

LOCAL DEPOSITION OF NANOPARTICLES ON A PDMS MICROFLUIDIC DEVICE

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ABSTRACT

The local deposition of metal patterns on polydimethylsiloxane (PDMS)-based microfluidic devices is usually obtained with methods based on photolithography and thin-film deposition techniques. As a result, it is time consuming and expensive. We present a cleanroom-free method to generate and locally (3D) print nanoparticles inside microfluidic structures using a prototype nanoparticle printer. Films of Pt or Ag nanoparticles were printed on a PDMS microfluidic device and used for two different applications: generation of pH gradients via bipolar electrochemistry, and localized sensing of chemicals via surface-enhanced Raman spectroscopy (SERS). The results show the versatility of the approach, allowing the integration of metal nanoparticles in specific regions of microfluidic devices for various applications.

KEYWORDS: metal nanoparticles deposition, PDMS, bipolar electrodes, surface-enhanced Raman spectroscopy.

INTRODUCTION

Polydimethylsiloxane (PDMS) is currently the most used material in the fabrication of micro- and nanoscale devices. The integration of noble metal nanoparticles (NPs) on PDMS provides flexibility in fabricating functional devices for applications such as stretchable electronics¹, chemical, and biological sensors². Conventional methods to achieve a local deposition of NPs require expensive vacuum processing and multiple steps, making the process complex and time-consuming. In this work, we locally deposit NPs generated by spark ablation in the chip chambers of a multiplexed PDMS microfluidic device using a nanomaterial 3D printer from the company VSParticle. The microfluidic devices integrated with Pt and Ag NPs were used for the generation of potential and pH gradients via bipolar electrochemistry and as surface-enhanced Raman spectroscopy (SERS) substrates for the detection of low-concentrated analytes, demonstrating the potential and versatility of this new fabrication method.

EXPERIMENTAL

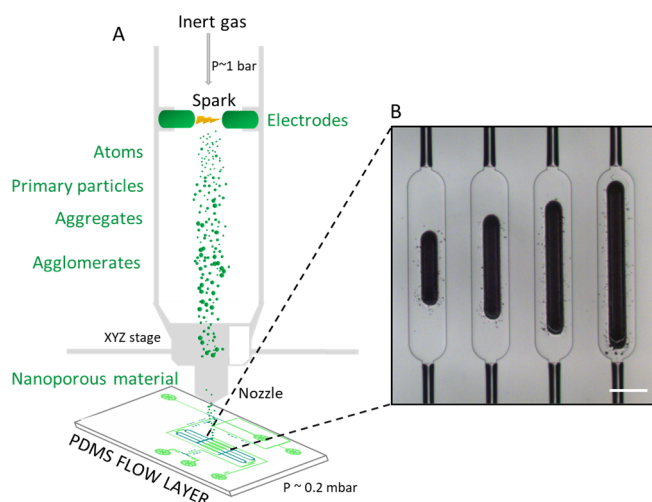


Figure 1: **A)** Schematic representation of the setup used to produce and print the nanoparticles on the PDMS substrate. **B)** Bright field image of layers of Pt nanoparticles printed in the chip chambers. Scale bar: 350 μm .

RESULTS AND DISCUSSION

Pt layers in the chip chambers were used as bipolar electrodes (BPEs), which consist of conductive materials immersed in an electrolyte and polarized wirelessly through an external electric field. The BPEs were tested towards

Pt and Ag NPs were produced and deposited directly on the PDMS substrates using a commercial particle generator (VSParticle-G1) and a prototype aerosol printer (VSParticle-P1). The particle generator contained 2x Pt (99.9%) or Ag (99.9%) electrodes and 1 slm Ar (99.9%) was used as carrier gas. The output of the particle generator is connected to a vacuum chamber equipped with a nozzle (throat diameter 0.1 mm) for focusing and printing the beam of NPs onto the substrate. The microfluidic devices consisted of PDMS chips with four independently addressable chambers. Their design and microfabrication are based on a previous work³. Briefly, the chips are made of two PDMS layers and a glass slide. The top layer contains the fluidic channels (height 50 μm) and chambers (width 350 μm , length 1850 μm), where the NPs are confined. Pneumatically actuated valves are placed on the bottom layer (channel height 20 μm), which is directly attached to a glass slide.

the water-splitting reaction, which induces changes in the pH of the electrolyte due to the O₂ and H₂ production at the edges of the BPEs, that act as anode and cathode. The use of a fluorescent pH-responsive dye in the electrolyte allowed the detection and comparison of the activity of the electrodes, which is proportional to their lengths (Figure 2B). The presence of valves in the microfluidic chip allowed the use of the electrodes both simultaneously (Figure 2A) and, by opening the valves of only one chamber, also independently (Figure 2C).

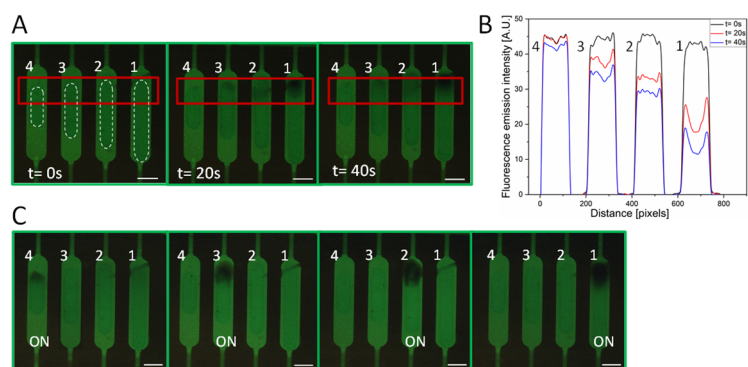


Figure 2: **A)** Fluorescence images showing the activity of BPEs used simultaneously upon the application of an external driving potential $E = 400$ V. **B)** Fluorescence emission intensity profile at the anodic poles of the electrodes. The change in the fluorescence intensity reflects the decrease in the pH of the solution, due to the O₂ production via water splitting. The available overpotential for O₂ production is proportional to the length of the electrodes. **C)** Fluorescence micrographs showing the BPEs used individually upon the application of an external driving potential $E = 500$ V. The PDMS valves can act as insulators by closing the conductive path through the channels. Scale bars: 350 μm .

In addition, Ag layers were used as SERS substrate for the detection of a solution of methylene blue (MB) $2.5 \cdot 10^{-5}$ M. As shown in Figure 3C, when the solution is detected on the bare PDMS, the MB peaks are not visible while the Ag NPs can show and enhance the MB signal. The Ag NPs showed an enhancement factor (EF) $\approx 1.7 \cdot 10^5$, comparable to typical average EFs values reported in the literature⁴ for Ag structures.

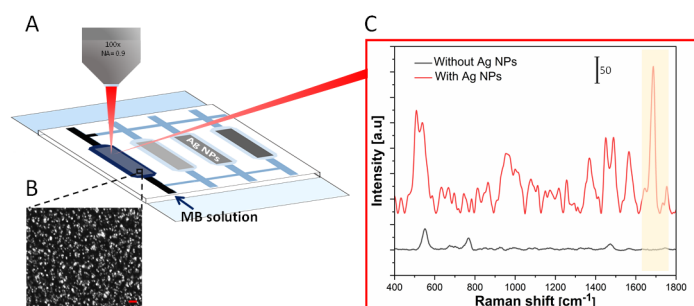


Figure 3: **A)** Schematic representation of the acquisition of the Raman signals from a PDMS chip with Ag NPs deposited in its chambers. **B)** Raman spectra of MB on the bare PDMS (in black) and Ag NPs (in red). The black curve only shows the PDMS peaks, while the red curve represents MB peaks, with the most intense highlighted and referred to C-C stretching. In both cases, the fluorescence background was subtracted. **C)** SEM image of Ag NPs deposited on the PDMS substrate. Scale bar: 200 nm.

CONCLUSION

We proposed a simple and one-step process to locally print patterns of NPs on PDMS. We demonstrate their use as electrodes and as SERS sensors. The results show the versatility and potential of the approach, which allows the easy integration of metal NPs in specific regions of microfluidic devices. This can lead to the fabrication of functional devices for applications that include but are not limited to screening and sensing platforms.

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