Direct printing of gold nanospheres from colloidal solutions by pyro-electrohydrodynamic jet allows hypersensitive SERS sensing

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Abstract: Pyro-electrohydrodynamic jet printing (p-jet) has been used to fabricate a nanostructured plasmonic sensor for SERS spectroscopy. The p-jet approach allowed us to have an assembly of nanoparticles with suitable geometry and size, which resulted in a sensing surface with intense SERS activity and a rather homogeneous response. Raman imaging measurements highlighted strong Enhancement Factors across the sensing area, exceeding those of the pristine colloidal solution by almost two orders of magnitude. The intense plasmonic effect was further demonstrated by the spectroscopic recognition of a metal-catalyzed dimerization process triggered to completeness at the metal surface. The results presented herein demonstrate the usefulness of the proposed SERS sensor for hypersensitive molecular analysis.

Keywords: SERS spectroscopy; sensors; jet-printing; colloids; plasmonic
1. Introduction

Surface Enhanced Raman Scattering (SERS) is a plasmonic process by which the signals arising from the inelastic scattering of a molecule are enhanced by several orders of magnitude, (typically $10^5 - 10^9$) resulting in drastically improved sensitivity of Raman spectroscopy measurements. The effect occurs when the target molecule is adsorbed on, or in close proximity to a metal surface with nanoscale morphology. In recent years, SERS has emerged as one of the leading techniques for molecular analysis both in fundamental studies and in an application-oriented perspective. Remarkable results have been recently reported in such diverse fields as the analysis of trace contaminants[1,2], catalysis[3,4], imaging and nanomedicine for diagnostic and therapeutic applications[5-7].

Several strategies have been developed to realize SERS sensors, the most effective being: i) synthesis of individual metal-nanoparticles in the form of colloidal solutions; ii) deposition of colloids onto suitably treated substrates; iii) fabrication of patterned nanostructures by electron beam lithography (EBL). Each of these methods has advantages and drawbacks. Colloid solutions are stable and easy to handle. They represent the main platform for biosensing and provide a highly uniform response, which is a major advantage in quantitative analysis. The signal intensity, however, may change significantly with time if kinetic effects control the adsorption process and/or in case of aggregation and consequent precipitation of the nano-objects. Furthermore, dilution may appreciably reduce the sensitivity. Planar structures obtained by colloid deposition (drop-casting) are, in principle, the most sensitive platform owing to the formation of a large number of hot-spots (1 – 5 nm gaps at inter-particle junctions), which greatly enhance the plasmonic effect[8]. However, uniform coverage of the substrate is difficult to achieve and most systems give rise to the so-called coffee-ring effect. The nanoparticles tend
to separate in the boundary region of the dried drop forming a characteristic pattern, which is detrimental not only for the consistency of the response, but also for the quality of the generated signals (fluorescence is frequently observed in areas with a high deposition density). These effects may severely limit the usefulness of planar substrates, especially in quantitative analysis. Conversely, EBL nanostructures are highly reproducible and essentially defect-free, thus providing very homogeneous response. However, their cost is conspicuous in comparison to other platforms and by this route it is difficult, to reproduce hot-spot morphologies, which tends to reduce the sensitivity.

In the context of the drop-casting strategy, the ability to confine the nanoparticle deposition within micrometric areas presents distinct advantages. The increased nanoparticle density largely enhances SERS sensitivity when the transfer of the analyte to the sensing surface is performed by immersion (dip-transfer). Drop-transfer can be advantageous whenever it is possible to realize a targeted deposition of microdroplets. Another situation in which confined nanoparticle deposition can be highly advantageous is when the sampling volume is very limited. This occurs, for instance, when SERS detection is combined to a preliminary separation step via GC/HPLC, which is becoming a viable route in proteomic/metabolomic research[9,10]. In these applications, micro/nanoliters of the analyte can be mixed with comparable volumes of the sensing colloid, followed by confined deposition of the resulting solution. The quality and intensity of the SERS signals can also be improved when the sensing area has a surface comparable to the laser spot. A typical objective lens used for semi-macro sampling (0.5×, NA = 0.02) produces – with a 632 nm laser line – a beam diameter at focus of around 50 µm, depending on the specific setup. Thus, a laser spot focused at the center of a sensing area limited to less than 100 µm would cover a substantial extent of the nanoparticle deposition, and the
SERS intensity sampled in this way would be more representative of the signal distribution compared to a deposition spread over a much larger surface.

In this paper, we propose a method for fabricating a SERS sensor characterized by a micrometric sensing surface having carefully controlled shape and size in the range 50 – 100 µm. This nanostructured plasmonic sensor is based on a colloidal solution of gold nanospheres synthesized by seed-mediated growth and characterized by uniform shape and narrow size-distribution. We used here a non-conventional technique that we call \textit{p-jet}, that stands for \textit{pyro-electrohydrodynamic jet[11]}, in order to achieve the confined sensing surface by direct printing of the colloidal solution. Compared to more conventional approaches, such as microcontact printing[12], photolithography[13], nanoimprint[14], EBL[15], focused ion beam[16] and direct laser writing[17], \textit{p-jet} is free from mold-based procedures and does not require the use of expensive equipment. The p-jet uses high electric fields generated pyroelectrically by lithium niobate (LN) and lithium tantalate (LT) crystals[18]. Inkjet printing by the use of electric fields generated by high voltage generators has been developed for different applications[19,20]. The p-jet used here has the additional advantage of being electrode-free and nozzle-free, thus allowing us to avoid external high voltage generators and nozzle-clogging drawbacks[21]. We have already demonstrated the success of p-jet for a wide variety of applications which include printing fine patterns[11,22], patterning tiny fibres[23], accumulation of biomolecules[23], formation of disperse sprayed droplets[24], manipulation of soft matter[25-28], just to cite some. Here the p-jet is used for the first time for direct writing of metal nanoparticles from colloidal solution. A complete characterization of the AuNPs is reported, by transmission electron microscopy (TEM), statistical image analysis (SIA) and UV/Vis spectroscopy. Furthermore, we evaluated the SERS performances of the nanoparticle assembly in terms of Enhancement Factor (EF) and response homogeneity by confocal Raman spectroscopy and Raman imaging. The
results demonstrate clearly how the proposed method is highly promising in nanotechnology research, as it enables the precise jetting of AuNPs for SERS detection.

2. Experimental section

2.1. Materials

Trisodium citrate (TC), gold(III) chloride trihydrate (H Au Cl₄ · 3H₂O), ascorbic acid (AA), sodium borohydride (NaBH₄), Cetyltrimethylammonium bromide (CTAB), ethanol and p-mercaptoaniline (pMA) were purchased from Sigma-Aldrich and used as received. Milli-Q water was used for the preparation of gold nanoparticles. The LN crystals were bought from Crystal Technology Inc. in the form of both sides polished 500 μm thick c-cut 3-in. wafers and were cut into square samples 2 × 2 cm² sized by a precision diamond saw. The deposition slide was a coverslip, bought from Sigma Aldrich, consisting of an untreated glass substrate 24 × 60 mm sized and 0.2 mm thick.

2.2. Fabrication of the SERS sensor

2.2.1. Pyroelectric effect

The c-cut LN is a ferroelectric crystal and, at room temperature, has a spontaneous polarization Ps conventionally oriented from the so-called c- face to the c+ face. At equilibrium, i.e. when there is no temperature variation, the polarization charge of the LN crystal is completely screened by external screening charges on the crystal surface and there is no electric field. When thermally stimulated, the magnitude of Ps changes and, consequently, a transient electrostatic state appears with uncompensated screening charges on the crystal surface[18]. This
phenomenon generates a high electric field that originates from the hot point of the crystal surface. This electric field can be exploited for a wide variety of applications ranging from biological to soft matter manipulation[23,29-31].

2.2.2. P-jet printing

Figure 1(a) shows the schematic view of the p-jet system used here for fabricating the sensing surface, while Figure 1(b,c) show schematically the formation of the jets by using the pyroelectric effect into the LN crystal.

Figure 1. Schematic view of (a) the p-jet system, (b) of the activation of the pyroelectric effect and the generation of the electric field (grey lines) when the thermal stimulation is ON (c) and of the droplet eject effect when the thermal stimulation is OFF.
We deposited a mother drop (0.2 µL) of the colloidal solution onto a round shaped tip by standard manual pipetting. The p-jet system is made of different elements mounted on three-axes precision translation stages, aligned vertically from top to bottom. The thermal source consists of a tungsten wire, which heats locally the LN crystal sample by Joule effect. The red rectangle in Figure 1(b) indicates schematically this hot point of the crystal, which corresponds to the area in which the pyroelectric effect occurs. The grey lines in Figure 1(b) show schematically the distribution of the electric field generated across the hot point of the crystal. We mount the deposition slide just under the crystal and we deposit the spots of the colloidal solution on the opposite side. The distance between the mother drop and the deposition surface is around 80 µm. A conventional optical path, consisting of a collimated LED, an optical microscope objective (10×) and a high-speed CMOS camera (Motion Pro Y3-S1, pixel size of 10.85 µm²), permit us to have a lateral view of the jetting events during the activation of the pyroelectric effect, as shown in Figure 1(a).

The electric field generated pyroelectrically by the LN crystal induces charge accumulation on the free surface of the mother drop by the electrostatic effect. The density of charge is high enough to induce a well-known Coulomb repulsion effect[32,33], which deforms the meniscus of the mother drop into the so-called Taylor cone. When the electric field exceeds the surface tension of the liquid, tiny droplets are ejected from the apex of the meniscus[34]. The daughter droplets generated by this p-jet system have volumes in the range of 80 pL. After the first spot we translate the deposition slide and we produce new spots of colloidal solution with gold nanoparticles at specific spatial confining.

2.2.3. Micro-heater system
The micro-heater is made of a pointed wire of tungsten (300 µm thick). The thermal stimulus was controlled by means of a power dissipation driven by a traditional voltage generator that is modulated by a conventional 5 V transistor-transistor logic (TTL) signal.

2.2.4. Synthesis of gold nanoparticles

The synthesis of the gold nanoparticles (AuNPs) was carried out in aqueous solution by using the seed-mediated growth method\[35\]. Briefly, a seeds (~3 nm) solution was prepared at room temperature by dissolving a certain amount of HAuCl₄ and TC in water to get a final concentration 2.5 × 10⁻⁴ M of both reagents. Then, under stirring, 600 µL of ice-cold NaBH₄ aqueous solution (0.1 M) were added and the color immediately turned pink, which is indicative of seeds formation. The prepared solution was left undisturbed at room temperature for 2 hours and then used for the particle growth step. Next, a growth solution (GS) was prepared by adding CTAB (final concentration 0.08 M) to a water solution containing 2.5 × 10⁻³ M of HAuCl₄. The mixture was heated at around 80°C until it turned clear orange and then it was cooled down to room temperature before use. For the nanoparticle growth, 1 mL of 0.1 M AA aqueous solution and the seed solution were added to GS, which immediately turned wine red, indicative of nanoparticles formation. The solution was stirred for 10 minutes and then centrifuged three times at 13,000 rpm, 35°C for 20 minutes to remove the free CTAB in solution. The AuNPs were re-suspended in water and kept at room temperature for further characterization.

2.2.5. Surface functionalization of the SERS sensor
The SERS sensor was washed several times with milli-Q water, dried under nitrogen flux and then functionalized with pMA. A 100 μM solution of pMA was prepared by dissolving a certain amount of the probe in ethanol. Then a self-assembled monolayer (SAM) of pMA on the gold surface was obtained by dropping 20μL of the pMA solution on the substrate in order to fully cover the whole spot. The SERS sensor was kept at room temperature, for a sufficient time, to allow ethanol evaporation. Before Raman characterization, the sensor was washed again with water to remove the excess of unreacted pMA and dried under nitrogen flux.

2.3. Techniques

2.3.1. Transmission electron microscopy (TEM)

The AuNPs shape and average diameter were estimated by bright field TEM performed on a FEI Tecnai G12 Spirit Twin (LaB6 source) equipped with a FEI Eagle 4 K CCD camera (Eindhoven, The Netherlands) operating with an acceleration voltage of 120 kV. Samples for TEM examination were prepared by immersing a carbon-coated copper grid in the colloidal solution, followed by drying. TEM images were acquired in different sample areas and were transferred to the MATLAB computational platform (Mathworks, Natick, MA, USA) for further processing. SIA was performed by the PLS/MIA toolbox, (Eigenvector Research Inc., Manson, WA, USA) running under the MATLAB environment.

2.3.2. UV-VIS spectroscopy
The optical properties of AuNPs and their molar concentration were measured by an UV spectrophotometer equipped with single monochromator (V-570 from Jasco, Easton, USA). Absorption spectra of the AuNPs colloids were collected using a 1.00 cm quartz cell with a scan speed of 400 nm/min in the wavelength range from 300 nm to 800 nm. For the quantitative analysis of the gold amount in the AuNPs solution a set of six standards were obtained by diluting the as-prepared gold nanoparticles solution batch. Complete reduction from Au(III) to Au(0) was assumed.

2.3.3. Raman Spectroscopy

The AuNPs SERS performances in solution were evaluated by Raman spectroscopy using pMA as molecular probe. The Raman and SERS spectra were collected by a confocal Raman spectrometer (Labspec Aramis, from Horiba-Jobin Yvon, Edision, NJ, USA) operating with a 632 nm diode laser as the exciting source. The 180° back-scattered radiation was collected by an Olympus metallurgical objective (MPlan 10x, NA = 0.25) with confocal and slit apertures set to 400 μm; a grating with 600 grooves/mm was used throughout. The radiation was focused onto a CCD detector (Synapse Mod. 354308) cooled at -70 °C by a Peltier module. The laser power measured at the output of the objective was 1.87 mW, which resulted in a power density of 1.9 mW/μm². The pMA reference spectrum was collected on a 10 wt% solution of pMA in ethanol while the SERS spectrum was collected after AuNPs functionalization with a 100 μM ethanol solution of pMA (AuNPs/pMA, v/v 1:1). Both spectra were collected with an exposure time of 10 s by using a quartz cuvette with chamber volume of 700 μL (Hellma GmbH & Co, Jena, Germany). The EF of the colloids was calculated according to our previous work[35].
The performances of the SERS planar sensor were evaluated by running Raman imaging measurements in the mapping mode: the SERS substrate was placed on a piezo-electrically driven microscope-stage with a x,y resolution of 10 ± 0.5 nm and a z resolution of 15 ± 1 nm. The stage was scanned at a constant speed in the x–y plane with a 2.0 μm step size. The spectra were collected by an Olympus metallurgical objective (MPlan 50x, NA = 0.75) with an exposure time of 1s. For the enhancement factor calculation of the planar SERS sensor the reference spectrum was collected on the bulk pMA (powder) by an Olympus metallurgical objective (MPlan 10x, NA = 0.25) with an exposure time of 4s. A 632 nm diode laser was used as the exciting source with confocal and slit apertures set to 400 μm. All the collected Raman data were converted into ASCII format and transferred to the MATLAB computational platform for further processing.

3. Results and discussion

3.1. Colloids characterization

The SIA was performed on a selection of TEM micrographs, which provided a total nanoparticles population of ≅ 300 units. Figure 2 shows a representative TEM micrograph of the AuNPs and the results of the SIA. According to our previous work\textsuperscript{35} the shape and shape distribution of the AuNPs were evaluated by means of the roundness parameter $R$ obtained from SIA, which is defined as:

$$
R = \frac{4 \times A}{\pi \times d_{max}^2}
$$

(1)
where, $A$ is the particle area and $d_{\text{max}}$ is the major axis. It was found that 98% of the population is characterized by a spherical shape ($R \geq 0.8$); it exhibits an average diameter of $16 \pm 3$ nm and a unimodal, Gaussian-like size distribution (cf Figure 2B). Only 2% of the total nanoparticle population was characterized by a rod-like shape ($R \leq 0.6$). In the whole set of TEM images, no particle aggregation was apparent.

![Image](image_url)

**Figure 2.** *A:* TEM micrograph of the gold nanoparticles. *B:* SIA of the TEM micrographs.

The AuNPs colloids exhibit a strong plasmon resonance (SPR) band around 526 nm with a narrow shape, which, according to the SIA results, is indicative of a unimodal distribution of particle sizes (see Figure S1, Supplementary Material). The Au molar concentration in the colloidal solution was evaluated by UV-VIS spectroscopy. The UV-VIS calibration curve was performed by collecting the spectra of six AuNPs standards prepared as explained previously. An accurate quantitative analysis of the gold amount in the AuNPs batch was possible since the absorbance (at 526 nm) vs concentration plot displays a Beer-Lambert behaviour (i.e., it is linear through the origin, correlation coefficient $R^2 = 0.999$, cf. Figure S2, Supplementary Material). After the UV calibration the AuNPs solution was centrifuged and re-suspended in water and an
UV absorption spectrum was collected, from which the Au molar concentration was estimated to be 2.6 mM. According to our previous work [35] by coupling the TEM geometrical parameters (size and shape) and the UV-VIS results ([Au]) the concentration of the colloid solution was estimated to be 21 nM. This AuNPs batch was used for the SERS sensor fabrication.

The SERS performances of the synthesized AuNPs in terms of absolute enhancement factor (EF) were evaluated by comparing the spontaneous and the SERS spectra of pMA. In particular, 

\[ EF = \frac{I_{SERS} \times N_{REF}}{I_{REF} \times N_{SERS}} \]

where \( I_{SERS} \) is the integrated area of a specific SERS signal (at 1583 cm\(^{-1}\)) and \( I_{REF} \) is the integrated area of the corresponding Raman signal (at 1598 cm\(^{-1}\)), both normalized for the exposure time. Analogously, \( N_{SERS} \) and \( N_{REF} \) represent the number of molecules contributing to the SERS and the Raman signal, respectively, and were evaluated according to the procedure described in our previous work[35] and detailed in the Supplementary Material (paragraph 2.1). The estimated EF value of the present colloid is \( 1.7 \times 10^5 \), a figure suitable for high-sensitive analytical applications of SERS spectroscopy.

3.2. SERS response of the plasmonic nanoparticle assembly

In order to test the SERS activity of the nanoparticle assembly and to verify the signal distribution over the sensing area, we performed a Raman imaging experiment. A (100 × 100) µm area was mapped with a spatial resolution of 2.0 µm; the resulting image, reconstructed by considering the intensity of the pMA peak at 1583 cm\(^{-1}\), is compared to the visible image of the same region (Figures 3a – 3b). The spatially confined assembly is evident in both images as a perfectly round disk with a diameter of 76 µm. In the visible micrograph (Figure 3a) a dark boundary highlights the region where the nanoparticles tend to accumulate (coffee-ring effect).
The Raman image shows a clear correlation between the SERS response and the nanoparticle density. Representative SERS spectra from selected points are shown in Figure 3c. They are highly reproducible, with a flat and consistent baseline denoting the absence of spurious signals and interfering fluorescence. SERS activity is maximized in the boundary region but the pMA spectrum is clearly detected also in areas outside the coffee-ring.

Figure 3. a: visible image of the plasmonic nanoparticle assembly. b: Raman image of the assembly. c: SERS spectra collected in different points of the plasmonic surface (locations labelled A, B and C in Figure 3b). Trace D corresponds to the SERS spectrum averaged over the whole dataset.

Figure 4 reports a comparison between the spontaneous Raman spectrum of pMA (10 wt% ethanol solution, blue trace), the SERS spectrum of the colloid (green trace) and the SERS spectrum collected on the nanoparticle assembly (point A of the Raman image, red trace). The
SERS spectrum of pMA in the colloidal solution closely resembles the spontaneous Raman spectrum, both in terms of peak positions and Relative Raman Intensity. All peaks in the explored frequency range shift downward by an amount ranging between 5 (at 998 cm\(^{-1}\)) and 15 cm\(^{-1}\) (at 1583 cm\(^{-1}\)), reflecting the interaction of the probe molecule with the metal surface. Conversely, the SERS spectrum of pMA on the micrometric plasmonic surface is largely different from the reference. Three new intense signals at 1139, 1391 and 1433 cm\(^{-1}\) are observed; the peaks at 1074 and 1573 cm\(^{-1}\) remain relatively unperturbed with respect to their counterparts in the colloidal solution and the peak observed at 825 cm\(^{-1}\) in the Raman spectrum, completely disappears.

\[\text{Figure 4. Blue trace: spontaneous Raman spectrum of pMA (10 wt\% ethanol solution). Green trace: SERS spectrum of the colloidal solution. Red trace: SERS spectrum collected on the nanoparticle assembly (point A of the Raman image in Figure 2).}\]
These findings can be interpreted by recalling that, in suitable conditions, under laser illumination the probe molecule can undergo a photochemical process, forming dimeric azo-species[36] (see Scheme 1).

Scheme 1. Schematic representation of the photocatalytic dimerization of pMA.

In fact, the strong peaks, at 1433, 1391 and 1139 cm\(^{-1}\) correspond to vibrational modes involving the newly formed N=N and N–C bonds [respectively, \(\nu(NN)/\beta(CCH)\), \(\nu(NN)/\nu(CN)\), \(\nu(CN)/\beta(CCH)\)], where the Greek letters have the usual meaning of stretching (\(\nu\)) and bending (\(\beta\)). The spectrum reported in Figure 4, red trace, is coincident with that of 4,4’-dimercaptoazobenzene (DMAB) adsorbed on a SERS-active Ag electrode[36], confirming the essentially complete conversion of the monomer in the azo-species. The results presented herein (see Figure 4) demonstrate that this process does not occur in the colloidal solution because the plasmonic effect is confined to the single nanosphere and is insufficient to trigger the photochemistry. On the nanoparticle assembly, the probe experiences strongly enhanced laser fields due to a substantial density of hot-spots, which result in the complete conversion of the monomer in the dimeric species. In fact, the Enhancement Factor evaluated in a region of high SERS activity (point A in Figure 3b) amounts to 2.8 \(\times\) 10\(^7\), while the average EF in the whole sensing area is 1.2 \(\times\) 10\(^7\). More details on the EF calculations are reported in the Supplementary
Material (paragraph 2.2). Thus, the proposed fabrication method brings about an $EF$ increase of about two orders of magnitude with respect to the conventional colloid platform and opens up the possibility of employing the present nanoparticle assembly for hypersensitive molecular analysis.

4. Conclusions

In the present contribution a novel fabrication technique to realize spatially confined nanoparticle assemblies is presented. The micro patterning process, based on a modification of the p-jet technique, allows the fabrication of a sensing surface made of an assembly of nanoparticles with suitable geometry and size in the range of 50 – 100 $\mu$m. These platforms are demonstrated to be efficient SERS sensors, exhibiting fairly homogeneous response and Enhancement Factors larger than those of the parent colloidal solutions by almost two orders of magnitude. The occurrence of largely enhanced laser fields was confirmed by the observation of a photo-induced dimerization reaction of the probe molecule on the metal surface. It is shown that the nanostructured plasmonic sensor realized by the p-jet technique can be suitable for hypersensitive analytical applications.

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