Maskless Preparation of Spatially-Resolved Plasmonic Nanoparticles on Polydimethylsiloxane via In Situ Fluoride-Assisted Synthesis

Stefano Mariani, Antonino Amedeo La Mattina, Alessandro Paghi, Lucanos Strambini, and Giuseppe Barillaro*

Here, a fluoride-assisted route for the controlled in-situ synthesis of metal nanoparticles (NPs) (i.e., AgNPs, AuNPs) on polydimethylsiloxane (PDMS) is reported. The size and coverage of the NPs on the PDMS surface are modulated with time and over space during the synthetic process, leveraging the improved yield (10×) and faster kinetics (100×) of NP formation in the presence of F⁻ ions, compared to fluoride-free approaches. This enables the maskless preparation of both linear and step gradients and patterns of NPs in 1D and 2D on the PDMS surface. As an application in flexible plasmonics/photonics, continuous and step-wise spatial modulations of the plasmonic features of PDMS slabs with 1D and 2D AgNP gradients on the surface are demonstrated. An excellent spatially resolved tuning of key optical parameters, namely, optical density from zero to 5 and extinction ratio up to 100 dB, is achieved with AgNP gradients prepared in AgF solution for 12 minutes; the performance are comparable to those of commercial dielectric/interference filters. When used as a rejection filter in optical fluorescence microscopy, the AgNP-PDMS slabs are able to reject the excitation laser at 405 nm and retain the green fluorescence of microbeads (100 µm) used as test cases.

1. Introduction

The fundamental properties of nanostructured materials depend not only on their size but also their collective distribution in a hosting material. Control of the nanoparticle (NP) size and distribution in a macroscopic material provides access to functionalities (e.g., optical, electrical, mechanical, magnetic) that are often difficult to obtain otherwise. Two main routes, namely, ex situ and in situ, have been pursued to date to integrate metal NPs in/with polymers. Ex situ approaches require pre-formation of NPs, which are mixed with a polymer in a solvent or assembled via layer-by-layer technique. These methods have issues related to tedious protocols, NP aggregation, long-term stability, decreased adhesion, and limited density. In situ approaches enabling the direct formation of metal NPs include metal salt reduction, irradiation of the metal precursor in a polymer, laser ablation, or the decomposition of the metal precursor mixed with the polymer matrix.

Most of these approaches exploit concentration, time, and temperature as parameters to control size and density of NPs deposited and/or formed on a material. However, controlling the variation of the NP features in the same material, for example, to produce a continuous change in the NP size and/or distribution in a specific direction to achieve a linear NP gradient, further requires a suitable design of the surface chemistry. For instance, NP gradients have been achieved by forming a chemical gradient of functional groups upon which the NPs will adsorb in a number density gradient or a homogeneously functionalized surface (e.g., with amine or thiol groups) on which the NPs adsorb in a gradient given by diffusion and electrostatic interactions.

Although tailoring the surface chemistry enables the design of NP gradients in advance, to some extent at least, this approach fails to provide the necessary flexibility to monitor and/or modify the gradient design in real-time during the processing and to design/fabricate complex NP patterns (e.g., non linear gradients, stepwise modulation, 2D gradients) in the same material. This limits the preparation of novel NP composite materials with advanced functionalities.

Polydimethylsiloxane (PDMS) is extremely popular in material science and technology thanks to the superior optical, mechanical, and chemical characteristics, as well as processing versatility and competitive cost. Applications include, but are not limited to, stretchable electronics and photonics, environmental cleaning, and soft robotics.
Incorporation of metal NPs in PDMS via ex situ\(^{[22–23]}\) and in situ\(^{[24–36]}\) approaches have been also exploited to prepare PDMS composites with novel functionalities, among which, flexible plasmonic components with NPs supporting localized surface plasmon resonance (LSPR). Spatial control of the metal nanostructures/NPs on PDMS has been demonstrated using ex-situ approaches by transfer-printing/stripping on PDMS of nanosized metal structures patterned on a host substrate.\(^{[17,27,28]}\)

However, to our best knowledge, no reports on in situ spatial modulation of NP size and/or distribution on either PDMS or other polymeric materials have been reported so far.

This is likely due, at least for PDMS, to the slow kinetics of in situ synthetic approaches, such as the spontaneous reduction of \(\text{M}^{n+}\) ions (salt or complex) at Si–H bonds of (uncured PDMS),\(^{[17,24]}\) which hinders the control of NP size and distribution on the same substrate with time. It is useful to point out that fluoride-free approaches have been used for the synthesis of metal NPs in situ, to date.

Here we report a novel route for the real-time modulation of size and coverage of metal NPs (i.e., \(\text{AgNPs}, \text{AuNPs}\)) synthesized via a fluoride-assisted in situ reduction of metal ions at the PDMS surface. We show that the presence of fluoride ions in the metal solution leads to an improved density (about 10\(\times\)) and kinetics (100\(\times\) faster) of the synthetic process, with respect to state-of-the-art approaches that are fluoride-free. This makes possible the control of both size and filling factor of NPs formed on the PDMS surface with time and over space during the processing, enabling the real-time preparation and monitoring of unique NP gradients and patterns in one and two dimensions on the same PDMS slab, not achievable with other in situ synthetic methods.

As a proof-of-concept application in flexible plasmonics/photonics, we demonstrate the in situ preparation of continuous and step-wise 1D and 2D NP gradients on PDMS slabs by controlling the insertion strategy and rate of the slab in the metal solution, enabling, in turn, the maskless fabrication of spatially-resolved plasmonic elements on PDMS; we further demonstrate the in situ 2D patternning of metal NPs on the PDMS surface by preliminary plasma inhibition of Si–H bonds in specific areas of PDMS and successive maskless formation of NPs in the complementary PDMS areas; eventually, we exploit the excellent light filtering properties (optical density (OD) tunable from 0.5 to 5 and extinction ratio (ER) from 20 to 100 dB) of AgNP-decorated PDMS plasmonic slabs achieved via the fluoride-assisted method to demonstrate their application as rejection filters in fluorescence microscopy.

2. Results and Discussion

In situ fluoride-mediated synthesis of Ag and Au NPs on PDMS slabs were achieved as sketched in Figure 1a. PDMS slabs 1 cm × 1 cm in size and 2 mm thick were prepared and dipped in an ethanolic fluoride-rich metal solution (i.e., \(\text{AgF}\) or \(\text{HAuCl}_4\cdot\text{NH}_4\text{F}\)) at room temperature (i.e., 20 °C), Ag and Au NPs were formed on the PDMS slabs by redox reaction occurring between unreacted Si–H bonds (of the curing agent) available at the PDMS surface and metallic cations \(\text{Ag}^+\) and \(\text{Au}^{3+}\) available in the solution.\(^{[24]}\) The PDMS slabs decorated with metal NPs were eventually dried under gentle nitrogen flow. Control experiments were carried out using fluoride-free ethanolic solutions of \(\text{AgNO}_3\) and \(\text{HAuCl}_4\) which are commonly used for the in situ synthesis of Ag and Au NPs on PDMS.\(^{[24]}\)

Ethanol was used as the solvent due to its higher (≈10×) permeation rate in PDMS \((9.8 \times 10^{-4} \text{ cm}^2 \text{s}^{-1})\) with respect to water \((9.1 \times 10^{-5} \text{ cm}^2 \text{s}^{-1})\).\(^{[29]}\) It has been reported that the synthesis rate of metal colloids in ethanolic solutions is higher compared to that in aqueous solutions.\(^{[24,30]}\)

Figure 1b shows different PDMS slabs decorated with Ag and Au NPs by immersion in fluoride-rich and fluoride-free (control experiment) ethanolic solutions of Ag and Au for different times, namely, from 1 to 270 min for AgNPs and from 24 to 96 h for AuNPs. Other pictures for additional decoration times are given in Figure S1, Supporting Information. In both cases, the PMDS slabs appeared brownish\(^{[30]}\) and red-violet\(^{[24]}\) after decoration with Ag and Au NPs, respectively, with color intensity increasing with the decoration time; this was ascribed to the LSPR absorption of NPs with increased density and/or surface coverage as the immersion time increased. Remarkably, a comparison of the color intensity of the slabs decorated in fluoride-rich and fluoride-free solutions for a given immersion time immediately points out that the presence of fluoride ions in the solution greatly accelerates the kinetics and increases the density of metal NPs on the PDMS surface. Slabs decorated in \(\text{AgF}\) for 1 and 4 min have similar intensities to those decorated in \(\text{AgNO}_3\) for 90 and 270 min, resulting in an about 100× improvement of the synthesis yield in the presence of F\(^{−}\) ions. Notice that, a total of 24 h of immersion in the \(\text{AgNO}_3\) solution produces AgNP-decorated slabs with color intensity lighter than that of slabs decorated in the \(\text{AgF}\) solution for only 8 min (Figure S1, Supporting Information). Similar results are achieved for AuNPs formed in the presence of fluoride ions, for example, compare slabs decorated in \(\text{HAuCl}_4\cdot\text{NH}_4\text{F}\) for 24 h vs. \(\text{HAuCl}_4\) for 96 h in Figure 1b. In agreement with the literature,\(^{[24,30]}\) the synthesis of AuNPs is intrinsically slower than that of AgNPs; yet, the presence of fluoride ions in the solution significantly improves the process yield, reducing, in turn, the synthesis time.

We speculate that the acidic equilibrium constant \((\text{pK}_a)\) of chemical species generated upon metal reduction at the PDMS surface plays a key role in improving yield and kinetic of NP formation in fluoride-rich metal solutions.\(^{[31]}\) The mechanism we propose for the fluoride-mediated synthesis of metal NPs is sketched in Figure 1c with specific reference to the formation of AgNPs. For both fluoride-rich and fluoride-free solutions, an \(\text{Ag}^+\) available in solution due to silver salt dissociation reacts with a \(\text{Si}–\text{H}\) bond available at the PDMS surface (due to curing agent) producing metal silver \(\text{Ag}^0\) on PDMS and releasing an \(\text{H}^+\) ion as byproduct. The released \(\text{H}^+\) binds to an \(\text{F}^-\) or \(\text{NO}_3^-\) ion available in the \(\text{AgF}\) and \(\text{AgNO}_3\) solution, respectively, resulting in dissociated moieties of HF and HNO\(_3\). Given that HF and HNO\(_3\) have significantly different \(\text{pK}_a\) values of 3.17 and −1.37,\(^{[22]}\) respectively, a much higher number of \(\text{H}^+\) ions couples with \(\text{F}^{-}\) ions in the \(\text{AgF}\) solution with respect to that coupling with \(\text{NO}_3^-\) in the \(\text{AgNO}_3\) solution.\(^{[32]}\) This reduces the concentration of \(\text{H}^+\) ions in \(\text{AgF}\) solution by about 5 orders
of magnitude with respect to that in the AgNO₃ solution. The lower H⁺ concentration in the fluoride-rich solution, compared to the fluoride-free solution, accelerates the reduction kinetics of Ag⁺ ions to metallic Ag⁰ and, in turn, the synthesis of AgNPs on PDMS, according to the chemical equilibrium (Le Châtelier’s) principle. Notice that, NP formation through silver auto-reduction in solution with AgF salt (i.e., Ag⁺ + F⁻ → Ag⁰ + F⁻) [33] can be ruled out. Room-temperature auto-reduction of AgF is promoted in aprotic solvents (e.g., acetonitrile, benzonitrile, and DMSO), and de-activated in protic solvents, [33] as well as in water and ethanol. [34] This was also confirmed here by acquisition of the transmission spectrum of an ethanolic solution of 15 mM AgF (in cuvette) after 16 min, from which the plasmonic resonance peak typical of AgNPs occurring around 400 nm [35] was barely visible (Figure S2, Supporting Information).

A thorough morphological characterization of the PDMS slabs decorated with AgNPs both in fluoride-rich and fluoride-free solutions was carried out by atomic force microscopy (AFM) and transmission electron microscopy with microanalysis (TEM-EDX).

AFM maps of PDMS slabs decorated in ethanolic solutions of AgF at 1, 4, and 12 min and of AgNO₃ at 30 and 90 min are shown in Figure 2a,b and Figure S3, Supporting Information. AgNPs with average size of 8.8 to 14.5 nm were achieved in AgF solution as the decoration time increased from 1 to 12 min (Figure 2c); NPs with larger size, of 11.2 and 15.8 nm were obtained after decoration for 30 and 90 min in AgNO₃ solution. Notice that, for both the solutions the size distribution of the AgNPs synthesized on the PDMS surface increased with the decoration time, though at significantly different timescales. Remarkably, a density of about 400–500 NPs per µm² was achieved for the fluoride-rich solution, which is independent of the decoration time, at least in the range 1–12 min investigated (Figure S4a, Supporting Information). This is a factor about 6× higher than the density obtained with the control fluoride-free solution, about 70–90 NPs per µm², in spite of a much longer decoration time. Consistently, a higher surface coverage (about 7x) is achieved in the fluoride-rich solution, with respect to fluoride-free one; specifically, the surface coverage increases from 7 to 10% as the immersion time in AgF solution.
increases from 1 to 12 min, consistently with the size increase of the AgNPs formed on the PDMS surface (Figure S4b, Supporting Information).

The high resolution (HR) TEM-EDX analysis of PDMS slabs decorated for 12 min in the AgF solution confirmed the crystalline nature of AgNPs synthesized on the PDMS surface with average size around 15 nm (Figure 2d,e). The Ag crystalline planes can be clearly appreciated in the NP shown in Figure 2e. Figure 2f,g shows elemental maps, that is, Ag, O, Si, C, and Ag intensity signals of AgNPs decorated in AgF for 12 min.

We further characterized the PDMS slabs decorated with Ag and Au NPs synthesized in fluoride-rich and fluoride-free solutions by transmittance spectroscopy. Figure 3a shows transmittance spectra (normalized to bare PDMS) of the PDMS slabs shown in Figure 1b and decorated with AgNPs in AgF solution at 1 to 12 min; for comparison, the transmittance spectrum of the slab decorated in AgNO₃ for 270 min is also shown. A characteristic transmittance drop centered around 403 nm is observed for all the decorated slabs, which is compatible with the LSPR peak of AgNPs with size of about 10 nm. Remarkably, the transmittance value at the plasmonic peak wavelength is 40 and 0.6% after only 1 and 4 min of immersion in AgF solution, respectively; additional 8 min of immersion in the solution further reduced the plasmonic peak transmittance well below 0.1%, together with a peak widening due to broader size distribution of AgNPs as the decoration time increased, in agreement with the AFM analysis (Figure 2a–c and Figures S3 and S4, Supporting Information). The decorated slabs retained a high transmittance value outside the plasmonic resonance region, regardless of the decoration time; for instance, a transmittance of 80 to 100% was measured at wavelengths >550 nm after 4 min of immersion in AgF solution.

Remarkably, control experiments in AgNO₃ solution highlighted that 270 min are needed to lower the transmittance value at the LSPR peak wavelength down to 1%; such a transmittance value is comparable to that achieved after 4 min in the AgF solution (Figure 3a) and confirms the much slower (<1/100) NP formation rate in a fluoride-free solution (Figure S5, Supporting Information). These results are fully consistent with the color intensity analysis of the decorated PDMS slabs discussed in Figure 1.

Similarly, the presence of AuNPs on PDMS slabs synthesized in HAuCl₄ solutions was corroborated by the occurrence of a transmittance drop at the plasmonic resonance peak of 530 nm (Figure S6, Supporting Information). The presence of F⁻ ions in the HAuCl₄ solution containing NH₄F leads to a reduced transmittance value at the plasmonic resonance wavelength for a given immersion time, with respect to pure HAuCl₄, thus corroborating the increased AuNP density/coverage on the PDMS surface in the fluoride-rich solution (Figure S6, Supporting Information). Figure S6, Supporting Information, shows that a synthesis of 4 h in the presence of a fluoride source (i.e., NH₄F) results in a density of AuNPs sufficient to reduce the...
transmittance value at the plasmonic peak wavelength down to about 80%, to be compared with a value of 70% achieved after 24 h of synthesis in pure HAuCl₄. More importantly, the standard synthesis with pure HAuCl₄ (i.e., without a fluoride source) does not allow to achieve an NP density high enough to reduce the transmittance value at the plasmonic resonant wavelength below 50%, regardless of the synthesis time (Figure S6c, Supporting Information, black squares); conversely, the addition of NH₄F to the standard HAuCl₄ solution leads to a significant improvement of the yield of the NP formation process, enabling to increase the NPs formed on the PDMS surface and reduce, in turn, the transmittance value at the LSPR wavelength down to 10% in 96 h (Figure S6c, Supporting Information, red dots). This enables the fabrication of AuNP-based composite materials with features not achievable otherwise.

The transmittance value of Ag and Au NPs at the plasmonic resonance wavelength provides a mean to investigate the kinetics of NP formation on the PDMS surface and, in turn, to monitor NP size/coverage modulation in real-time during the processing.

Time-resolved transmission spectra were acquired during the synthesis of Ag NPs, and the transmittance value of the LSPR wavelength was tracked over time; ethanolic solutions of AgF 15 mM, as well as of AgNO₃ 15 mM (negative control) and of AgNO₃ 15 mM mixed with NH₄F to provide a source of F⁻ ions (positive control) were used for the synthesis. Figure 3b shows the time-resolved transmittance map of a PDMS slab immersed in the AgF solution for 14 min; transmittance is normalized to that of bare PDMS immersed in the solution, acquired at t = 0 s. The transmittance value at 403 nm (i.e., at the local surface plasmon resonance wavelength) versus immersion time is reported in Figure 3c-black trace (and Movie S1, Supporting Information). Immersion of the PDMS slab in the solution led to the appearance of a transmittance dip at 403 nm after a few seconds, consistent with the formation of AgNPs on the PDMS surface; as the immersion time increased, the transmittance dip became more pronounced reaching a value of about 40% after 1 min and less than 1% after 4 min, in agreement with the augmented AgNP surface coverage with the immersion time (Figure 1b, and Figures S3 and S4, Supporting Information). Thus, monitoring the transmittance value of the LSPR wavelength provides a quantitative method to control/monitor size and coverage of the NPs synthesized on PDMS in real-time.

Immersion of PDMS in the control fluoride-free AgNO₃ solution also led to a similar transmittance behavior, though over a significantly different timescale of 100 min compared to several seconds in AgF (Figure 3c-red trace and Figure S7a, Supporting Information). The addition of a fluoride source, that

![Figure 3. Optical features of plasmon-encoded AgNP-PDMS slabs prepared via fluoride-assisted synthesis. a) Transmission spectra of PDMS slabs decorated with AgNPs in a 15 mM AgF ethanolic solution for 1, 4, and 12 min, normalized to the transmission spectrum of bare PDMS. The transmission spectrum of a PDMS slab decorated for 270 min in an ethanolic solution of AgNO₃ 15 mM (i.e., fluoride-free) is also shown for comparison. b) Time-resolved transmission spectrum of a PDMS slab decorated with AgNPs in a 15 mM AgF solution for 14 min. c) AgNP synthesis kinetics, namely, transmittance at 403 nm vs decoration time, measured on PDMS slabs immersed in an ethanolic solution of AgF 15 mM, as well as of 15 mM AgNO₃:NH₄F and 15 mM AgNO₃ solutions. d) Transmission spectra of PDMS slabs decorated with AgNPs using ethanolic solutions of AgF at different concentrations (i.e., 5, 7.5, 15, 30, and 45 mM) for 1 min, normalized to the transmission spectrum of bare PDMS. e) Transmittance values at the plasmonic peak wavelength of the AgNP-decorated PDMS slabs reported in (d). f) Transmission spectra of PDMS slabs with different base:curing ratios (i.e., 20:1, 10:1, and 5:1 w/w) decorated with AgNPs in a 15 mM AgF ethanolic solution for 1 min.](image-url)
is, NH$_4$F, to the pure AgNO$_3$ solution resulted in a significant improvement of the AgNP formation kinetics (Figure 3c-green trace and Figure S7b, Supporting Information), confirming the role of F$^-$ ions.

The kinetics of AgNP formation on PDMS with the different solutions tested was compared using as a parameter of merit the time at which the transmittance of the decorated PDMS slabs reduced to a value of 50%, namely, $t_{50}$. We found that $t_{50}$ was about 50 s for the AgF solution, increasing to 215 s (about 4 min) in the AgNO$_3$:NH$_4$F solution and to 6180 s (103 min) in the AgNO$_3$ solution. Thus, the presence of F$^-$ ions in AgF solution improves the synthesis/yield of AgNPs on PDMS by more than 2 orders of magnitude (a factor of about 125) compared to the fluoride-free AgNO$_3$ solution; further, the addition of NH$_4$F to the AgNO$_3$ ethanolic solution accelerates the Ag reduction on the PDMS surface by more than 1 order of magnitude (a factor about 30).

We next investigated the flexibility of the fluoride-assisted process using ethanolic solutions with different AgF concentrations (oxidizing agent) and PDMS slabs with different base-to-curing (reducing agent) ratios (Figure 3d-f and Figure S8a–d, Supporting Information).

Figure 3d shows the transmission spectra of PDMS slabs immersed for 1 min in ethanolic solutions at different AgF concentrations in the range 5–45 mM. The transmittance value at the plasmonic peak wavelength exponentially reduces with the AgF concentration from 81.6% at 5 mM to 1.2% at 45 mM (Figure 3e). This is consistent with a more efficient synthesis of AgNPs on the PDMS surface as the AgF molar concentration increases, once the immersion time is chosen. A similar behavior was observed with the increase of the curing agent in the PDMS slabs (Figure 3f). Once the immersion time of 1 min and AgF concentration of 15 mM were chosen, the transmittance value at the plasmonic peak wavelength reduced linearly with the curing agent concentration, from about 68% to 13% for base:curing agent ratios of 20:1 and 5:1, respectively (Figure S8c,d, Supporting Information).

Eventually, we tested the adhesion properties of AgNPs formed on PDMS slabs in a 15 mM AgF ethanolic solution for 4 min (Figure S9a–d, Supporting Information).

Two commercial tapes, standard and with high tensile strength (26 N cm$^{-1}$), as well as a bare PDMS slab, due to the excellent adhesive properties of PDMS that is commonly used in the literature for the transfer-printing of nanosized materials,[37] were employed for the adhesion test. The tape was stuck in the literature for the transfer-printing of nanosized materials, and Figure S7b, Supporting Information), confirming the excellent adhesive properties of PDMS that is commonly used in the literature for the transfer-printing of nanosized materials.

Figure 4a-1 shows a PDMS slab decorated with a 1D gradient of AgNPs with continuous-modulation of NP size/coverage. The slab was prepared using a constant insertion rate of 1/18 mm s$^{-1}$, for a total time of 12 min. The AgNP gradient possesses unique spatially-modulated plasmonic features that confers to the PDMS slab a transmittance spectrum tunable with the interrogation point over a large range (Movie S2, Supporting Information), as detailed later in this work. By using a step-wise insertion strategy, a PDMS slab with step-wise change of the size/coverage of AgNPs is achieved, as shown in Figure 4a-2 (Figure S10, Supporting Information). To further prove the flexibility of the proposed synthetic approach, we prepared 2D gradients of AgNPs on PDMS by superposition of two linear 1D gradients formed along the x (first gradient) and y (second gradient, upon rotation of the slab of 90°) directions, each one at a constant insertion rate of 1/18 mm s$^{-1}$ for 6 min. Figure 4b shows the 2D gradient of AgNPs. The NP distribution and size are linearly modulated from 0 to 6 min in the x and y directions, and from 0 to 12 min along the xy diagonal.

Remarkably, the transmittance spectra acquired on spatially-modulated slabs in surface points corresponding to 1, 4, and 12 min of decoration (Figures S10 and S11, Supporting Information) were in good agreement with those acquired on spatially-uniform slabs decorated with AgNPs for the same immersion times (Figure 3a). This is a clear indication of the good control and reliability of the decoration process with the immersion time, both at low and high insertion rates.

Additional experiments were carried out to further highlight advantages and flexibility of the proposed fluoride-assisted approach in the direct patterning of NPs. We first performed inhibition of the Si–H groups at the PDMS surface by selective oxygen plasma using a shadow mask containing a 2D array of holes with diameter ranging from 50 to 400 µm; maskless and selective formation of AgNPs on the PDMS areas not exposed to the oxygen plasma was then performed by immersion of the slab in a 15 mM AgF solution for 12 min. Results on the 2D NP patterning are summarized in Figures S12a–d, Supporting Information. Figure S12a, Supporting Information, shows the AgNP pattern formed on the PDMS surface; thanks to the efficient and fast NP synthesis, the plasma treatment was sufficient to inhibit the Ag$^+$ reduction on the PDMS surface and all the circular features were resolved (Figure S12b,c, Supporting Information). PDMS slabs treated with oxygen plasma over the whole surface were used as negative control and confirmed
no significant formation of AgNPs on the PDMS surface after 12 min immersion in the AgF solution (Figure S12d, Supporting Information).

Remarkably, the patterning cannot be achieved using the standard fluoride-free solution (i.e., 15 mM AgNO₃ in ethanol) (Figure S12e,f, Supporting Information). In this case, due to the poor yield/kinetic of the NP synthetic process, a synthesis time of more than 12 h is required to achieve a surface coverage/plasmonic resonance peak comparable to that obtained in 12 min in the 15 mM AgF solution. Oxygen plasma inhibition of Si–H groups at the PDMS surface is metastable, so that it fails in avoiding reduction of Ag⁺ ions at the PDMS surface at such longer synthesis times, resulting in the full coating of the PDMS surface with AgNPs. Direct patterning of metal NPs on the PDMS surface in a relatively short processing time opens up remarkable opportunity in flexible electronics, though not limited to.

We eventually characterized the AgNP-decorated PDMS slabs as plasmon-encoded flexible filters in terms of OD and ER (Figure 4c and Figure S13, Supporting Information), which are two key parameters commonly used to point out the quality of commercial filters. ⁴⁰ OD⁺ of the spatially-modulated slabs at the plasmonic resonance wavelength, namely, the logarithmic intensity ratio of the light falling upon the material to the light transmitted through the material, can be effectively tuned from 0 up to 5 by tuning the immersion time in the AgF solution from 0 to 12 min (Figure 4c, left axis). The experimental OD values (using a bare PDMS slab as reference) were about 0.5 after 1 min and 5.1 after 12 min of immersion in AgF, meaning that the 10-nm-thin layer of AgNPs grown on the PDMS surface can be used to attenuate light around 403 nm up to a factor 10⁵, namely, up to 5 orders of magnitude; this is comparable to OD values of commercial dielectric glasses and 3 order of magnitudes better than plasmonic nanolayers reported so far (Figure S14, Supporting Information). Consistently with values reported in the literature, 270 min of decoration with the fluoride-free AgNO₃ solution resulted in an OD value of 2, thus confirming that the fluoride-assisted AgNP synthesis enables the preparation of plasmonic PDMS slabs with features not achievable.

Figure 4. 1D and 2D spatially-resolved AgNP-decorated PDMS slabs and application of AgNP-PDMS slabs as optical filters in fluorescence microscopy. a) 1-Picture of an AgNP-PDMS slab featuring a continuous 1D gradient/modulation of the NP surface coverage and size, achieved in a 15 mM AgF solution with a constant insertion rate of 1/18 mm s⁻¹ for 12 min. 2-Pictures of 4-cm-long PDMS slabs with a step-wise spatial modulation of AgNP size/distribution, achieved by controlled immersion of the slab in a 15 mM AgF solution for 1, 4, and 12 min. b) Picture of an AgNP-PDMS slab featuring a continuous 2D gradient/modulation of the NP surface coverage and size, achieved in a 15 mM AgF solution with a constant insertion rate of 1/18 mm s⁻¹ for 6 min, first along the x-direction and then along the y-direction. c) Experimental OD and ER values measured at 403 and 635 nm on AgNP-PDMS slabs in points corresponding to immersion times of 1, 4, and 12 min in a 15 mM AgF solution. OD and ER values measured on slabs decorated in a 15 mM AgNO₃ solution (fluoride-free) are also reported for comparison. The error bars represent one standard deviation with respect to average values achieved over a number of 3 samples per decoration time. d,e) Imaging of fluorescent (510 nm) microbeads acquired with a bright-field optical microscope (Leica DM2500 M) using an AgNP-decorated (15 mM AgF solution for 4 min) PDMS slab as a rejection filter placed between the microbeads and the microscope objective d). Control images are acquired using a bare PDMS slab e). All the images are acquired using a 403 nm laser diode as the excitation source. Scalebar is 500 μm (200 μm in the inset). f) Photoluminescence spectrum of fluorescent microbeads and 403 nm laser diode acquired through the bare PDMS slab (black trace) and AgNP-PDMS filter (red trace).
with standard synthetic methods. Further, the ER\[^{[41]}\] of the decorated slabs, namely, the logarithm intensity ratio of light transmitted through the material at a given wavelength outside the plasmonic region (i.e., 635 nm) to the light transmitted at the plasmonic peak wavelength (i.e., 403 nm), was as high as 100 dB after 12 min of decoration in AgF solution (Figure 4c, right axis); 270 min in AgNO\(_3\) solution yielded ER = 40 dB, to be compared with a similar ER value achieved after 4 min in AgF solution.

Remarkably, the optical properties of AgNP-decorated PDMS slabs (4 min in a 15 mM AgF solution) were proved to be insensitive to slab bending and incidence angle. Figure S15, Supporting Information, shows that the optical properties of AgNP-decorated slabs were unchanged over different bending radii, for multiple (>100) bending/release repetitions. Insensitivity of the transmittance to angle and bending is consistent with the plasmonic nature of AgNP-decorated PDMS filter, for which the resonance wavelength is mainly dependent on size and distribution of the NPs on the PDMS surface; indeed, being AgNPs randomly arranged on the PDMS surface, their size and distribution do not significantly change with incidence angle and bending, at least for the values tested in this work. Figure S16a, Supporting Information, shows the angle-resolved transmittance map acquired on an AgNP-decorated slab (4 min in a 15 mM AgF solution) for incidence angles 0 to 55°. The transmittance spectra acquired over the different incidence angles are given in Figure S16b, Supporting Information. The transmittance properties of the slab did not change with incidence angles in the range 0–45°; a slight broadening of the plasmonic peak associated with a small decrease of the transmittance (yet around 80%) at longer wavelengths was appreciable beyond 45°.

We next investigated uniformity and reliability of the decoration process in an AgF solution over a larger area to demonstrate that the process can be easily up-scaled. Figure S17, Supporting Information, shows an optical picture and transmittance spectra of a 9-cm-long AgNP-decorated slab immersed in a 15 mM AgF solution for 4 min. A uniform decoration with AgNPs is apparent over the whole area, as indicated by the even color intensity appreciable by naked eye and quantified by the excellent superposition of transmittance spectra acquired at different points of the slab. These latter were also in good agreement with those achieved on smaller samples with same decoration time.

Eventually, we verified the application of AgNP-PDMS slabs prepared in AgF ethanolic solution as rejection filters in fluorescence microscopy. An AgNP-decorated PDMS slab (4 min in a 15 mM AgF solution) with OD = 2.6 was placed between the objective lens of a commercial bright-field optical microscope and a glass slab containing fluorescent beads (\(\Delta_{\text{res}} = 510\) nm) of diameter 105–126 \(\mu\)m. A commercial laser diode at 403 nm was used as the excitation source. A bare PDMS slab (without AgNPs) was used to acquire control images. Figure 4d–f summarizes the results of the experiments. The AgNP-PDMS filter was able to effectively reject the excitation light thanks to the high OD value at 403 nm, further retaining the green fluorescence of the microbeads (Figure 4d,f, red trace). Control images acquired through the bare PDMS slab clearly show the leakage of the 403 nm laser light that shields the green fluorescence of the beads (Figure 4e,f, black trace).

3. Conclusions

The fundamental advance of this work is in real-time and in situ control of the metal NP patterning during the synthetic process—we demonstrated the maskless preparation of 1D and 2D gradients and patterns of metal NPs on PDMS via modulation of the size and surface coverage of NPs (Ag and Au NPs) formed through in situ reduction in metal solutions containing fluoride ions.

We showed that the presence of F\(^{-}\) ions in the metal solution improves density and kinetics of the NP formation process up to a factor of 10 and 100, respectively, with respect to fluoride-free solutions, by tremendously lowering the concentration of H\(^{+}\) ions released upon reduction of metal ions (Ag\(^{+}\) and Au\(^{3+}\)) at the PDMS surface. This enables the modulation of size and coverage of the NPs formed on the PDMS surface with time and over space by controlling the insertion strategy and rate of the PDMS slab in the metal solution and/or by former metastable inhibition of Si—H groups at the PDMS surface with oxygen plasma.

We further demonstrated that 1D and 2D AgNP gradients formed on PDMS possess wavelength- and spatially-resolved plasmonic performance comparable to those of dielectric/interferometric optical filters; specifically, AgNP gradients with OD variable from 0.5 to 5 and ER variable between 10 and 100 dB were fabricated on PDMS slabs in 12 min. Application of AgNP-PDMS slabs in fluorescence microscopy resulted in an effective rejection of the excitation laser light at 403 nm, enabling acquisition of fluorescent emission/images at wavelength higher than 510 nm.

We envisage that this work will have implications in a number of application areas beyond those discussed here, including flexible electronics, sensing, water cleaning, photovoltaics, bactericide surface. The unique features of the NP synthesis in fluoride-rich metal solutions, in terms of efficiency, tunability, speed, reliability, will play a relevant role in the preparation of composite nanostructured materials, providing access to functionalities (e.g., optical, electrical, mechanical, magnetic) that are otherwise difficult (or impossible) to achieve with state-of-the-art fluoride-free methods.

Furthermore, building on our results, the fluoride-assisted synthesis of NPs can be immediately extended to other metals (e.g., Pt, Pd) and substrates (e.g., silicon), with respect to those discussed in this work, further broadening the impact of the proposed route both in material science and applications.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors thank Tecla Radaelli, Paolo Targa, and Francesco Somaini of the Physics Lab at ST Microelectronics for their support with TEM-EDX characterization. G.B. also acknowledges the support of Italian Ministry of Education, University and Research (MIUR) in the framework of the CrossLab project (Departments of Excellence).
Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

Keywords
fluorescence microscopy filters, fluoride anions, gold nanoparticles, in situ synthesis, nanoparticle gradients, polydimethylsiloxane, silver nanoparticles, spatially resolved plasmonics

Received: January 24, 2021
Revised: March 25, 2021
Published online: May 4, 2021

[1] Z. Nie, A. Petukhova, E. Kumacheva, Nat. Nanotechnol. 2010, 5, 15.
[2] J. D. S. Newman, G. J. Blanchard, Langmuir 2006, 22, 5882.
[3] E. K. W. Tan, P. K. Shrestha, A. V. Pansare, S. Chakrabarti, S. Li, D. Chu, C. R. Lowe, A. A. Nagarkar, Adv. Mater. 2019, 31, 1901802.
[4] G. Hu, T. Albrow-Owen, X. Jin, A. Ali, Y. Hu, R. C. T. Howe, K. Shehzad, Z. Yang, X. Zhu, R. I. Woodward, T. C. Wu, H. Jussila, J. B. Wu, P. Peng, P. H. Tan, Z. Sun, E. J. R. Kelleher, M. Zhang, Y. Xu, T. Hasan, Nat. Commun. 2017, 8, 278.
[5] Y. Kim, J. Zhu, B. Yeom, M. Di Prima, X. Su, J.-G. Kim, S. J. Yoo, C. Uher, N. A. Kotov, Nature 2013, 500, 59.
[6] E. Yilmaz, G. Ertas, E. Bengu, S. Suzer, J. Phys. Chem. C 2010, 114, 18401.
[7] A. K. Yetisen, I. Naydenova, F. Da Cruz Vasconcellos, J. Blyth, C. R. Lowe, Chem. Rev. 2014, 114, 10654.
[8] G. V. Ramesh, S. Porel, T. P. Radhakrishnan, Chem. Soc. Rev. 2009, 38, 2646.
[9] R. R. Bhat, J. Genzer, Nanotechnology 2006, 18, 025301.
[10] C. Hsuwiler, T. P. Kunzler, M. Textor, J. Vörös, N. D. Spencer, Langmuir 2007, 24, 5929.
[11] R. V. Goreham, R. D. Short, K. Vasilev, J. Phys. Chem. C 2011, 115, 3429.
[12] J. Sindram, K. Volk, P. Mulvaney, M. Karg, Langmuir 2019, 35, 8776.
[13] A. O. Lundgren, F. Björefoer, L. G. M. Olofsson, H. Elwing, Nano Lett. 2008, 8, 3989.
[14] A. Lundgren, M. Hulander, J. Brorsso, M. Hermansson, H. Elwing, O. Andersson, B. Liedberg, M. Berglin, Part. Part. Syst. Charact. 2014, 31, 209.
[15] M. Hulander, A. Lundgren, L. Faxälv, T. L. Lindahl, A. Palmquist, M. Berglin, H. Elwing, Colloids Surf., B 2013, 110, 261.
[16] J. Zhou, D. A. Khodakov, A. V. Ellis, N. H. Voelcker, Electrophoresis 2012, 33, 89.
[17] M. P. Wolf, G. B. Saleib-Beugelaar, P. Hunziker, Prog. Polym. Sci. 2018, 83, 97.
[18] D. Qi, K. Zhang, G. Tian, B. Jiang, Y. Huang, Adv. Mater. 2020, 33, 2003155.
[19] L. Li, H. Lin, S. Qiao, Z.-Y. Huang, J.-Y. Li, J. Michon, T. Gu, C. Alosno-Ramos, L. Vivien, A. Yadav, K. Richardson, N. Lu, J. Hu, Light: Sci. Appl. 2018, 7, 17138.
[20] D. Zhu, S. Handschu-Wang, X. Zhou, J. Mater. Chem. A 2017, 5, 16467.
[21] C. Majidi, Adv. Mater. Technol. 2019, 4, 1800477.
[22] I. Pastoriza-Santos, J. Pérez-juste, G. Kickelbick, L. M. Liz-Marzán, Nanoosci. Nanotechnol. 2006, 6, 453.
[23] C. Li, M. Liu, L. Yan, N. Liu, D. Li, J. Liu, X. Wang, J. Lumin. 2017, 190, 1.
[24] Q. Zhang, J.-J. Xu, Y. Liu, H.-Y. Chen, Lab Chip 2008, 8, 352.
[25] A. Goyal, A. Kumar, P. K. Patra, S. Mahendra, S. Tabatabaei, P. J. J. Alvarez, G. John, P. M. Ajayan, Macromol. Rapid Commun. 2009, 30, 1116.
[26] J. R. Dunklin, G. T. Forcherio, K. R. Berry, D. K. Roper, ACS Appl. Mater. Interfaces 2013, 5, 8457.
[27] M. G. Millyard, F. M. Huang, R. White, E. Spigone, J. Kivioja, J. J. Baumberg, Appl. Phys. Lett. 2012, 100, 073101.
[28] S. Song, X. Ma, M. Pu, X. Li, K. Liu, P. Gao, Z. Zhao, Y. Wang, C. Wang, X. Luo, Adv. Opt. Mater. 2017, 5, 1600829.
[29] Y. Tamai, H. Tanaka, K. Nakanishi, Macromolecules 1995, 28, 2544.
[30] Y. S. Li, T. Verbiest, R. Strobbe, I. F. J. Vankelecom, J. Mater. Chem. A 2013, 1, 15031.
[31] Y. Lee, S.-G. Oh, Colloids Surf., A 2014, 459, 172.
[32] R. Rich, in Inorganic Reaction in Water, Springer Berlin Heidelberg, Berlin 2007, pp. 25–35.
[33] K. Maity, D. K. Panda, E. Lochner, S. Saha, J. Am. Chem. Soc. 2015, 137, 2812.
[34] J. Clayden, N. Greeves, S. G. Warren, in Organic Chemistry, Oxford University Press, Oxford 2012.
[35] G. Milczarek, T. Rebis, J. Fabianska, Colloids Surf., B 2013, 105, 335.
[36] S. Aghiroti, S. Mukherji, S. Mukherji, RSC Adv. 2014, 4, 3974.
[37] A. Carlson, A. M. Bowen, Y. Huang, R. G. Nuzzo, J. A. Rogers, Adv. Mater. 2012, 24, 5284.
[38] T. Trantidou, Y. Elani, E. Parsons, O. Ces, Microsyst. Nanoeng. 2017, 3, 16091.
[39] J. X. J. Zhang, K. Hoshino, in Micro and Nano Technologies, 2nd Ed., Academic Press, Oxford 2019.
[40] Thorlabs UV/VIS Bandpass & Laser Line Filters, https://www.thorlabs.com/newgrouppage.cfm?objectgroup_id=1001 (accessed: April 2021).
[41] C. DeCusatis, in Handbook of Fiber Optic Data Communication, 4th Ed., Academic Press, Oxford 2013.