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Surface Functionalization of Cyclic Olefin Copolymer by Plasma-Enhanced Chemical Vapor Deposition using Atmospheric Pressure Plasma Jet for Microfluidic Applications

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Lab-On-A-Chips promise solutions for high throughput and specific analysis for environment and health applications, with the challenge to develop materials allowing fast, easy and cheap microfabrication and efficient surface treatment. Cyclic Olefin Copolymer (COC) is a promising thermoplastic, easily microfabricated for both rapid prototyping and low-cost mass production of microfluidic devices, but still needing efficient surface modification strategies. This study reports for the first time the optimization of an easy COC silica coating process by Plasma-Enhanced Chemical Vapor Deposition at Atmospheric Pressure (APPECVD) with plasma jet and tetraethylorthosilicate (TEOS) as precursor, leading to a 158±7 nm thickness and a 14 days stability of hydrophilic properties for a COC-embedded microchannel (100 μm), paving the way for a simplified and controlled COC surface modification.

1 Introduction

Lab-On-A-Chip (LOAC) technology promises solutions for high throughput and highly specific analysis for environment and health applications. The choice of the material to engineer them is crucial. Indeed, each material has its own physicochemical properties which determine the microfabrication method. Moreover, it is sometimes necessary to modify the physico-chemical properties of the microchannel surface for subsequent functionalization and/or fluid flow control. Therefore, the challenge is to develop LOAC materials allowing fast, easy and cheap microfabrication methods and efficient surface treatment. Since nearly 20 years poly(dimethyl siloxane) (PDMS) has been a popular material for the fabrication of microfluidic devices due to its easy microfabrication method, its elastic and transparency properties and its biocompatibility.^[1,2] However, there is nowadays a move towards thermoplastic materials for their reduced cost and easier microfabrication.^[3-7] Among the various thermoplastics, cyclic olefin copolymer (COC) has emerged as it offers a high chemical resistance and exhibits an optical transparency close to that of glass (for wavelengths over 300 nm).^[8] COC microsystems are furthermore easily micro fabricated allowing for both rapid prototyping and low-cost mass production.^[9,10] Despite all these advantages, COC's main drawbacks as a material for microfluidics are its surface chemical inertness and its hydrophobic properties. In the case of LOACs, the integration of the different steps of an analytical chain (pre-concentration, separation and detection) in microchannels mainly implies a chemical modification of the COC surface. Some COC microchannel treatments provide hydrophilic properties to control electrokinetic separations^[11-15] or to integrate chemical reactive groups for ligands^[12,13,16-19] or monolith^[20-22] immobilization. Moreover, surface functionalization of COC micro channels minimizes the adsorption of analytes in particular biological molecules.^[11,14,18,23] Nowadays, three main

66 COC surface functionalization strategies are commonly used: UV/ozone oxidation,^[24,25]
67 photografting^[11,13,15,20,21,23,26–29] and plasma processes^[16,19,30–36].

68 The UV/ozone oxidation procedure relies on the exposition of the COC surface under a
69 mercury lamp and in an air-filled chamber at atmospheric pressure resulting in the generation
70 of ozone. This treatment permits to confer hydrophilic properties to COC surfaces.^[24,25]

71 Photografting is performed by a photoinitiator under a UV light, which excitation promotes
72 abstraction of hydrogen atoms from the COC surface, leading to the formation of radicals
73 which then initiate a surface grafting polymerization process.^[37] Generally, photografting is
74 performed through a single step, that can lead to a significant amount of ungrafted
75 polymer.^[23]

76 Plasma is widely used for COC surfaces treatment^[16,19,30–35,38], so as to shift the COC surface
77 to a hydrophilic one, due to its oxidation, molecule chain scissions, substitution and
78 recombination^[31,38]. Several gases or gas mixtures have been extensively used for plasma
79 generation such as oxygen, argon or nitrogen.^[30–32,38] The main advantages of this surface
80 treatment are that it is an environmentally benign process and leads to a homogeneous
81 surface.^[30–32,38]

82 One renowned plasma process to deposit chemical layer on surfaces is Plasma-Enhanced
83 Chemical Vapor Deposition (PECVD).^[39] This low-pressure plasma process consists in the
84 fragmentation of a precursor inside gas plasma. Organosilicon-oxygen mixtures are widely
85 used to generate thin silica film deposition, notably for microfluidic applications.^[35–36] The
86 thin silica layer confers hydrophilic properties allowing the generation of a controlled
87 electroosmotic flow for electrokinetic separations inside COC microchannels.^[40] Moreover,
88 the presence of reactive chemical functions, such as silanol groups (SiOH), due to plasma
89 polymerization of organosilicon precursors,^[35–36] could allow the grafting of several chemical
90 entities^[41–42]. Da Silva et al. have shown the possibility to deposit by PECVD at low pressure
91 thin layers of silica (700 nm thickness) on COC surface.^[36] This layer was characterized by

water contact angle (WCA), X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FTIR) and ellipsometry measurements, showing the presence of a silica film on the COC substrate. Ladner et al. demonstrated the activation of COC surface by a plasma at low pressure composed of 1-bromopropane as the brominated precursor and of argon gas, to create brominated functionalities that could permit to immobilize ligands through subsequent chemical modifications *via* a click chemistry reaction.^[19]

The main drawback of many plasma treatments is the use of low pressures leading to expensive and cumbersome plasma equipments hardly adapted for industrial continuous operations.^[43] Moreover, generation of a vacuum could take several hours, depending on the vacuum required, and increase the overall process time. To overcome this, plasma surface treatments were further developed at atmospheric pressure. A study has demonstrated the possibility to deposit a thin silica film in few minutes inside COC microchannels at atmospheric pressure with organosilicon precursor.^[35] The silica layer was deposited with a helium-oxygen plasma generated between two electrodes integrated outside the chip and an organosilicon precursor circulating inside the COC channel.

This study reports, for the first time, the deposition of a silica coating inside COC microchannel with a plasma jet at atmospheric pressure. Plasma jet is advantageous over plasma treatments at atmospheric pressure proposed by Theelen et al.^[35] Indeed, it does neither need the integration and the alignment of electrodes outside the chip, nor a gas flow through the microchannel, which greatly simplifies the microfabrication steps and avoids the use of several external equipments. Moreover, the plasma jet permits to treat several microchannels simultaneously in a few seconds. The experimental conditions for this COC surface modification with tetraethylorthosilicate (TEOS) were optimized so as to obtain a homogeneous density of silanol groups on its surface, for further functionalization and for the generation of an electroosmotic flow inside COC microchannels. Experimental conditions were optimized in terms of distance between the nozzle and the substrate, TEOS and carrier

air flow rates, and number of treatment cycles. The treatment of COC channels by the Atmospheric Pressure plasma jet proved to be fast and easily transposable for industrial applications. This process does not require complicated microfabrication steps, is environmentally friendly and will allow to design new LOACs involving COC materials.

2 Materials and Chemicals

COC plates (Topas® grade 8007, $T_g = 75^\circ\text{C}$, 1 mm thickness) were purchased from Microfluidic ChipShop. Brass mold (8 cm * 8 cm * 5 mm) was purchased from GREM (France). Silica wafers (4 inches, 500 μm of thickness) were purchased from Prolog Semicor (Ukraine). Tetraethylorthosilicate (TEOS, 98%), was purchased from Sigma-Aldrich. 2-propanol (99.9%) was purchased from GPR Rectapur. Ultra-pure water (resistivity ≥ 18.2 M Ω , Purelab Flex, Elga Veolia, France) was used.

3 General Procedure for the Silica-Like Deposition Using AcXys® plasma jet on COC Surface

In this study, the silica thin film has been deposited with an atmospheric pressure plasma system produced by AcXys® Technologies (Saint Martin le Vinoux, France). This system is composed of three command modules and a moving nozzle. The frequency is set with ULS command module where the power and the gas throughout are displayed. Thus, the APPJ (Atmospheric Pressure Plasma Jet) nozzle is mounted on a motorized xyz table (controlled using the Quickset module) so that it can sweep the surface of the sample at constant speed

(fixed at 150 mm/s) in order to deliver a homogeneous treatment. The plasma jet is generated by introducing air (35 L/min) into the plasma torch. The ULC module is used to inject the liquid organosilicon precursor (TEOS) contained in a pressurized tank into the treatment nozzle at a flow rate between 10 μ L/min and 500 μ L/min. The carrier gas (at a flow rate between 5 L/min and 25 L/min) vaporizes the liquid precursor which is then injected in post-discharge *via* pipes placed on each side of the nozzle. It should be noticed that the liquid precursor is controlled by a liquid flow meter before being nebulized by the venturi effect. The precursor thus nebulized is transported by the carrier gas to the deposition nozzle. The system operates at room temperature.

Figure 1. Picture of the torch plasma AcXys®.

4 Microfabrication of COC Channels

The design of channels was performed with the 3D CAO software Inventor® and then transposed on a brass mold with micro-molding technic (Minitech®). Afterwards, hot embossing was applied to COC (75 mm * 25 mm * 1 mm) plates, inside a 3 tons hydraulic

press (Scannex[®]) at 150°C, under a 15 bars pressure for 30 min. The system was then cooled at room temperature before shutting off the pressure. The dimensions of simple COC rectangular microchannels used during the study are of 6 cm length, 100 µm width and 30 µm height.

5 Characterizations of the Silica-Like Deposition on COC Surface

COC raw plates and COC treated plates are characterized by the following methods. Infrared spectra were acquired using a Fourier Transform Infrared Spectrometer (Cary 660 Spectrometer, Agilent) with an Attenuated Total Reflectance module (GladiATR, Pike). The ATR-FTIR spectra were collected from 4 000 to 500 cm⁻¹, at a resolution of 4 cm⁻¹. 100 scans were made for each measurement. The background (air) was taken before each measurement. Static ultrapure water (resistivity ≥ 18.2 MΩ) contact angle (WCA) measurements were done thanks to a DSA25-Drop Shape Analyser from Krüss. A 2 µL droplet was released from a syringe and placed slowly on the surface which contact angle was measured after 30 s. Similar experiments were conducted on the modified material after 14 days of storage in a petri dish at room temperature and at atmospheric pressure to simulate the COC microchips storage conditions. Images of droplet formation captured using a high-resolution camera were analyzed with the Advance Image Analysis Software. The reported contact angle values are an average at least three measurements at various locations on COC plates. Optical microscopy (Axio Observer A1, Zeiss) was performed with a CCD digital camera (Pike F145B, Allied Vision Technologies Stadtroda, Germany) and an image acquisition software (Hiris, RD Vision, France). Images were reprocessed *via* Image J software. Spectroscopic ellipsometry (UVISEL, Horiba Jobin Yvon) was performed at an incidence angle of 60°, with a 75 W Xe lamp over a spectral range of 245±2100 nm (i.e., 0.6±5 eV). Ellipsometry is based on variation of light polarization, which is reflected by the sample.^[44] As COC substrates do not reflect light,^[8] a silica wafer was chosen as model substrate to

determine the thickness of silica deposits^[19]. The reported thickness values are an average of at least three measurements at various locations on modified of plate surfaces.

6 Results and Discussion

As a preliminary treatment, COC plates were sonicated in isopropanol and then water (during 3 min). When treated with the plasma jet, COC plates were attached with carbon tape on a holder. So as to remove eventual low molecular weight fragments at the topmost COC surface layer,^[36] they were pre-treated by Air Plasma at Atmospheric Pressure (APAP) at 80 kHz (987 W, 35 L/min air) with a nozzle speed of 150 mm/s. Indeed, oxygen radicals and excited molecules produce volatile organic and inorganics compounds such as CO, CO₂, H₂O molecules, eliminating low molecular weight oxidized fragments. In a second step, a silica film was then deposited on COC surfaces by APPECVD process, under an air plasma to decompose TEOS 80 kHz (1030 W, 35 L/min air) with a nozzle speed of 150 mm/s. The APPECVD process could be applied several times, “a treatment cycle” being defined as one APPECVD process.

The influence of several experimental parameters on the silica coating of COC substrates (2 cm²) was studied. These parameters are the distance between the nozzle and the substrate surface (from 16.5 to 31.5 mm), the TEOS flow rate (from 100 µL/min to 200 µL/min), the carrier air flow rate (from 5 to 20 L/min), and the number of treatment cycles (from 1 to 5). The COC plates before treatment, after the APAP step, and after APAP + APPECVD were characterized by ATR-FTIR, WCA and optical microscopy. The thickness of silica layers was measured by ellipsometry.

6.1 Characterizations of Untreated and Plasma Treated COC Plates

Figure 2. COC substrate characterizations before any treatment (bottom graph and image), after APAP treatment (middle graph and image) and after APAP + APPECVD treatments (upper graph and image) by (a) ATR-FTIR, and (b) optical microscopy. Experimental conditions for APAP: 16.5 mm between torch and surface and 150 mm/s nozzle speed (~300 ms treatment time). Experimental conditions for APPECVD: 16.5 mm between torch and surface, 200 $\mu\text{L}/\text{min}$ TEOS, 5 L/min carrier air and 150 mm/s nozzle speed (~300 ms treatment time).

Untreated COC surfaces present an ATR-FTIR spectrum (Figure 2.a) with absorption bands located at 2947 and 2868 cm^{-1} which are assigned to carbon/hydrogen stretching vibration modes of $-\text{CH}_2$ and $-\text{CH}_3$ groups from the polymer backbone. The band around 1456 cm^{-1} corresponds to the wagging mode of $-\text{CH}_3$ groups.^[36] The WCA measurements of untreated COC plate ($95 \pm 1^\circ$) confirmed the hydrophobic properties of the polymer.^[8] Optical

microscopy characterization showed that the COC surface was transparent and homogeneous (Figure 2.b).^[8]

The ATR-FTIR spectrum of APAP-treated COC surface did not present any difference with that of the untreated COC surface (Figure 2.a). After APAP treatment, the WCA values dropped from $95\pm 1^\circ$ to $48\pm 7^\circ$. This can be explained by the insertion of polar functional groups onto the surface of the raw hydrophobic COC substrate after APAP treatment,^[30,33,34,38,45] leading to a more hydrophilic surface. ATR-FTIR spectroscopy is not sensitive enough to detect the presence of polar groups deposited by APAP treatment. Roy et al. have suggested a possible reaction mechanism on COC surface during plasma treatment^[38], the electrons, ions and free radicals generated during high energy plasma irradiation promoting breakage of the C-H and C-C bonds. This would lead to shorter polymer carbon chain, the formation of other molecules through recombination reaction and also crosslinking.^[38] As nitrogen and oxygen atoms are present, chemical interactions between the radicals from air and thermoplastics occur, which promote the insertion of polar groups like hydroxyl, ketone or carboxylic acid for example.^[32] Optical microscopy characterization showed that APAP-treated COC surface did not present any difference compared to untreated COC (Figure 2.b). APAP treatment preserved the optical transparency of the substrate.

After APPECVD treatment, three new ATR-FTIR bands appeared in addition to the characteristic bands of COC backbone. During APPECVD treatment, a silica layer was deposited due to the reaction between oxygen reactive atoms and the precursor, generating emission of carbon dioxide and water.^[36] The two bands at 1225 cm^{-1} and 1078 cm^{-1} correspond to the Si-O-Si asymmetrical and symmetrical stretching modes, respectively.^[36,46] The band located at 3342 cm^{-1} is assigned to hydroxyl group (stretching mode). This band is related to the presence of Si-OH groups, as the interaction between the $-\text{SiO}_2$ layer and the air

leads to the formation of –OH groups at the outer surface of the coating.^[36] The initial bands originating from the COC thermoplastic backbone (2947, 2868 and 1456 cm⁻¹) were still present due to the low thickness of the silica layer (39±5 nm) compared to the depth to the analysis.^[36] The WCA values dropped from 48±7° to 27±2° for APAP- and APAP + APPECVD-treated COC surface, respectively, evidencing the deposition of a more hydrophilic layer. Optical microscopy characterization shows that APPECVD treatment induced micro-cracked surface layer (**Figure 2.b**).

In order to generate a homogeneous immobilization of ligands/monoliths or a repeatable electroosmotic flow between various batches of COC LOACs, the surface layer should be as homogeneous as possible. Micro-cracks may be due to the generation of an elevated temperature during plasma treatment that could degrade the surface. By increasing the distance between the nozzle and the substrate, temperature during the treatment should be lowered.

6.2 Influence of the Distance Between the nozzle and the Surface on the Silica Coating

To avoid the presence of cracks evidenced on APAP + APPECVD-treated COC surface, probably caused by a too high treatment temperature process, the distance between the torch and the substrate was increased, step by step (by 5 mm), from 16.5 mm and 31.5 mm. The increase in this distance should allow reducing the temperature during the treatment. The study was performed in the same experimental conditions as previously described except for the distance between the torch and the substrate. For each distance, the thickness of the silica layer was measured by ellipsometry and the presence of cracks was checked by optical microscopy (Table 1).

Table 1. Influence of the distance between the torch and the COC surface on the silica layer thickness determined by ellipsometry. For experimental conditions for silica deposition, see Figure 2.

Distance between the torch and the surface of the substrate [mm]	Silica coating thickness [nm]	Presence of cracks
16.5	39±5	Yes
21.5	43±11	Yes
26.5	38±8	Yes
31.5	20±3	No

When torch/substrate distance was increased, the silica layer thickness decreased concomitantly. This can be explained by the fact that, air/TEOS plasma spot reaches the COC surface with a large diameter, leading to less TEOS reactive species density onto the COC surface. The cracks were no more visible when applying a distance of 31.5 mm. For all the tested distances, the wettability did not change, with a constant value of ~30°.

6.3 Influence of the TEOS flow rate and number of treatment cycles

The influence of the TEOS flow rate (100 and 200 µL/min) and the number of treatment cycles (1, 3 and 5) on the properties of the deposited silica layer were studied by ATR-FTIR, WCA and ellipsometry (**Figure 3**). For this study, the carrier air flow rate was fixed at its high value (20 L/min) to consider a high silica and silanol density, for a better sensitivity with ATR-FTIR measurements.

Treatment cycles	WCAs ($^{\circ}$)	Silica coating thickness (nm)
1 cycle	32 ± 1	37 ± 6
3 cycles	24 ± 2	43 ± 2
5 cycles	$<10 \pm 0$	74 ± 4

Treatment cycles	WCAs ($^{\circ}$)	Silica coating thickness (nm)
1 cycle	$36 \pm 1^{\circ}$	$44 \pm 2 \text{ nm}$
3 cycles	$16 \pm 3^{\circ}$	$87 \pm 4 \text{ nm}$
5 cycles	$<10 \pm 0^{\circ}$	$158 \pm 7 \text{ nm}$

Figure 3. COC substrate characterizations (ATR-FTIR, WCA and ellipsometry) after the overall plasma treatment: (APAP followed by 1 (~300 ms), 3 (~900 ms) or 5 (~1.5 s) APPECVD treatment cycles. Experimental conditions for APAP pre-treatment: 31.5 mm between torch and surface, 1 cycle treatment (300 ms). Experimental conditions for APPECVD: 31.5 mm between torch and surface, (a) 100 or (b) 200 $\mu\text{L}/\text{min}$ of TEOS and 20 L/min of carrier air flow rate.

For each TEOS flow rate, the peak intensities attributed to the silica thin film (3342, 1225 and 1078 cm^{-1}) increased with the number of treatment cycles. On the other side, peak intensities originating from the thermoplastic backbone (2947, 2868 and 1456 cm^{-1}) decreased when increasing the number of cycles (**Figure 3**). These results are consistent with an increase in silica deposit with the number of cycles. These results furthermore indicate that wettability increased with the number of treatment cycles. Concerning ellipsometry measurements, the layer thickness was confirmed to increase with the number of treatment cycles. Moreover, the TEOS flow rate played a key role on the silica layer characteristics. The intensity of the band attributed to -OH groups from silanol (3342 cm^{-1}) was twice higher at 200 $\mu\text{L}/\text{min}$ (5 cycles) compared to 100 $\mu\text{L}/\text{min}$ (5 cycles) of flow rate (**Figure 3**). The higher the flow rate, the more hydrophilic the treated surface and the thicker the layer. This result is in accordance with previous studies.^[47] So a higher silica density was deposited with the higher TEOS flow rate on COC surface. Optical microscopy characterizations were done to verify the absence of visible cracks with all combinations of experimental conditions tested. For all of them, no crack on the surface treated by APAP + APPECVD were noticed (data not shown).

6.4 Influence of the Carrier Air Flow Rate

Another experimental parameter for the optimization of the silica layer is the carrier air flow rate, which was varied from 5 to 20 L/min . For each flow rate, ATR-FTIR, WCA and ellipsometry measurements were performed and the presence of cracks was checked by optical microscopy (**Figure 4**).

Figure 4. COC substrate characterizations by (a) ATR-FTIR, (b) WCA and ellipsometry, and (c) optical microscopy after APAP and 5 APPECVD treatment cycles. Experimental conditions for APAP pre-treatment: 31.5 mm between torch and surface, 1 cycle (300 ms). Experimental conditions for APPECVD: 31.5 mm between torch and surface, 200 $\mu\text{L}/\text{min}$ of TEOS, 5 treatment cycles (1.5 s) and 5 (blue) or 20 L/min (red) of carrier air flow rate.

ATR-FTIR spectra indicate that the absorbance of the bands attributed to the silica layer (3342, 1225 and 1078 cm^{-1}) increased with the carrier air flow rate, whereas the absorbance of the bands originating from the thermoplastic backbone (2947, 2868 and 1456 cm^{-1}) decreased (**Figure 4.a**). The thickness of the silica layer increased from 78±2 nm to 158±7 nm, when the carrier air flow increased from 5 L/min to 20 L/min (**Figure 4.b**). It therefore seems that the increase in carrier air flow leads to higher silanol density on plasma treated COC thermoplastic (**Figure 4.a and 4.b**). This can be explained by an increase in interaction between SiO_2 layer and the air, as reported in the literature.^[38] With 5 L/min and 20 L/min carrier air flow rates, the optical characterizations of the surface proved the absence of crack

on the silica deposit (**Figure 4.c**). Therefore, the objective to obtain a sufficient and homogeneous surface silanol density for further functionalization^[41-42] can be reached with the following APPECVD conditions: a 31.5 mm distance between the torch and the surface, 200 μ L/min TEOS flow rate, 20 L/min carrier air flow rate and 5 treatment cycles. This COC surface modification should allow the generation of a controlled electroosmotic flow inside COC microchannels^[40]. The silica layer was then of 158 ± 7 nm thickness with a contact angle of less than 10° . These performances are similar to the ones of other plasma processes on COC surfaces for silica deposition in terms of layer thickness (between 250 nm^[35] and 700 nm^[36] for atmospheric pressure and low pressure plasma respectively) and wettability ($\sim 10^\circ$). The plasma process described herein relies on simplified conditions in terms of equipments, treatment rapidity and costs^[41] and allows generating the deposition of a silica layer on COC surface with a similar wettability and the same order of magnitude for the silica layer thickness (between 100 and 900 nm) as the plasma process at low pressure

6.5 Stability of the Silica Layer

The stability of the silica layer deposited using the optimized experimental conditions (APPECVD: 31.5 mm between torch and surface, 200 μ L/min TEOS flow rate, 20 L/min carrier air flow rate and 5 treatment cycles) was studied by WCA measurements. APAP + APPECVD-treated COC plate was stored in a petri-dish at room temperature and at atmospheric pressure for 14 days to simulate the COC microchips storage conditions. As a matter of comparison, untreated COC surface and APAP-treated COC plates were stored and studied under the same conditions (**Figure 5**).

Figure 5. Evolution of WCA measurements in function of storage time (0 to 14 days) for raw (COC), pre-treated with APAP (COC + APAP) and fully treated (COC + APAP + APPECVD) COC surface. Storage conditions: in petri-dish at atmospheric pressure and room temperature. Experimental conditions for APAP: 31.5 mm between torch and surface and 1 cycle (300 ms). Experimental conditions for APPECVD: 31.5 mm between torch and surface, 200 μ L/min TEOS flow rate, 20 L/min carrier air flow rate and 5 treatment cycles (1.5 s).

As shown in **Figure 5**, silica layers deposited on COC surface are stable over 14 days, in accordance with another study.^[36] The COC plates with a APAP + APPECVD plasma treatment can thus be stored during 2 weeks at atmospheric pressure and room temperature before further processing.

6.6 Optical Characterization of Plasma Treated COC Microchannels

So as to evaluate the transposition of our process into COC microchannels, preliminary experiments were conducted using optimized conditions for silica coating in single COC

microchannels of 6 cm length, 100 μm width and 30 μm height. Optical characterizations of COC microchannels were performed before and after APAP + APPECVD treatment, as illustrated in Figure 6.

Figure 6. Optical characterizations of COC microchannels (a) before and after (b) silica coating by plasma treatment at atmospheric pressure. Experimental conditions for APAP and APPECVD: see Figure 5. Fully treatment time (COC + APAP + APPECVD) microchannel is ~ 2.4 s. The black line is 100 μm bar scale.

This figure shows that scratches inside COC microchannel due to the brass mold can be observed (Fig 6 a). After APAP + APPECVD treatment, almost all scratches disappeared, probably screened by the deposition of a thin silica layer into the microchannel (**Figure 6.b**). The thin silica layer overlaid the defects inside COC microchannels. These results prove the efficient transposition of the *in situ* plasma process, inside microdevices.

7 Conclusion

This study reports for the first time a new plasma process for simplified, quick and efficient silica layer deposition on COC surfaces. This new procedure employs Plasma-Enhanced Chemical Vapor Deposition at Atmospheric Pressure (APPECVD) with a plasma jet, TEOS as precursor and air gas. The optimization of different experimental conditions allowed to generate a homogeneous silica coating on COC surface. The optimal experimental conditions permitted to deposit a 158 ± 7 nm hydrophilic silica layer that proved to be stable over 14 days stored at room temperature and atmospheric pressure.

This fast and versatile plasma process compared to the ones generated at low pressure, allowed to deposit thin silica layers of similar properties on COC substrate. This plasma jet treatment also allowed *in situ* treatment of COC microchannels, that is to say fast and easy microfabrication process of the microchips, is environmentally friendly and can be further used for industrial application, among which the production of COC LOAC.

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