Construction of an Array of Photonic Crystal Films for Visual Differentiation of Water/Ethanol Mixtures

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ABSTRACT: A photonic crystal film (PCF) which consists of a porous layered structure with a highly ordered periodic arrangement of nanopores has been used to differentiate between various mixtures of water and ethanol (EtOH). The refractive index difference between the wall (silica) of the empty nanopore and air which occupies it results in the structural color of the PCF. This color disappears when the nanopores are infiltrated by a liquid with a similar refractive index to silica (or silicon dioxide). The disappearance of the structural color provides a means to construct a colorimetric sensor to differentiate between various water/EtOH mixtures based on their wettability of the nanoparticles in the PCF. In this study, an array of silica-based PCFs was synthesized on a silicon substrate with a precise control of nanopore properties using the co-assembly/sedimentation method. Using this method, we benefited from having different PCFs on a single substrate. Chemical coatings, neck sizes, and film thicknesses on each PCF were the three factors used to adjust the wettability of the pores. Nanopore wetting by water/EtOH mixtures was studied in a systematic manner based on the three factors, and the findings were used to develop a sensor for visual differentiation of various water/EtOH mixtures. The final developed sensor consisting of an array of six PCFs was able to differentiate between seven different water/EtOH mixtures: W10, W20, W30, W40, W50, W60, and W70, in which W10 means 10% of water in EtOH.

1. INTRODUCTION

Photonic crystals (PCs) are periodic nanostructured materials which can control how photons are absorbed by or reflected from them. Color displays, inks and paints, optical switches, lasers, filters, solar cells, and sensors are applications in which PCs have been used.<sup>1−6</sup> PCs with different compositions have been developed to be used as chemical sensors for sensing pH, solvents, and so on.<sup>7−11</sup>

Photonic crystal films (PCFs) possess structural color which originates from the refractive index difference between the matrix material (in which nanopores are formed) and air (which occupies the empty nanopores).<sup>12−16</sup> For PCFs to be used as chemical sensors, the surface of the nanosized pores inside the PCFs is typically coated by hydrophobic/oleophilic materials such as fluoroalkylchlorosilanes.<sup>17−11</sup> These coating materials will cause the pores to be wetted or not wetted by certain liquids (Figure 1). When dry, the PCF is shown with its structural color (Figure 1A). When a liquid with a similar refractive index to the matrix (i.e., silica) wets the nanopores, the structural color disappears because of the refractive index matching between the liquid and matrix (Figure 1B).

The disappearance of the structural color provides a way to differentiate between various liquids with different compositions based on the wettability of the nanopores.

Silica-based PCFs with a chemically functionalized nanopore surface offer a selective wettability threshold to differentiate between liquids of different chemical compositions. There are two main approaches for liquid identification using PCFs: (1) based on color change of PCF due to the infiltration of a liquid with a different refractive index compared to air; (2) based on color disappearance, in which colored (nonwetted) and dark (wetted) regions are observed. In the first approach, color changes may be small and angle-dependent, and this is complicated for nontrained persons to discern. On the other hand, the second approach is easier to use as compared to the first approach.<sup>18</sup>

Aizenberg and her research team have developed PC sensors with patterned chemical coatings on surfaces throughout their 3D porous structures. Patterned chemical functionalities in different regions on the sensor was achieved using oxygen plasma with removable masks. Using these sensors, they were

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**Figure 1.** Sensing of liquid on PCF due to color disappearance caused by nanopore-wetting behavior; (A) nonwetted PCF, (B) wetted PCF.
successful to differentiate between three pure liquids, such as isopropanol, acetone, and water. Various pure alcohols (e.g., methanol, ethanol, and isopropanol), different pure alkanes (hexane, heptane, octane, nonane, and decane), and different auto fuels (gasoline and diesel) have also been differentiated. They were also able to differentiate between different compositions of a two-component mixture, that is, water/EtOH mixtures of W50, W22 (W22 is a mixture of 22% water and 78% EtOH), W15, and W0. In another work, they were able to differentiate between water/EtOH mixtures of W10, W15, W20, W25, and W50. The selectivity of their sensors has shown a remarkable improvement in another report. By applying new chemical gradients on their well-ordered PCs, they have been able to differentiate between water/EtOH mixtures of W7.5, W5, W2.5, and W0 which have very small differences in surface tension. Among these cases, they are not able to differentiate between water/EtOH mixtures with the ethanol content lower than 50%. By replacing conventional alkyldichlorosilanes by a co-polymer based on a hydrophilic electrolyte monomer (acrylic acid) and a hydrophobic chromophore and applying different exposure times of ultraviolet light for photopolymerization, they could modify the wettability of the pores of the sensor and differentiate between water/EtOH mixtures of W100, W97.5, W95, W92.5, W90, and W87.5 but not with the ethanol content higher than 78%. By replacing conventional alkyl chloride monomers with acrylic acid, they could modify the wettability of the pores of the sensor and differentiate between water/EtOH mixtures of W100, W97.5, W95, W92.5, W90, and W87.5 but not with the ethanol content higher than 78%.2 In these reports of differentiating between water/EtOH mixtures, they did not manage to differentiate mixtures that have EtOH contents less than 50% (e.g. W60), possibly because of the inability to find a suitable hydrophilic chemical coating.

Various groups have previously developed sensor strips for differentiation of hydrocarbon mixtures with close chemical compositions. The wettability threshold for each sensor was tuned using a combination of different chemical coatings and neck angles. In this way, gasoline/EtOH mixtures of E10 (10% EtOH in gasoline), E5 (5% EtOH in gasoline), and pure gasoline have been differentiated by the sensor.22 The developed sensors have also been shown to be capable of differentiation of gasoline/oil mixtures with gasoline-to-oil ratios of 16:1, 20:1, 25:1, 32:1, 40:1, and 50:1 which are typical compositions. The wettability threshold for each sensor was tuned using a combination of different chemical coatings and neck angles. In this way, gasoline/EtOH mixtures of E10 (10% EtOH in gasoline), E5 (5% EtOH in gasoline), and pure gasoline have been differentiated by the sensor.22 The developed sensors have also been shown to be capable of differentiation of gasoline/oil mixtures with gasoline-to-oil ratios of 16:1, 20:1, 25:1, 32:1, 40:1, and 50:1 which are typical compositions.

Many methods reported to fabricate PCF have the inflexibility of building only one PCF on a substrate at a time. Therefore, different PCFs cannot be easily achieved on one single test strip. To overcome this inflexibility, the PCFs will have to be diced into square pieces and assembled on a separate solid support to create a test strip, and this complicates the scale-up process in manufacturing. In this study, we have achieved the following objectives: (1) using evaporative sedimentation method to synthesize PCFs which brings about the advantage that we can have an array of several PCFs on a single substrate; (2) performing parallel liquid mixture analysis on several PCFs on the strip in order to multiplex the analysis of different liquid mixtures.

The reported method offers several advantages as follows: (1) this way of constructing an array of PCFs on the same substrate will be less costly and more efficient as compared with other methods because this will not require subsequent dicing and assembling of different PCFs on a support. (2) As compared with many other reported methods, the fabrication process of PCFs using this technique takes shorter time; from the manufacturing standpoint, this aspect makes our method economically more efficient.

The final sensor strip that consisted of an array of six PCFs was designed and fabricated by using an optimized combination of the neck angle, film thickness, and surface chemical coating. The sensor strip has been shown to have the capability to differentiate between seven different liquid mixtures with a simple-to-read wetted/nonwetted platform.

2. EXPERIMENTAL SECTION

2.1. Materials. Circular silicon wafers (4-inch diameter) were provided by University Wafer, Inc. (Boston, MA, USA). Poly(methyl methacrylate) (PMMA) nanospheres (1% solid content) with a diameter of 318 ± 12 nm were purchased from Sigma-Aldrich, Inc. (Oakville, ON, Canada). Trichloro(3,3,3-trifluoropropyl)silane (3FS) was obtained from Sigma-Aldrich (Oakville, ON, Canada); nonafluorohexyltrichlorosilane (9FS) was provided by Gelest, Inc. (Morrisville, PA, USA); trichloromethylsilane (99%) (TMS) was purchased from Sigma-Aldrich (Oakville, ON, Canada); 3-(trichlorosilyl)propyl methacrylate (TPMA) was obtained from Fluka (Buchs, Switzerland). Dimethylchlorosilane solution (2% w/v) in octamethylcyclotetrasiloxane (or Repel-silane) was purchased from GE Healthcare (Uppsala, Sweden).

2.2. PDMS and Silicon Preparation. The polydimethylsiloxane (PDMS) mold with six trenches was designed and fabricated to construct an array of PCFs on a silicon substrate. Six trenches, with dimensions of 2.5 mm width—20 mm length—1 mm depth, were cut on the PDMS slab (1 mm thickness) using a knife blade. Circular silicon wafers (4 inch diameter) were cut by a diamond glass cutter into two equal pieces, making two semicircles. After the semicircular silicon substrate was cleaned using Sparkleen detergent [Sparkleen powder (10% w/v) dissolved in DI water] followed by rinsing with DI water, the substrate was sealed to the PDMS mold. Then, the substrate was placed in a Pyrex dish containing 100 mL of piranha solution [sulfuric acid (98%) and hydrogen peroxide (30%) mixed in a 7:3 ratio] for 1 h to create a hydrophilic surface on the substrate. It was then removed from the dish and rinsed with water, ethanol (95%), and water successively and blow-dried.

2.3. PMMA/TEOS Mixture Preparation. A mixture of 0.01 M HCl, tetraethyl orthosilicate (TEOS), and anhydrous ethanol (EtOH) was prepared in a glass vial (a ratio of 1:1:1.5 w/w/w HCl/TEOS/EtOH) and used as the matrix solution. This solution was mixed thoroughly using a magnetic stirrer at 200 rpm for 1 h. PMMA nanospheres, which were suspended in water, were used as the template. The PMMA stock bottle was sonicated for 30 min to homogenize the colloids before use. Aliquots of PMMA colloids and the matrix solution were added to a definite amount of DI water to form the PMMA/TEOS mixture in a tube. The mixtures were then capped and sonicated for 1 h.

2.4. PCF Fabrication. In order to synthesize an array of silica-based PCFs, the PDMS mold consisting of six trenches was sealed on the silicon substrate (Figure 2A). The PMMA/TEOS mixture was then introduced into the trenches. This mold allows separate deposition of six different PMMA/TEOS mixtures on one silicon substrate without any liquid leakage. After deposition of the PMMA/TEOS mixtures, the mold substrate was placed in a covered plastic Petri dish in which the humidity was kept high (using wet tissues) to reduce solvent
Using a micropipette, a small droplet of liquid (10 \( \mu L \)) was placed on the surface of the silicon substrate (Figure 2B), and then, it was placed in a programmable oven for calcination. The oven temperature was ramped up to 500 °C over 3 h. In order to confirm complete removal of the coating, the sample should pass the water wetting test; the removal of the coating was verified by the disappearance of the blue structural color of the PCF upon its immersion in water.

### 3. RESULTS AND DISCUSSION

#### 3.1. Interfacial Properties of Water/EtOH Mixtures.

The interfacial properties of various water/EtOH mixtures on four different silane coatings were investigated. These silanes are 3FS, 9FS, TMS, and TPMA.

Figure 3 shows the contact angles of various water/EtOH mixtures measured on flat silicon substrates that were coated with TPMA, TMS, 3FS, and 9FS. The water/EtOH mixtures are designated by the percentage of water in the mixtures, shown by the number after the letter "W", for example, W60 is the mixture of 60% water and 40% EtOH. The six mixtures are W100, W80, W60, W40, W20, and WS. Based on Figure 3, as the water contents of these mixtures decrease, the contact angles decrease because water has a higher surface tension (72.01 mN/m at 25 °C) as compared to EtOH (21.82 mN/m at 25 °C).

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**Figure 2.** Steps of PCF fabrication (A) sealing the PDMS mold to the silicon substrate, (B) six white-colored strips formed after solvent drying, (C) an array of six blue PCFs was synthesized on the silicon substrate.
In addition, the value of the contact angle for a specific water/EtOH mixture on silicon coated with 9FS is higher than that with 3FS. This indicates 9FS is more hydrophobic than 3FS, possibly because of a strong force within 9FS and hence low interaction between 9FS and the liquid. On the other hand, TPMA produces the lowest contact angle, showing it to be a more polar molecule as a result of the presence of two carbon–oxygen bonds in its molecular structure as compared with TMS. The contact angle values of water/EtOH mixtures obtained on TMS and 3FS are in a good agreement with an earlier reported work.20

3.2. Effect of the Neck Angle on Wetting Behavior of PCFs. In this section, the effect of only the neck angle on the wetting behavior of PCFs was studied, and so, we fixed the coating (i.e., 9FS) and the number of film layers (the amounts of PMMA and water used were 20 and 430 μL, respectively, to achieve PCFs with four layers; the determination of the number of layer was shown in the Supporting Information). To adjust the neck angle, the amount of TEOS in the PMMA/TEOS mixture used for each PCF was increased, that is, from 1.1 μL in PCF 1 (on the left on Figure 4) to 3 μL in PCF 6 (on the right). Based on Figure 4, increasing the amount of TEOS results in a decrease in the neck angle from $32^\circ \pm 2^\circ$ to $20^\circ \pm 2^\circ$. When the PCF sample was immersed in W25, the six PCFs remained nonwetted because the contact angle of W25 ($\theta_C = 34^\circ \pm 1^\circ$) is greater than neck angles ($\phi_0$) of all PCFs ($\theta_C > \phi_0$ is required for wetting). When the sample was immersed in W10, all PCFs were wetted because the contact angle of W10 ($\theta_C = 19^\circ \pm 1^\circ$) is smaller than the neck angles of the PCFs. By changing the amount of TEOS, it is possible to control the values of neck angles in the PCFs and hence the wettability of the PCFs.

3.3. Effect of Chemical Coatings on Wetting Behavior of PCFs. In this section, the effect of only chemical coating on the wetting behavior of PCFs is investigated, and so, all six PCFs have the same composition and film thickness. Figure 5 represents the effect of chemical coatings (i.e., TPMA, TMS, 3FS, and 9FS) on the wetting behavior of an array of PCFs, with the uncoated PCFs as the control. The TPMA-coated sample remained nonwetted when it was immersed in W80 and W85, but it was wetted when immersed in W75 or in mixtures of higher EtOH contents. The higher the water content in the water/EtOH mixtures is, the higher is the contact angle of the mixtures, and it is more difficult for them to wet the PCFs. We define the boundary of wetting and nonwetting as the wetting threshold, that is, for a TPMA-coated sample, the wetting threshold is between W75 and W80 (i.e., $W75–W80$).

As a result of high hydrophobicity of the TMS-coated PCFs, the wetting threshold was shifted to mixtures with lower EtOH contents, that is, ($W60–W65$). When the samples were coated with 3FS and 9FS with greater hydrophobicities, the wetting thresholds were further shifted to W40–W45 and W15–W20, respectively. Therefore, by using different chemical coatings, the wettability of the PCFs can be tuned as indicated by the wetting thresholds.

3.4. Effect of Film Thickness on Wetting Behavior of PCFs. In this section, the effect of PCF thickness (in terms of number of layers) on wetting behavior of PCFs is investigated; see Figure 6. Two PCFs were fabricated using PMMA, TEOS, and water amounts of 45, 2.8, and 1300 μL (for three layers) and 50, 3.1, and 510 μL (for eight layers), respectively; the determination of number of layers was shown in the

Figure 3. Measured contact angles from six different water/EtOH mixtures on the silicon substrate when coated with; 9FS, 3FS, TMS, and TPMA.

Figure 4. Effect of the neck angle on the wettability of PCFs. In the image of the silicon strip, PCFs 1–6 are arranged from left to right. The various TEOS amounts in the PMMA/TEOS mixtures are shown; in all cases, the amounts of PMMA and water used were fixed to be 20 and 430 μL, respectively. These PCFs were coated with 9FS.
Supporting Information. Because the TEOS/PMMA ratio for both samples was fixed to 0.062, we expect the PCFs should have the same neck angle and have the same wetting threshold for the same coating (i.e., 9FS). However, while the three-layer sample was wetted in W15, the eight-layer sample was not wetted in W15. Therefore, the film thickness is another factor that can be used to tune the wettability of PCFs.

3.5. Combinations of the Neck Angle, Film Thickness, and Chemical Coating to Tune Wettability. In this section, the neck angle, thickness, and chemical coating are combined to tune wettability of PCFs for differentiation of various water/EtOH mixtures.

To understand the combination of the three factors in a systematic way, we perform wetting tests, determine the wetting thresholds, and then plot these in terms of film thickness (number of layers) and neck angle. To represent the neck angle, we defined a parameter called the excess ratio over the theoretically required amount of TEOS (EXR); this is a quantity that can be calculated based on the actual amount of TEOS used in the PMMA/TEOS mixture to fabricate a PCF. For example, for a PCF with the amount of PMMA, TEOS, and water of 45, 2.8, and 1300 μL, respectively, the theoretical...
amount of TEOS to fill 26% of the volume of the PCF is 1.4 μL. However, the actual amount of TEOS used to fabricate the PCF was 2.8 μL. Then, by dividing 2.8 μL (actual amount used) over 1.4 μL (theoretical amount needed), the EXR is calculated to be 2. We believe the greater is the value of EXR, the thicker are the walls of the PCF, and the lower is the value of the neck angle, the lower is the tendency of pore wetting. We used the theoretical matrix volume of 26% (or pore volume of 74%) as a reference point to calculate EXR values for all the samples without loss of generality, even though we know the theoretical values based on 2, 3, and 5 layers have been computed to be 32, 30, and 28%, respectively. Table S1 in Supporting Information shows the details for the compositions of the five PCF samples with different thicknesses and EXR values that are fabricated.

Figure 7 shows the wetting results of TPMA-coated samples after being immersed in various water/EtOH mixtures. In each PCF sample, the value of EXR increases from PCF 1 to PCF 6 (left to right). The different numbers of layers add another quantifier to these PCFs, that is, (A) two layers, (B) three layers, (C) four layers, (D) six layers, and (E) eight layers. For instance, for PCFs with six layers, they are called PCFs D1-6, and for eight layers, they are called PCFs E1-6. In the case of eight layers, W65 wetted PCF E1 but not E2-6, but W60 wetted all PCFs E1-6. In the case of six layers, W65 wetted PCFs D1-4 but not D5-6, but W60 wetted all PCFs D1-6. Therefore, in order to differentiate between W60 and W70, TPMA-coated samples with six or eight layers can be used.

The wetting results of TMS-coated, 3FS-coated, and 9FS-coated PCF samples after being immersed in various water/EtOH mixtures are shown in Figures S3, S4, and S5, respectively, as shown in the Supporting Information. Based on Figure S3, in order to differentiate between W60 and W50, TMS-coated samples with 3, 4, and 6 layers can be used. Also, to differentiate between W50 and W40, TMS-coated samples with eight layers can be used. Based on Figure S4, in order to differentiate between W40 and W30, 3FS-coated samples with three, four, and six layers can be used. Based on Figure S5, in order to differentiate between W25 and W20, TPMA-coated samples with two layers can be used. Also, to differentiate between W20 and W10, 9FS-coated samples with four, six, and eight layers can be used.

The wetting threshold based on EXR and number of layers for the mixtures of W75, W70, and W65 can be obtained from Figure S3. Based on Figure 7, when a two-layer (A) TPMA-coated PCF is used, W75 wetted PCF A1-2 but not PCF A3-6. From Table S1, EXR for A2 and A3 are 3.3 and 4, respectively, and so, the wetting threshold can be obtained by calculating the average EXR value, which resulted in 3.7. Similarly, when a three-layer (B) TPMA-coated PCF was used, W75 wetted PCF B1 but not PCF B2-6; the wetting threshold was given by the average of EXR values for PCF B1 (2) and for PCF B2 (2.7), which resulted in 2.4. These two wetting thresholds for W75, that is, (EXR = 3.7, layer number = 2) and (EXR = 2.4, layer number = 3), were then plotted in Figure 8, and the two data points were joined to give the wetting threshold line in blue on the far left. The same procedure was followed to find other average EXR values and number of layers for the wetting thresholds of two other mixtures, that is, W70 and W65, and the wetting threshold lines were plotted in orange and gray on the middle and far right, respectively. The obtained plot, as shown in Figure 8, shows the three wetting threshold lines, in which the wetted regions are on the left sides of the lines, designated with green points, whereas nonwetted regions are on the right sides of the lines. The wetting thresholds for PCFs coated with TMS, 3FS, and 9FS using different liquid mixtures are also extracted and plotted in Figures S6, S7, and S8, respectively.

3.6. Development of a Sensor to Differentiate Water/EtOH Mixtures. Based on the wetting threshold graphs obtained in Section 3.5, a sensor strip platform was designed in order to differentiate between various water/EtOH mixtures. As it is shown in Figure 9, six different PCFs were produced with different chemical coatings, EXR, and film thicknesses. In order to differentiate between W70 and W60, an eight-layer PCF was fabricated with an EXR of 1.6 and with TPMA as chemical coating, see the red dot in Figure 8. To differentiate between W60 and W50, a three-layer PCF was fabricated with an EXR of 3.6 and coating of TMS, and to differentiate between W50 and W40, an eight-layer PCF was fabricated with different chemical coatings, EXR, and film thicknesses.
an EXR of 2.1 which was coated with TMS; see the two red dots in Figure S6. In order to differentiate between W40 and W30, a six-layer PCF was fabricated with an EXR of 1.6 which was coated with 3FS; see the red dot in Figure S7. To differentiate between W30 and W20, a two-layer PCF was made with an EXR and chemical coating of 3 and 9FS, respectively, and between W20 and W10, a six-layer PCF was produced and coated with 9FS and the EXR was designed to be 1.8; see the two red dots in Figure S8. The schematic diagram of the ideal sensor using the PCF design is shown in Figure 9, in which the liquid differentiation can be achieved by counting the number of wetted/nonwetted PCFs on the sensor strip.

Figure 10 shows the image of the fabricated sensor and wetting results in seven water/EtOH mixtures: W10, W20, W30, W40, W50, W60, and W70. Based on Figure 10, the differentiation of these water/EtOH mixtures have been accomplished successfully. The final sensor strip shows six wetted PCFs when immersed in W10 (or a mixture with higher EtOH contents). If only one, but not two, PCF is not wetted after immersion in a water/EtOH mixture, the mixture is considered to be W20. The final sensor shows 2, 3, 4, 5, and 6 nonwetted PCFs when immersed in W30, W40, W50, W60, and W70 (or a mixture with lower EtOH contents), respectively.

The present work is compared with previous reports, as shown in Table 1. Here, the PCF preparation time, chemical coating, liquid mixtures for differentiation, and differentiation methods reported in the literature are summarized. In this study, the PCF preparation time of 17 h was achieved which is lower than the previously reported times (55 h). The final sensor in the present study can be used to differentiate between a wider range of water/ethanol mixtures (W10 to W70) as compared to the previous work. Moreover, the differentiation method in the present study is based on counting the number of wetted/nonwetted PCFs, which is more easily interpreted than the method of considering color pattern changes found in some of the previous reports.

4. CONCLUSIONS

In this study, an array of six PCFs was fabricated on a single silicon substrate using co-assembly sedimentation. The effects of chemical coating, neck angle, and film thickness on the PCF wettability were studied systematically. A more hydrophobic chemical coating, a smaller neck angle, and a larger film thickness result in more difficult wetting of PCF pores. Combinations of these three factors were used to tune the

![Figure 10. Differentiation of seven water/EtOH mixtures: W10, W20, W30, W40, W50, W60, and W70 using an array of six PCFs on a single-sensor strip substrate.](image-url)

Table 1. Summary of PCF Preparation Time, Chemical Coating, Liquid Mixtures for Differentiation, and Differentiation Methods Reported in the Literature

<table>
<thead>
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<th>Reference</th>
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<th>Liquid Mixtures</th>
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<td>21</td>
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<td>13FS, DEC, JBS, TMS</td>
<td>(W0−W15, W22−W50)</td>
<td>wetted/nonwetted color patterns</td>
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<tr>
<td>22</td>
<td>55 h</td>
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<tr>
<td>23</td>
<td>17 h</td>
<td>3FS, 9FS</td>
<td>(W0−W2.5, W5−W7.5)</td>
<td>wetted/nonwetted color patterns</td>
</tr>
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</table>

References:
1. 3FS: trichloro(3,3,3-trifluoropropyl)silane, 9FS: nonafluorohexyltrichlorosilane, 13FS: trichloro(1H,1H,2H,2H-perfluorooctyl)silane, TMS: trichloromethylsilane, DEC: n-decylsilyl, 5FP: pentafluorophenylpropyl, PTOL: p-tolyl, respectively.
wettability of the PCFs for various water/EtOH mixtures with 5% EtOH difference. Based on the optimized combinations of the three factors, a final sensor strip platform was designed to differentiate between seven water/EtOH mixtures. The final developed sensor allows us to differentiate between seven water/EtOH mixtures: W10, W20, W30, W40, W50, W60, and W70 by counting the number of wet and non-wetted PCFs. The results of six, five, four, three, two, one, and zero wetted PCFs after immersion in a water/EtOH mixture can be attributed to the presence of W10 (or a mixture with a higher EtOH content), W20, W30, W40, W50, W60, and W70 (or a mixture with a lower EtOH content).

**ASSOCIATED CONTENT**

5 Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02947.

Top-view SEM image of a PCF showing occupation of 24 particles in an area of 2.187 × 10−6 mm²; cross-sectional SEM image of a PCF with six layers; effect of thickness on the wettability of PCFs when coated with TMS; effect of thickness on the wettability of PCFs when coated with 3FS; effect of thickness on the wettability of PCFs when coated with 9FS; wetting threshold based on EXR and number of layers for TMS-coated PCFs; wetting threshold based on EXR and number of layers for 3FS-coated PCFs; wetting threshold based on EXR and number of layers for 9FS-coated PCFs; composition of six PCFs on a silicon strip with thickness of two, three, four, six, and eight layers; and PCFs 1–6 arranged from left to right in the images of the silicon strip (PDF)

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