Invited Paper

Wetting in Color: From photonic fingerprinting of liquids to optical control of liquid percolation

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ABSTRACT

We provide an overview of our recent advances in the manipulation of wetting in inverse-opal photonic crystals. Exploiting photonic crystals with spatially patterned surface chemistry to confine the infiltration of fluids to liquid-specific spatial patterns, we developed a highly selective scheme for colorimetry, where organic liquids are distinguished based on wetting. The high selectivity of wetting, upon-which the sensitivity of the response relies, and the bright iridescent color, which disappears when the pores are filled with liquid, are both a result of the highly symmetric pore structure of our inverse-opal films. The application of horizontally or vertically orientated gradients in the surface chemistry allows a unique response to be tailored to specific liquids. While the generic nature of wetting makes our approach to colorimetry suitable for applications in liquid authentication or identification across a broad range of industries, it also ensures chemical non-specificity. However, we show that chemical specificity can be achieved combinatorially using an array of indicators that each exploits different chemical gradients to cover the same dynamic range of response. Finally, incorporating a photo-responsive polyelectrolyte surface layer into the pores, we are able to dynamically and continuously photo-tune the wetting response, even while the film is immersed in liquid. This *in situ* optical control of liquid percolation in our photonic-crystal films may also provide an error-free means to tailor indicator response, naturally compensating for batch-to-batch variability in the pore geometry.

Keywords: colorimetric sensing, inverse opals, photonic crystals, surface chemistry, wetting, structural color, photobleaching

1. INTRODUCTION

Chemical sensing has been the focus of extensive research in recent years with rapid advances in areas ranging from single molecule detection to low-cost sensors for medical diagnostics [1-3]. However, the high cost and complexity of many conventional chemical-sensing technologies limits their applicability [4]. A popular approach to low-cost chemical sensing is to exploit colorimetric indicators. The use of color as a reporter of chemical information makes this information accessible to users with limited resources and/or training. Colorimetry has expanded to include a diverse set of powerful sensors that are able to identify substances based on a wide array of properties. However, the expansion of colorimetric sensors to new sensing problems always comes with the added challenge of linking color to a specific physical property or molecular response. The application of structural color has the potential to greatly expand the availability of colorimetric solutions for sensing problems [5-14]. Structural color can be tuned through changes in physical properties, and thus imparts no specific restrictions on the chemistry of the material. This facilitates enormous flexibility for the types of materials that can be used to design structural color sensors aimed at specific applications.

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We have recently developed a colorimetric sensing platform, hereafter referred to as a Wetting in Color Kit (WICK), that connects wetting behavior to structural color changes in 3-D inverse opal films (IOFs) [15-17]. Highly ordered and crack-free, the IOF pore structure displays a natural iridescence [18]. When the structure is wetted with a liquid, the iridescence disappears due to the reduced refractive index contrast. By controlling the geometry and surface chemistry of this structure, the percolation of liquids can be controlled with high spatial and liquid selectivity. The selectivity of this wetting response is made possible by the highly symmetric pore structure. By spatially modifying the surface chemistry using simple laboratory protocols, it is possible to selectively tune the infiltration of different liquids to specific patterns. The resulting product is a highly selective sensor that is able to differentiate organic liquids based on wetting, with access to low surface-tension liquids (e.g. $\gamma \sim 20$ mN/m). Furthermore, the application of horizontally or vertically orientated gradients in surface chemistry allows a unique response to be tailored for specific organic liquids [15]. Most recently we have expanded the sensing platform to allow for *in situ* optical control of wetting. By incorporating a photo-responsive dye in the pores of the IOFs, the wettability can be optically tuned by photobleaching. This further expands the sensing capabilities by allowing for dynamic tuning, and is a useful approach for applying horizontal gradients in surface chemistry. The *in situ* optical tuning also provides a new approach to compensate for variability in the pore geometry of IOFs.

The use of wetting, a generic fluidic phenomenon, as a basis for colorimetric sensing makes this platform highly versatile, and applicable in principle to any sensing problem involving liquids. However, this versatility comes hand-in-hand with intrinsically limited specificity, since any liquid or liquid component is also capable of interfering with the response. We achieved high chemical specificity without sacrificing the breadth of applicability by using a combinatorial sensing approach. Previously, high chemical specificity was achieved by using the response from an array of six IOFs. Each IOF had a unique gradient of surface chemistry and the combined response from all six was sufficient to significantly increase chemical specificity compared to an individual IOF [17].

In its current embodiment, WICK has great potential to compete with conventional sensing technologies. However, before the technology can be commercialized, performance must be optimized and the most promising applications must be identified. Specifically, a more robust combinatorial sensing approach is needed to probe a larger range of liquids with higher specificity. This Proceeding reviews the development of this technology and discusses its current status from an applications viewpoint, highlighting the most promising applications and the most important work that needs to be addressed.

2. OVERVIEW

WICK exploits the use of structural color from highly ordered crack-free IOFs. The structural color is derived from the index contrast and wavelength-scale periodicity provided by spherical air-pores ($r_{\mathrm{pore}} \sim 140$ nm) in a SiO_2 slab, organized in a face-centered-cubic (fcc) lattice [18]. Adjacent pores are connected by small openings (hereafter referred to as necks) as shown in the scanning electron microscope images in Fig. 1A (left). The wetting properties of the IOFs are ultimately controlled by both the pore geometry and intrinsic wettability that depends on the interaction between the liquid and the surface chemistry [16]. Whether or not infiltration of fluid proceeds spontaneously from one pore to the next is determined by the free energy trade-off between the unfavorable creation of the liquid-air interface and the energetically favorable replacement of solid-air interfaces with liquid-solid interfaces (the wetting threshold occurs in the intrinsic wetting regime, $\theta_c < 90^{\circ}$) [16].

$$\Delta G = \gamma_{la} \pi R^2 (\sin^2\varphi - \sin^2\varphi_0 - 2\cos\theta_c(\cos\varphi_0 - \cos\varphi)) \qquad (1)$$

Here γ_{la} is the liquid-air surface tension, R is the pore radius, φ is the azimuthal angle that the liquid creates within the pores, φ_0 is the neck angle, and θ_c is the intrinsic contact angle [15,16]. The intrinsic contact angle is obtained by performing contact-angle measurements on a flat surface (e.g. silicon wafer) with the same surface chemistry as the IOF. The difference in the normalized Gibbs free energy for these two cases of fluid flow in the IOF is shown in Fig. 2B for a linear chain of pore-connectivity. A metastable non-wetting state exits when $\theta_c > \varphi_0$ (Fig. 2B). Unfilled regions display bright iridescent color, while filled regions become transparent due to the reduced refractive index contrast, revealing the color of the underlying substrate (Si wafer). The visual (optical images) and spectral (reflectance) changes of an IOF in air and water are shown in Fig. 1B. The selectivity of the wetting transition is ultimately controlled by the short-range disorder (<1mm) and surface chemistry [15]. The structural symmetry of the pore structure is what facilitates the sensitivity to small differences in wettability, while the re-entrant geometry [19] allows for access to very low surface-tension liquids ($\gamma \approx 20$ mN/m).

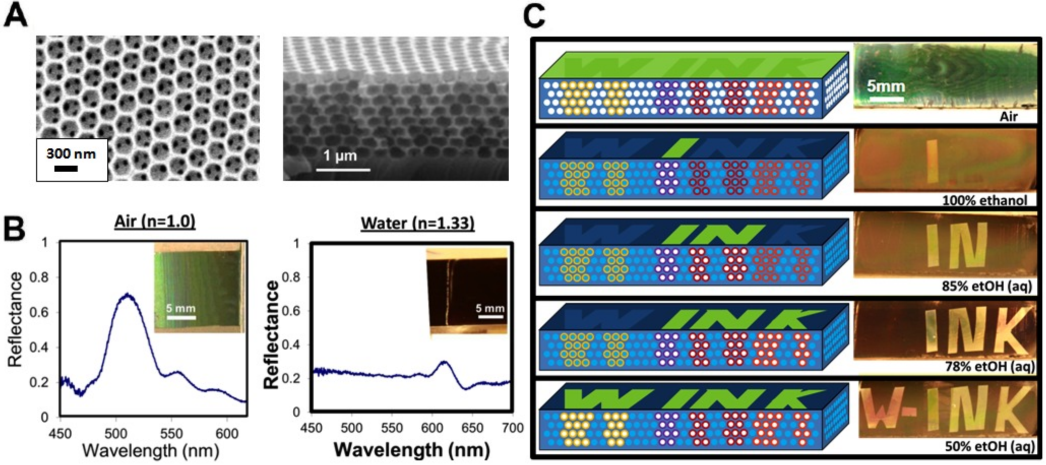

Figure 1. A) Scanning electron micrographs of IOFs. B) Optical images and reflectance spectra of air and water filled inverse opal photonic crystals. C) Optical images of the word "W-INK". "W-" TMS, "I" 13FS, "N" DEC, "K" 3FS, background ROH.

Using iterations of silanization and masked oxygen plasma exposure to selectively pattern different regions of the IOF with different chemical functionalities (e.g. DEC: n-decylsilyl, TMS: trimethylsilyl, 13FS: 1H,1H,2H,2H-tridecafluorooctyl, 3FS: 3,3,3-trifluoropropylsilyl as shown in Fig. 1C) [16], we facilitate the selective wetting of different liquids to different combinations of these regions. These wetting combinations cause the IOF to display color patterns that give information about the liquid's identity. In addition to the applications in colorimetry that will be elaborated upon hereafter, this ability to encode multiple levels of liquid specific color patterns (hidden when dry) also has potential as a form of encryption for applications in security and authentication. Our ability to encrypt immensely complicated multi-level patterns in this platform is leveraged by the diverse commercial availability of chlorosilanes with different functional groups. In addition, the fact that the device requires no power is attractive for many types of security applications where resources are limited or complexity (or the perception of complexity) is desired. However, a major drawback for encryption applications is that wetting with liquids is required for message decryption, which might not be desirable authentication of items such as paper currency.

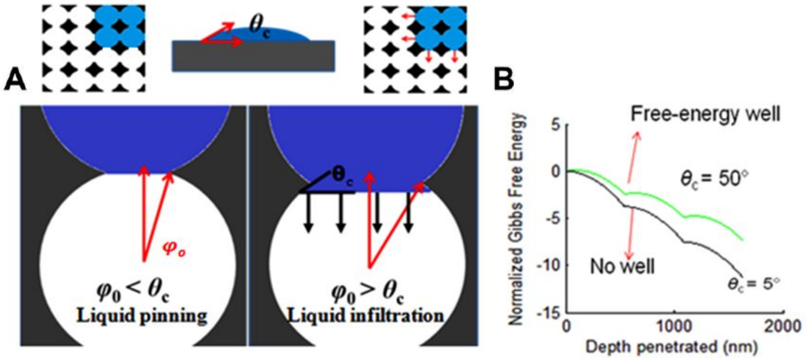

Figure 2. A) Schematic depicting the difference between liquid pinning and liquid infiltration throughout the pore structure of the IOF. B) Normalized Gibbs free energy as a function of penetration depth within the IOF for a 1D necklace model, illustrating the presence of metastable non-wetting states for $\theta_c > \varphi_0$ (shown here, $\varphi_0 = 20°$).

3. OPTIMIZATION OF PERFORMANCE

In the development of WICK for sensing applications, we focused on the optimization of several specific performance properties that are important for utility. These are as follows: (i) ***selectivity*** (What is the smallest difference in wettability or intrinsic contact angle that WICK can detect?), (ii) ***customizability*** (What tools do we have to design a WICK to differentiate a set of liquids that are specified by a customer?), (iii) ***chemical specificity*** (Given that wetting is a generic property of liquids, is there any way to extract chemically specific information from the WICK platform?), (iv) ***ease of use*** (While it is easy to say that WICK is easy to use since it is a colorimetric test, is this actually true in practice? Does practical use require specific lighting conditions or viewing angle, etc.?), and (v) ***reproducibility*** (How amenable is the fabrication protocol to the implementation of quality assurance and quality control procedures?). The following subsections summarize our optimization of WICK with respect to each of the above parameters.

3.1. Selectivity

Determining the selectivity of the WICK relies on the determination of both the smallest change in θ_c that induces a visible color change and how this sensitivity compares to the variability in the response that can be induced by environmental noise (e.g. small variations in pressure, temperature, etc.). We found that the selectivity is predominantly limited by local variability in the pore geometry, namely the size of the inter-pore necks and therefore their relative capacity to pin liquid fronts [15]. Estimating this geometric variability using SEM image analysis, we determined the correlation between the selectivity limits and this geometric variability using both percolation modeling [15] and basic optical simulations.

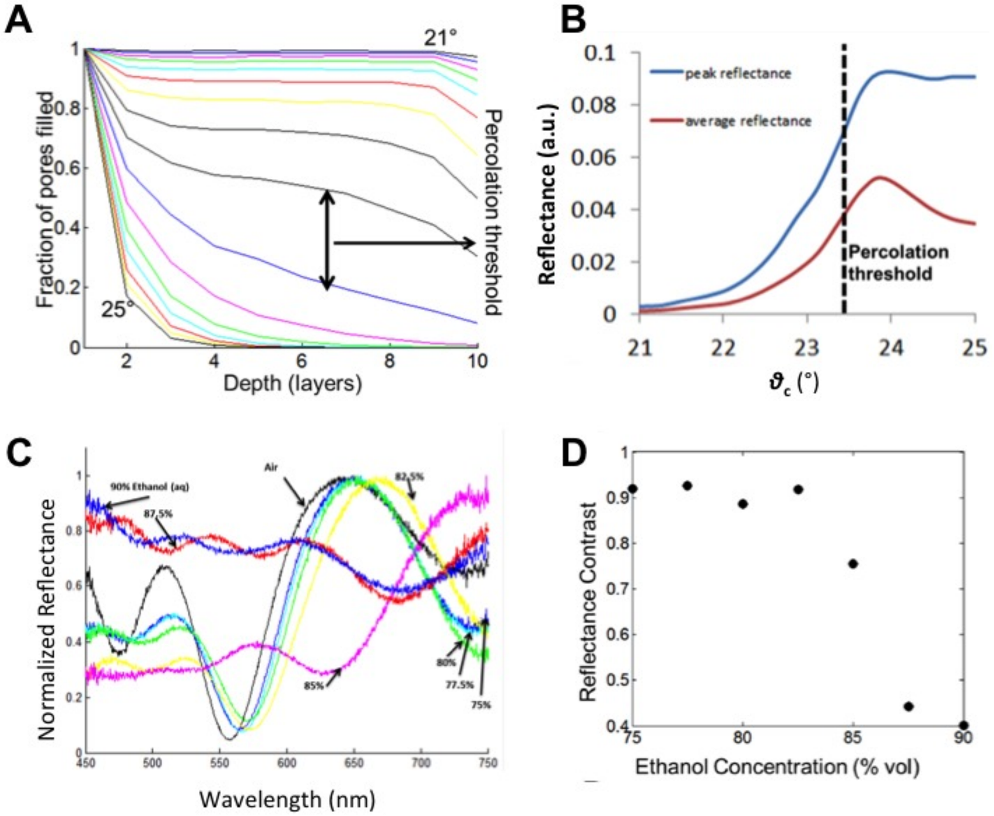

Figure 3. A) Percolation simulations for contact angles varying between 21° and 25°. B) The peak and average simulated reflectance as a function of the intrinsic contact angle. C) Measured reflectance spectra and D) reflectance contrast for a DEC functionalized IOF submerged in various ethanol-water solutions.

Studying percolation phenomena in IOFs is fairly straightforward because of their highly regular fcc structure. Percolation theory for highly ordered systems such as this are well studied and percolation thresholds are known beforehand [20]. Percolation simulations were used to derive the expected equilibrium filling states in the IOFs from bond connectivity determined for a given θ_c. Bond connectivity was determined by the distribution of neck angles estimated from electron micrographs. The simulation filled all pores with paths of fluid inter-pore connectivity (i.e. where $\theta_c < \varphi_0$). The filled pores were connected to the top layer of the IOF that was set to be completely filled at the beginning of the simulation since the top layer consists of half spheres, which have no re-entrant curvature [15].

We estimated the effects of percolation on total reflectance using a simplified Finite-Difference-Time-Domain (FDTD) optical simulation. To correlate the filling profiles of IOFs and the total reflectance in a computationally inexpensive manner, the layer-by-layer filling statistics of the 3D percolation simulations were projected onto a 2D optical model. In the simulations it was assumed that there was perfect refractive index matching (n=1.4 for both IOF and liquid) and that the IOF was completely submerged in the liquid. Irradiation of the IOF was achieved using a plane wave propagating at normal incidence, and the resulting reflectance was monitored by transformation to the far field. Fig. 3B depicts the computed peak reflectance and average reflectance, as a function of θ_c, calculated from the optical simulations. The reflectance saturation occurs near the percolation threshold, which is intuitive given the assumption that there are empty layers at certain depths in the IOF below this threshold [15]. For comparison, Fig. 3C shows the measured optical reflectance spectra of an IOF (DEC-functionalized) that is immersed in ethanol water solutions varying by 2.5%. The small oscillations in the filled spectrum (90% ethanol) indicate the lack of perfect refractive index matching. Large changes in reflectance are evident with changes as small as 2.5% in ethanol-water solution concentration indicating the remarkable selectivity of the sensors response. A large drop is noticeable between 85% (percolation threshold) and 90% ethanol solutions. This transition corresponds to the threshold when the structure is completely infiltrated with liquid.

The modelling and simulation data presented here describes the remarkable selectivity of the WICK. However, it does not explicitly identify the minimum visually distinct difference in reflectance of an IOF than can be identified using the naked eye. This information is a better indication of the effective selectivity that a user can expect when employing WICK, and is thus of great significance from a commercialization perspective. The simplified optical model suggests that the transition from disappearance to saturation of the reflectance peak occurs over a range of about 3°. While it also suggests that smaller changes are spectrally detectible, using complete disappearance of the reflectance peak as a measure of colorimetric certainty (implying a resolution of ~3°) ensures that only easy-to-read color changes are being considered. This is of great significance from a commercialization perspective for ease-of-use applications.

3.2. Customizability

The ability to pattern the surface chemistry of IOFs is useful for applications in encryption, but pre-determined functional groups (e.g. from store-bought chlorosilanes) are only applicable to unique liquids. In order to produce a sensor that is truly versatile and can be tailored to produce a desired response to an arbitrary organic liquid, it is necessary to have the ability to fine-tune the surface chemistry over a continuous scale. We have demonstrated three different methods to accomplish this type of continuous tuning. Two of these techniques work based on the principle of tuning the wetting response over a range between that produced naturally by functionalizing the pore surfaces uniformly with two different commercially available silanes. Suppose that two liquids, A and B, both infiltrate IOFs with DEC functionalization, and neither infiltrate 13FS-functionalized IOFs. In order for an IOF to colorimetrically differentiate A and B, it needs to have a functionality that shows different wetting patterns in A and B. The first approach we developed entails the deposition of a mixed functionality from the evaporation of a liquid mixture of two different chlorosilanes. Changing the relative concentrations of the two functionalities allows continuous tuning of the global response [15].

The second approach entails vertically grading the surface chemistry to cover the continuous range of responses between those offered by two given chemical functionalities [15]. This is accomplished by first exposing the entire film to the chlorosilanes with the more hydrophobic pendant group (13FS in our case). A short (typically <1min) oxygen plasma exposure follows. It re-activates the surface with vertically graded efficiency, the hydrophobic pendant groups being removed from the surface most effectively at the top of the structure, while the lowest layers are almost unaffected. Once this plasma exposure has been performed, a second less hydrophobic functionality is deposited via silanization. As shown in Fig. 4B, the resulting vertically graded wettability causes liquids to fill to a fixed penetration depth [15]. The naturally varying total thickness gives rise to distinct "rainbow" patterns, where each color is indicative of a different degree of liquid penetration [15]. Using a second round of selective plasma oxidation, background regions can be re-activated to allow for the appearance of specific patterns (e.g. letters or "teeth" as shown in Fig. 4), enhancing the readability of the indicator. Overall, the vertical gradient technique has the advantage that a single functionalized region produces many possible responses.

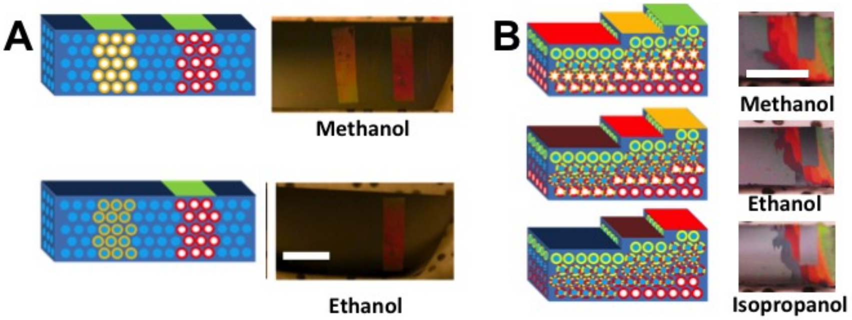

Figure 4. Scale bars: 5mm A). An IOF using a pattern of locally uniform functionalities to differentiate methanol and ethanol. B) IOFs functionalized with a vertical gradient of DEC→13FS and used to differentiate various alcohols.

Most recently, we have developed a third method to continuously adjust the response through the incorporation of a dynamic surface functionality whose wetting properties can be changed *in situ*. We functionalized the surface of IOFs with an acrylic-acid-based polyelectrolyte monolayer containing an azobenzene chromophore (poly(acrylic acid)-co-(Disperse Red 1 methacrylate)) [21]. While a wetting threshold was observed at around 20% ethanol (aq) with this functionality, the threshold was found to be continuously tunable through exposure to UV light, due to photobleaching of the dye. The final wetting threshold of the IOF was found to be controllable by varying the UV exposure dose (shown in Fig. 5). As shown in Fig. 5B, the regions that were exposed to UV light for longer periods of time have a higher wettability, evident from the disappearance of iridescence when submerged in a liquid. For example, the section of the IOF shown in Fig. 5B that received five minutes of UV exposure is wetted in the 5% ethanol solution, but not water, while the section exposed to UV for ten minutes is wetted in both liquids. This method also allows for *in situ* tuning so that an IOF can be put in any desired liquid, exposed to light, and tuned such that its wettability threshold corresponds to the surface tension of that liquid. While presently the utility of this technique is limited to a relatively narrow range of liquids with comparatively high surface tension (e.g. <20% ethanol in ethanol-water mixtures), this dynamic tuning capability provides an exceptionally simple way to adjust a WICK response to a specific target liquid. This *in situ* method also provides robustness against small inter-sample variation in the pore geometry (i.e. since the adjustment is a post-process).

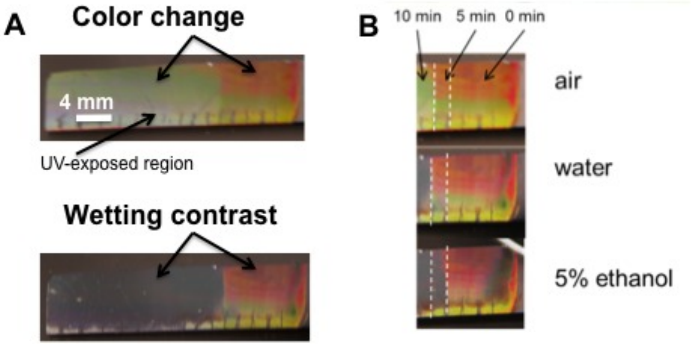

Figure 5. (A) Photobleaching-induced increase in wettability in IOFs functionalized with a polyelectrolye layer containing an azobenzene dye. The photobleached regions (clearly visible through color contrast in air) match the regions where wetting is observed once the film is submerged in water. (B) An IOF in air and submerged in water and a 5% aqueous solution of ethanol, showing UV-dose-dependent wetting.

3.3. Chemical Specificity

The inherent advantage of WICK is that it senses a property universal to all liquids. This universality can also be a disadvantage, as it results in chemical non-specificity (i.e. two different liquids with the same intrinsic contact angle on a given surface can produce the same response for a particular functionalized IOF). Due to this non-specificity, it is impossible to identify an unknown liquid using a single chemically patterned IOF without having any prior information about the liquid. This also makes liquid identification in a mixture more challenging. We were able to enhance the chemical specificity of WICK using combinations of responses from an array of chemically patterned IOFs. An example of how an array of IOFs with different chemical gradients can increase specificity is shown in Fig. 6B [17]. Here n-octane and ethanol are used to wet two different IOFs each with unique gradients in surface chemistry. For the IOF on the right, n-octane wets less than ethanol as seen by the presence of more colored layers while for the IOF on the left side, n-octane wets more than ethanol. This simple example shows how more information about a liquid is encapsulated in the wetting response from a combination of two chemically functionalized IOFs as opposed to one. The implication of this is such that ethanol could be diluted with a higher surface tension liquid (i.e. water) to produce the wetting pattern of n-octane on the right, but not on the left, since the wetting trend is reversed. We extended this concept to six different functionalities and found that a considerable degree of chemical specificity could be achieved (see Fig. 6B) [17].

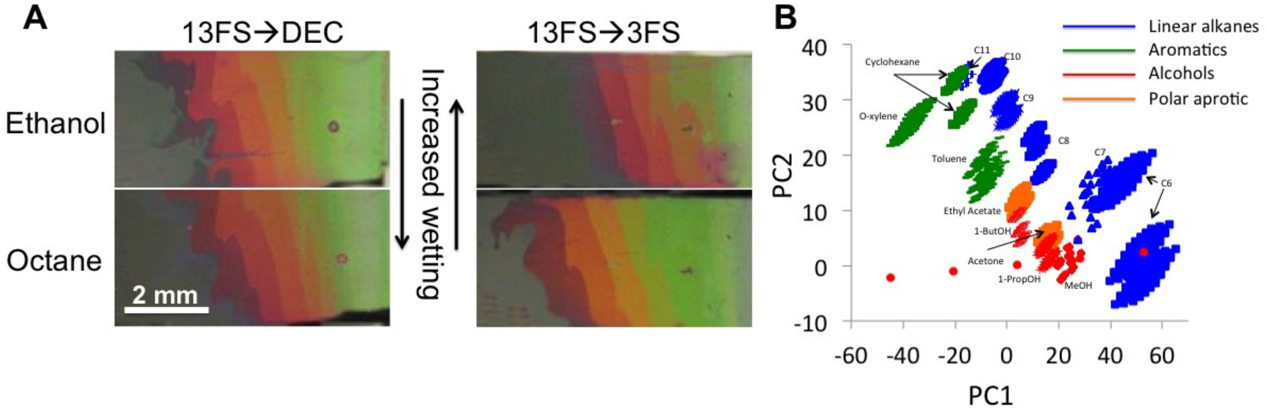

Figure 6. A) Sensor array with sufficient chemical specificity. IOFs on the left side are functionalized with vertical gradients of DEC→13Fs while samples on the right side are functionalized with 3FS→13FS. The reversal of the relative wetting trend between ethanol and octane illustrates the chemically specific information contained in the array that is not discernible from a single element. For example, a water dilution of ethanol could mimic the pattern shown on the right, but not the one on the left. B) Principal component analysis of the 6-element array showing the separation of linear alkanes, aromatics, alcohols and polar aprotic solvents.

In order to make the responses of different liquids easy to compare for a user, we developed a scoring system based on reference liquids to allow conversion of qualitative wetting patterns to numerical values. Each array of sensors was first characterized in reference solutions (ethanol-water solutions and isopropyl alcohol) and then wetting patterns were compared to patterns of the array in the reference solutions. Scores for liquids wetting patterns in the array were assigned based on which reference solution looked the most similar. This quantitative approach allows for easy interpretation, while also potentially offsetting some batch-to-batch variability in the IOF pore geometry (i.e. since the same neck distribution is compared for the reference and test liquids, regardless of how it compares to the distribution of other IOFs).

3.4. Ease of Use

Simplicity is arguably the most important aspect for the design of new sensing platforms. WICK is exceptionally easy to use, as liquid-specific responses are encapsulated in visually distinct optical readouts with *countable* differences. The importance of encoding the sensing output in a countable pattern (rather than in color) is apparent, recalling that structural color most often depends on viewing angle. Counting allows the sensor's response to be clearly identified regardless of the users' viewing angle, and this facilitates users with minimal training and essentially no technical knowledge to effectively use the technology. Furthermore, after use, samples can be dried off and re-used. Simple re-use is an attractive feature of WICK, but one must keep in mind that one-time use may be preferred in certain situations, especially for applications that require high specificity (e.g. to test unknown liquids where the effect of the initial test on the sensor may not be robustly quantified).

3.5. Reproducibility

The highly symmetrical and crack free structure of inverse opal photonic crystals facilitates sharply defined wetting patterns with remarkable selectivity [16]. However, batch-to-batch variability in pore geometry and neck angles adversely affects the reproducibility of the IOFs wetting response. We have explored three approaches that can be used for quality control to maintain sufficient reproducibility: (i) post selection, (ii) combinatorial scoring, and (iii) optical tuning.

Post selection is perhaps the most intuitive and simplest approach for solving the lack of reproducibility. In this approach, all new IOFs are DEC functionalized and then immersed separately in 85% and 90% ethanol solutions. IOFs must display a wetting response in 90% ethanol and a non-wetting response in 85% ethanol solutions to pass post selection. This ensures that the geometry of the IOF pores in each sample falls within an appropriate range thus providing sufficient reproducibility [15]. Despite its simplicity, the disadvantage is that approximately 1/3 of all IOFs are discarded.

The second approach exploited a combinatorial method to mitigate the disposal problem while still addressing the issue of reproducibility [17]. Scores were assigned to sample responses in organic liquids using ethanol solutions as a reference (refer to section 3.3). Regardless of the variability in a samples response, all that mattered was the response of a sample relative to a specific reference ethanol solution. This method is more laborious and complex than post selection, however it eliminates the inefficiency of sample discarding.

Finally, we have briefly outlined a third method using photo-switchable wetting discussed in section 3.2. This method involves optically tuning the wettability of each sample by photo-bleaching a chromophore-containing polyelectrolyte layer deposited on the surface of the pores. Sample variability means different bleaching times are required for each sample but all samples can be calibrated to a specific wettability threshold *in situ*, thus ensuring reproducibility. This method is the most complex of the three, but eliminates sample disposal.

4. OUTLOOK

WICK has many attractive features that facilitate an immense number of applications. The relatively low cost and simple optical readout give this technology a competitive edge in comparison to conventional sensing technologies. The fact that a user can, without any technical knowledge and essentially no training, use WICK to obtain meaningful information about an unknown liquid is an important advantage. However, chemical non-specificity remains a key limitation, and necessitates improved combinatorial scoring. The key to increasing chemical specificity is to increase the effective dimensionality of the arrays (i.e. number of independent measurements made for a specific liquid). However, there will always be a tradeoff between increased dimensionality and increased complexity. Scale-up of production presents an additional challenge, as current methods have been optimized for lab-scale production. Additional research is needed to investigate the potential large-scale production of functionalized IOFs.

Furthermore, it is desirable to expand the variety of substrates on which films can be deposited, and to accelerate the film growth. Large-scale fabrication procedures could make use of continuous processes instead of batch processing to reduce overall fabrication time. Currently, development of WICK has focused on glass or silicon substrates for film growth. However, commercialization opportunities in markets such as security may require the IOFs to be grown on additional substrates, such as paper bills and metal. One solution to this problem that is currently being researched is the incorporation of IOF fragments into paint. One could simply use this IOF paint to apply the IOF directly onto any substrate. Another potential approach would be to incorporate the IOF into a sticker that could then be applied to any surface. The application of WICK to flexible substrates may prove challenging due to the brittle nature of the IOFs. One possible solution could be to replicate the IOF structure in a flexible material, such as polydimethylsiloxane.

Apart from simple use in laboratories for liquid identification, WICK could also be used for consumer products. Contrary to applications in industry, there is a lesser need to have high specificity for some of these products, which allows for less stringent fabrication procedures. This ensures that fabrication remains relatively simple and inexpensive. One current commercialization project focuses on the application of WICK to shot glasses as a novelty item. The goal of the project is to develop a glass that can display desired patterns when filled with different liquors. Furthermore, one can imagine any number of consumer products where the addition of WICK could be an inexpensive and simple extension. WICK also has numerous industrial applications. In-field applications, where portability and simplicity are more important than absolute performance, are the most promising for this technology. The simplicity and power-free approach of WICK allows for use in extreme environments, where more complicated equipment may not be practical and where perfect specificity may not be required. A great example of this would be liquid identification during chemical spills in remote locations. Moreover, industrial applications would likely exploit the use of WICK as an inexpensive method of quality control where surface tension is a relevant factor. For example, the technology could find use in mass transfer processes during oil and gas production or even alcohol production processes as a simple method for quality control. Additional applications are also likely to be centered on the encryption capabilities. The vast number of chemical functionalities and wetting patterns that can be generated allow for complex multi-level encryption in a simple device. Finally, there is also great potential to use WICK as an educational tool for nanotechnology. The relative simplicity, visual nature and breadth of scientific concepts covered by WICK, may make it a useful as a hands-on learning tool that is appropriate for a wide range of students.

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