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BRIEF COMMUNICATION

A microstructure for the detection of vapor-phase analytes based on orientational transitions of liquid crystals

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Abstract
We report on the implementation of a microstructure comprising an array of micropillars to create a thin and stable film of nematic liquid crystal (LC), 5CB: 4′-pentyl-4-cyanobiphenyl, and the use of the microsystem for the colorimetric detection of vapor analytes. The microstructure uses capillary force generated by an array of cylindrical micropillars to steadily support a 22 μm thin film of LC, and overcomes susceptibility to gravity and shock. The feasibility of using the microsystem for gas phase detection is demonstrated by using dimethyl methylphosphonate (DMMP) gas to change the orientation of the LC and hence modulate the intensity of light transmitted through a crossed pair of polarizing films. The microstructure potentially offers a simple and portable solution to toxic gas detection.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Chemical and biological sensors which are highly sensitive, portable and cost-effective are needed for many applications including chemical warfare detection [1] and point of care diagnostics [2]. Considerable research is ongoing in this area. Some of the detection methods include fluorescence [3], absorbance spectroscopy [4], gas chromatography [5], mass spectrometry [6] and liquid crystals (LC) [7, 8]. An LC is a *smart material* which offers high sensitivity to targeted analytes, with simple and portable detection equipment, and relatively low cost. Interfacial molecular interactions at the surfaces of nematic LCs have been used to trigger orientational transitions of the molecules within the LC [7–9] resulting in the modulation of light intensity transmitted through a pair of crossed polarizing films. Vapor-phase analyte concentrations down to the ppb range have been successfully detected [10, 11].

This paper addresses the design and implementation of a microfabricated structure that can host LCs to be used for chemical and biological sensing. In one embodiment of LC-based sensors, a stable, micrometer-thick film of LC supported on a transparent substrate is used. Capillary forces which are dominant at the micrometer scale provide a method to realize this goal. To this end, structures such as polyurethane wells [10] and metallic grids [9] have been used.

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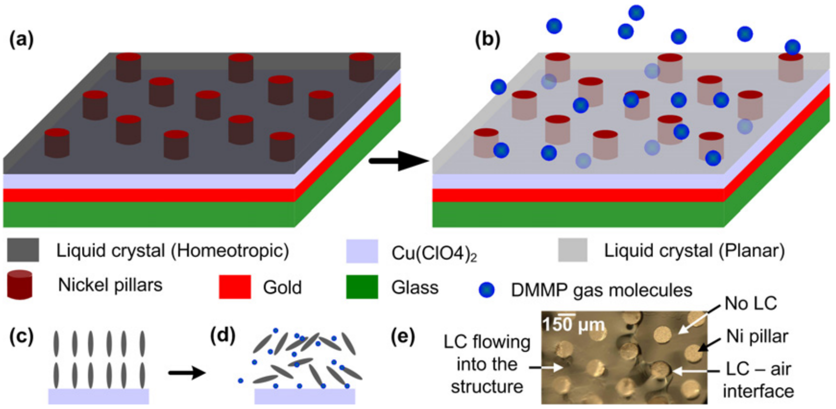

Figure 1. Schematic representation of the sensor. (a) The sensor before introducing DMMP vapor—molecules within the LC are oriented, on average, perpendicular to the substrate (c). No light is transmitted by the LC sandwiched between a pair of crossed polarizing films. (b) When exposed to DMMP, the LC loses its homeotropic orientation (d) and can now transmit light. (e) The fabricated device.

Although these structures can be used to host LCs for sensing applications, the procedures used to fill these structures are laborious and require careful handling of small volumes of LCs. Furthermore, the metallic grids are easily displaced from surfaces by mechanical forces, and thus they form the basis of a useful system for laboratory studies but not a portable microtechnology. To overcome these drawbacks, we present here a *smart microstructure* that is designed to exploit capillary forces generated by an array of nickel (Ni) micropillars electroplated on a glass substrate. Similar microstructures have been employed in the context of multiphase reactions [12], liquid chromatography [13] and air to liquid sampling [14]. The sensor is tested with DMMP vapor (a simulant for Sarin gas) and the LC designated 5CB (4′-pentyl-4-cyanobiphenyl).

2. Operating principle of the sensor

Figure 1 is a schematic representation of the sensor. An LC film is stabilized by the capillary force generated by an array of Ni micropillars fabricated on a glass substrate. The molecules comprising the LC orient perpendicular to the substrate (homeotropic orientation—figures 1(a) and (c)) by forming a coordination complex with a layer of copper perchlorate ($Cu(ClO_4)_2$) salt supported on a gold film deposited on the microstructure [10]. The orientation of the LC at the free surface (interface between the LC and air) is also homeotropic. In this orientation, the LC does not change the polarization of incident light transmitted through the film, and the LC appears dark when viewed between two crossed polarizing films placed on either side of the LC film. Upon exposure to DMMP vapor, DMMP diffuses through the film of LC and binds to the $Cu(ClO_4)_2$. In doing so, the LC is displaced from its coordination interaction with the $Cu(ClO_4)_2$ and the LC loses its homeotropic orientation [10] (figures 1(b) and (d)). This orientation of LC changes the polarization of transmitted light, causing an increase in the intensity of light passing through the crossed polarizing system.

3. Fabrication

The fabrication involves liquid-phase photopolymerization (LP^3) [15], Ni electroplating [16], gold (Au) evaporation and deposition of a $Cu(ClO_4)_2$ layer [10]. These are briefly described below. A glass substrate is sputtered with titanium/copper/titanium (Ti/Cu/Ti) layers, where Cu is used as a seed layer for electroplating. A 50 μm tall cavity is formed between the substrate and a film photomask, having the pattern of the micropillar array, by using adhesive tape. A photopolymerizable pre-polymer liquid comprising of a monomer (isobornyl acrylate), photoinitiator (2,2-dimethoxy-2-phenylacetophenone) and cross-linker (tetraethylene glycol dimethacrylate) is flowed into the cavity. The device is exposed to ultraviolet light to polymerize the exposed regions and the unpolymerized regions are flushed with ethanol. Any residual polymer is removed with oxygen plasma. After removing the top Ti protective layer, Ni is electroplated until the required pillar height is obtained. The pillar height determines the height of the LC film. The polymer mold is removed by soaking the device overnight in a bath of acetone/methanol and the metal layers are etched without releasing the pillars. A thin film (~20 nm) of Au is evaporated, followed by the formation of a carboxylic acid-terminated thiol monolayer by immersing the device into a 2 mM ethanolic solution of 11-mercaptoundecanoic acid for ~1 h. $Cu(ClO_4)_2$ is deposited onto the monolayer by soaking the device in a 25 mM ethanolic solution of $Cu(ClO_4)_2$ for 5 min followed by a thorough rinse with ethanol. Excess $Cu(ClO_4)_2$ is deposited by spin-coating 4.5 mM $Cu(ClO_4)_2$ in ethanol at 3000 rpm for 60 s [10].

4. Experiments and results

We observed the LC to spontaneously spread into the void spaces between the micropillars to form a thin film. The capillary forces lead to the formation of a stable film that was found to be resistant to gravity (tilting of the device) and shock. The capillary force generated by the structure increases with the total interfacial line of contact between the LC and the micropillar array, i.e. $F = n(\pi d)\gamma$, where F = capillary

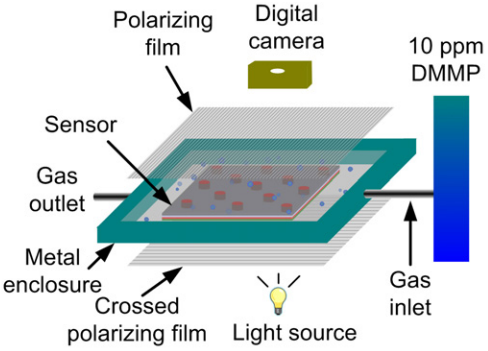

Figure 2. The experimental set-up. The sensor is placed in a metal enclosure having an inlet and outlet for DMMP vapor. Two crossed polarizing films are placed on top and bottom of the sensor. White light is used as an illumination source. A cylinder of 10 ppm DMMP feeds the sensor at a flow rate of ∼500 sccm. The status of the sensor is continuously captured by a digital camera connected to a computer (not shown).

force, n = total number of pillars, d = diameter of each pillar and γ = surface tension of LC. Although increasing the diameter of a pillar increases the perimeter of that pillar, the total number of pillars (n) that can be accommodated within a given area (A) of the device will decrease. There exists an optimal value of d, and hence n. Adjacent pillars are separated by d and form an equilateral triangle pattern which is replicated throughout the device area. In our experiments, we observed that $d = 150\ \mu\text{m}$, $h = 22\ \mu\text{m}$, $n = 1020$ and $A = 78.5\ \text{mm}^2$ provide sufficient capillary force to form a stable and robust thin film of LC (h = thickness of LC film). These values, however, do not necessarily represent the optimal ones for the formation of thin film LC microsystems.

We confirmed that the presence of the $Cu(ClO_4)_2$ layer created a homeotropic orientation of the LC by observing the conoscopic image (an interference pattern formed at the focal plane of the objective lens of a microscope) on a microscope equipped with a Bertrand lens. The device was then placed into the testing apparatus, as shown in figure 2. The sensor was sandwiched between two crossed polarizing films and was exposed to a source of 10 ppm DMMP vapor flowing at a volumetric rate of 500 sccm. This assembly was illuminated by a white light source and the transmitted light was captured by a digital camera and stored periodically on a computer. The initial homeotropic orientation of LC resulted in a dark optical appearance (figure 3(a)), as described above. Upon exposure to DMMP, the LC underwent an orientational transition to a tilted state that led to changes in the polarization of light transmitted through the film of LC. We observed the optical appearance of the LC to become bright, as shown in figure 3(b). With increasing time of exposure, the bright regions of LC spread throughout the device (figures 3(c) and (d)). We note that the response time of the device described here is substantially slower than that reported previously. The reasons for the slower response have not been identified, but may be related to the geometry (influence of the pillars), thickness of the LC film and/or the method of deposition of the metal salts. The results of an investigation of the dynamics of the LC in this geometry will be reported elsewhere.

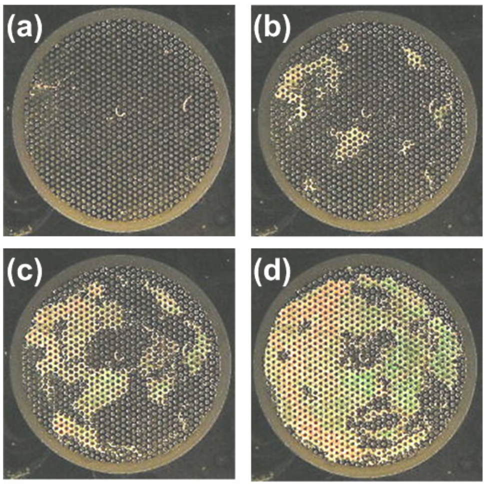

Figure 3. Response of the sensor to DMMP. (a) Before introducing DMMP. There is no transmission of light through the crossed polars due to the homeotropic alignment of LC. (b) At $t = 1783$ s after the introduction of DMMP. A few regions (appearing bright) of the sensor have started to respond. (c) At $t = 1964$ s. (d) At $t = 2291$ s. Most of the regions have responded to DMMP and there is a significant change in the intensity of the transmitted light.

5. Conclusions

The main conclusion of this study is that a micropillar system provides a convenient and robust approach to create stable, thin films of LC for use in sensing systems based on orientational transitions of LCs. The system employs the micropillars to create capillary forces that stabilize the LC. Preliminary studies demonstrate the feasibility of using this geometry for gas phase sensing, although the role of the geometry on the dynamics and sensitivity of the LC sensor remain to be fully elucidated.

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