Direct laser writing of submicron photonic arrays for vapor-responsive sensing

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Abstract: A two photon polymerization technique was used to fabricate 2D photonic crystals based on a vapor-responsive hydrogel. By testing their vapor sensing performance, these photonic arrays were found to exhibit dynamic stimulus responses and show excellent structural and color reversibility. © 2022 The Author(s)

People marvel at the vibrancy and diversity of bio-photonic crystal structures occurring in nature. The emergence of novel photoresists and direct laser writing based on two photon polymerization (2PP) has made possible the fabrication of complex microscopic biomimetic-inspired structures. To date most reports of photonic crystals printed by 2PP in the literatures use commercial non-responsive photoresists [3-4]. The fabrication of photonic crystals based on responsive hydrogels opens the pathway to a wide range of applications. Their low manufacturing cost, high printing accuracy and high stimulus sensitivity make them promising candidates in sensing and anti-counterfeiting to name just two examples [1, 2]. Up to the present time there few reports on photonic array fabrication using self-designed vapor-responsive hydrogels, or the use of such structures for vapor-sensing based on spectral changes of the photonic crystals.

In this work, we report a newly-designed monomeric cocktail composition, which is vapour-responsive acrylamide-based hydrogel. Samples with size of 300 μm were printed on fused silica using 780 nm femtosecond laser excitation coupled though a 63X objective in oil immersion configuration.

Firstly, we show an example of a grid structure, shown in Fig 1(a), that was fabricated and experimentally characterised. The optical spectra of the fabricated photonic crystals structures are in good agreement with those calculated using Lumerical FDTD software. The influence of the structure dimensions (i.e. structure height (h), line width (d), height of IPA in holes (h_{IPA}) and grid hole size (a)) and environmental factors (i.e. refractive index of material (RI) and refractive index of the ambient medium (RI_{bg})) on the transmission spectrum were investigated. Increasing the height of the structure (h), the linewidth (d) and the refractive index of the material (RI) causes a redshift of the transmission spectrum, while increasing the refractive index of the ambient medium (RI_{bg}) and the height of the IPA in the pores of grid structures (h_{IPA}) results in a blue shift of the transmission spectrum.

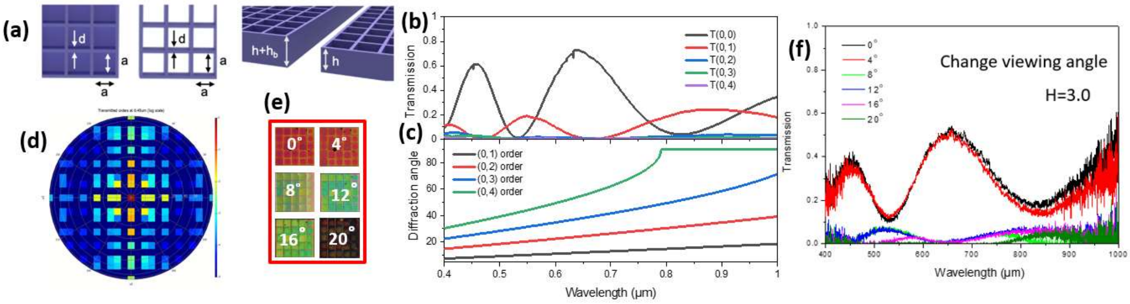

Fig. 1. (a) Schematic of the grid structure design [2]. (b) FDTD simulated transmission spectra of the 0, 1st, 2nd, 3rd and 4th diffraction order (d=0.5 μm, a=2.75 μm, h = 3.0 μm). (c) FDTD simulated diffraction angle for 1st, 2nd, 3rd and 4th diffraction order (d=0.5 μm, a=2.75 μm, h = 3.0 μm). (d) Farfield image shows the diffraction order at 450 nm. (e) Angle-resolved CCD images of sample (h = 3.0 μm). (f) Angle-resolved transmission measured by our home-built angle-resolved setup [2].

Fig. 1. (b) and (d) shows the grid structure exhibits the strongest transmission intensity in the zero order diffraction. From Fig. 1(c) we know that the first order starts at around 7 degree in 400nm. Fig. 1. (e) shows the vivid CCD images captured by our own angle-resolved setup. Structural color change (from red to green) at 8 degree which matches well with FDTD diffraction order calculations. Fig. 1. (f) is experimental angle dependent transmission

spectra which corresponds well with FDTD results. The results demonstrate that it is important to choose a suitable objective lens with small NA to isolate and monitor the the zero-order transmission.

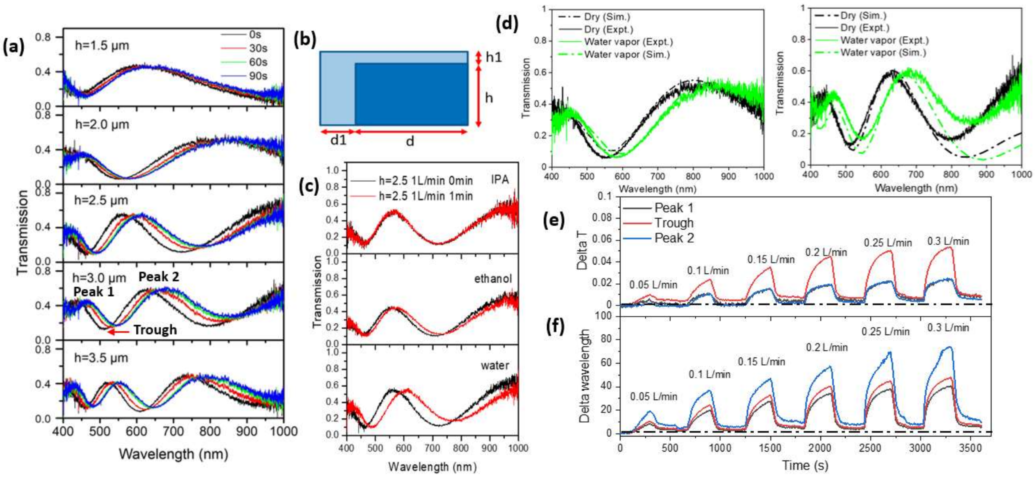

Fig. 2. (a) Transmission spectra of the photonic structures of different designed heights (top to bottom: 1.5 µm, 2.0 µm, 2.5 µm, 3.0 µm and 3.5 µm) at different time points, under a 1 L/min flow of water vapour [2]. (b) Schematic of volume expansion. (c) Transmission spectra of sample (h=2.5 µm) exposuring on IPA (top), ethanol (middle) and water (bottom) vapours for 1 minute under 1 L/min flowrate. (d) FDTD expension results compared with experimental results for samples with h = 2.0 µm and 3.0 µm, assuming a 5% volume expansion under exposure to water vapor at 1 L/min for 90 s [2]. (e) and (f) T and wavelength differences at peak and trough wavelength between each response spectra and the original spectrum for the h = 3.0 µm sample. Different water vapour concentrations with a dry period between each exposure are shown.

Fig. 2. (a) shows the gradual redshift of the transmission spectra of 5 grid structures of varying height under exposure to water vapour at a flow rate of 1L/min. The redshift of the spectrum is seen to be a result of a 5% volume expansion, as shown in Fig. 2. (b). Fig. 2. (d) shows the FDTD simulation results compared with experimental results. This is minimum volume expansion under a 1 L/min flow of water vapour.

To further demonstrate the vapour sensing performance of photonic sensors based on this responsive hydrogel, a sample with h = 2.5 µm was tested under different vapours, as shown in Fig. 2. (c). Interestingly, this photonic sensor exhibits different degrees of response to different vapours (water > ethanol > IPA). This important feature makes it possible to measure mixed vapours. The grid sample with h=3.0 µm was used to do consecutive water vapor measurenments over 1 hour, with the zero order transmission spectrum measured for varying vapor response as a function of time, as shown in Fig. 2. (e) and (f). The change in transmission, Delta T, and change in wavelength, Delta wavelength, show varying levels of sensitivity at different flow rates. Both Delta T and Delta wavelength exhibit reversibility and repeatability, as they always return to 0 during drying phase of the process, a feature that is critical to sensor design.

In conclution, the experimentally tested vapor response show that this bio- and environmental-friendly material combined with photonic crystals structure has enormous potential for vapor sensing devices in homes, labs and factories with concentration sensitivity and structural color reversibility. This zero order transmission of the 2D photonic sensors is most sensitive to water vapour, with a response time of less than 30 s. The 0 order structural color change is mainly attributed to the structural volume expansion and the main structural feature influencing the change in colour is the height increase.

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