Spatiotemporally Resolved Dual-band Hyperchromatic Structural Color with a Mesoporous Metamaterial

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Abstract: We present an approach to achieve highly responsive structural color utilizing dual-band porous silicon rugate filter metamaterials combined with dichromatic laser illumination. Spatiotemporally resolved sensing experiments are reported.

1. Introduction

Responsive structural color devices present exciting possibilities for various sensing and display technologies [1], including applications in point-of-care diagnostics, portable or wearable sensors, and low-power full-color displays. One prospective advantage of such colorimetric devices is that they can offer a more affordable and accessible sensing option compared to bulky laboratory equipment. This is especially true when it comes to performing measurements with spatial and temporal resolution. Instead of requiring complex equipment, colorimetric devices only need a light source, sensor, and a method of observation. This makes them ideal for use with simple tools such as smartphones, microscope cameras, or even the naked eye.

One of the main difficulties faced by responsive structural color devices and sensors is their limited capability to generate a significant color change, dE_{00}, in response to small changes in input stimuli, dS. Recently, our group introduced a concept called "hyperchromatic structural color" (HSC) as a solution to this challenge [2]. HSC combines a highly sensitive material system (e.g., mesoporous silicon) with strong spectral sensitivity $d\lambda/dS$ and an optical design that exhibits pronounced colorimetric sensitivity $dE_{00}/d\lambda$. Importantly, the optical design should encompass both the illuminant's spectral properties and those of the structural color object/filter.

In this study, we present dual-band HSC which relies on dichromatic laser illumination of a responsive mesoporous metamaterial with engineered spectral shapes in the vicinity of the illumination frequencies. Specifically, we realize our scheme using a lithography-free mesoporous silicon dual-band rugate filter combined with fiber-coupled red/green laser illumination. Speckle free laser imaging is facilitated by using light diffusing optical fiber and/or agitated multi-mode fiber. Our design achieves not only a high colorimetric sensitivity, $dE_{00}/d\lambda > 10\ nm^{-1}$, but also facilitates a quantitative mapping between the observed color and the device's spectral shift, thus circumventing the need for a spectrometer and/or hyperspectral camera to perform similar sensing tasks. Consequently, the observed chromaticity values can be directly linked to the physical characteristics of the applied stimuli (e.g., analyte concentration). We also experimentally investigate and validate the spatiotemporally resolved performance of such devices in three illumination/observation formats: specular projection onto a viewing screen, direct viewing of scattered light, and direct imaging in a microscope camera.

2. Experimental Approach and Results

P-type <100> silicon wafers with a resistivity of 0.01-0.02 Ω-cm were cut into approximately 2 × 2-inch pieces and subjected to anodization in around 65 mL of an ethanol based solution containing 15% hydrofluoric acid. To create the dual band mesoporous silicon rugate filter, a current density waveform J(t) consisting of two cosine terms with frequencies of 0.077 Hz and 0.1 Hz was applied using a Keithley 2601A instrument, where the minimum and

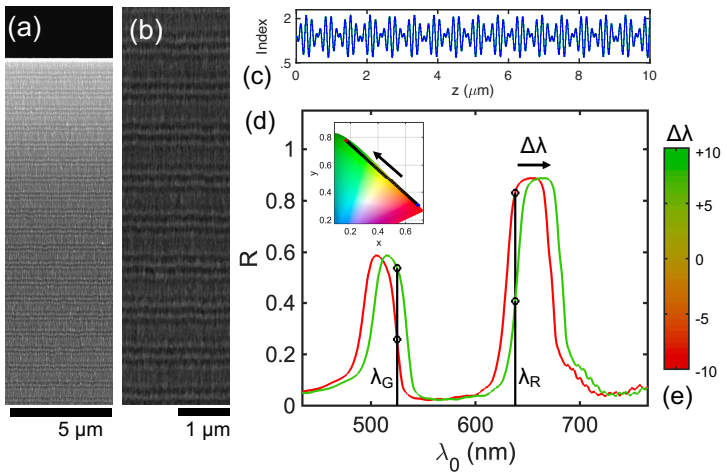

Figure 1(a, b) Dual band pSi rugate filter metamaterial SEM images, (c) refractive index profile, (d) reflectance spectra under perturbation from an input refractive index stimulus. Inset and part (e) show the predicted colorimetric response to wavelength shift.

maximum current densities were set at values of ~7.9 mA/cm² and ~47.25 mA / cm² respectively. The samples underwent oxidation at a temperature of 600°C for a duration ranging from 5 to 30 minutes in an ambient box furnace, to stabilize the structure and convert the internal mesoporous surface into silica thereby facilitating subsequent surface functionalization. As illustrated in Fig. 1a-c, this fabrication process achieves precise control over the effective refractive index $n(z)$ through self-organizing electrochemistry, a characteristic well-known to mesoporous metamaterials [3-5], but otherwise challenging to realize through lithographic methods. Our anodization recipe generates a refractive index profile of the form: $n(z) = \delta n/4*[\cos(2\pi z/\Lambda_G) - \cos(2\pi z/\Lambda_R)] + n_{avg}$, where δn is the index contrast, Λ_G and Λ_R are the green and red Bragg periods, and n_{avg} is the average refractive index.

We discovered that an optically lossy filter of this type, e.g. made from lightly oxidized mesoporous silicon, can naturally achieve excellent suppression of sidelobes and high extinction at the desired band edges. This design eliminates the need for apodization or quintic matching layers typically required in gratings or multi-layers. We also found that other combinations of +/- $\sin(2\pi z/\Lambda)$ and +/- $\cos(2\pi z/\Lambda)$ summations yielded less desirable spectral shapes. It is important to note that achieving adequate sidelobe suppression is crucial for an accurate one-to-one mapping between spectral shift and induced color response, while the sharpness of the band edges inversely affects the dynamic range.

Examples of spatially and spatiotemporally resolved structural color are shown in Fig. 2a and Fig. 2b respectively. In the first experiment, the surface is functionalized with two small molecules, first with a broad aminosilanization covering the entire chip, followed by a local binding of a monoloayer of Sulfo-NHS-Biotin. Despite the nanoscopic thickness of the applied surface adlayer, it is readily detected – producing a strong red-to-green color transition.

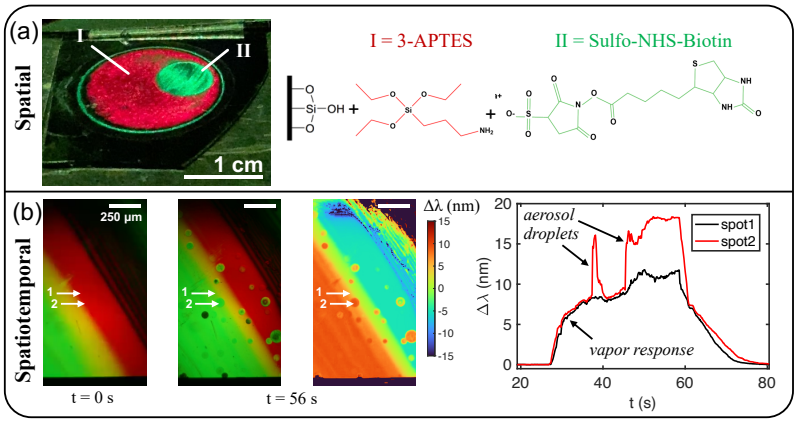

Figure 2. (a) Experimental demonstration of red-to-green color transition by surface functionalization, as photographed by a smartphone camera in a scattering configuration, and (b) spatiotemporal monitoring of IPA aerosol and vapor adsorption in a microscope configuration.

Fig. 2b highlights the spatiotemporal resolution of the dual band HSC technique. Here a small color gradient in the corner of the chip is imaged in a microscope. Exposure of the sample to isopropanol (IPA) aerosols and vapors, produces a highly dynamic and responsive color change. Initially, a sweeping shift in the background color is noted, corresponding to vapor adsorption within the pores. The interaction of aerosol microdroplets with the porous silicon surface is similarly monitored in real time, capturing adsorption events and subsequent evaporation dynamics both spatially and temporally. Further studies reveal ~100 ppm IPA vapor concentrations induce colorimetrically measurable responses which are ~30-40x larger than empirically determined resolution limit, which indicates the potential for ~ppm level detection capabilities using structural color. We note that aside from the sensitive optical design, the fine resolution is also aided in part by (i) measuring signals in the chromaticity plane rather than along intensity axis, and (ii) averaging multiple pixels while discarding outlier pixels.

3. Conclusion

We have successfully demonstrated dual-band HSC using dichromatic laser illumination alongside a responsive and spectrally engineered mesoporous metamaterial. Our method enables quantitative imaging through a direct mapping between the sensor's spectral shift and resulting chromaticity and presents a promising avenue for accurately analyzing and spatiotemporally measuring dynamic processes involving nanoscale analytes and other sensor stimuli.

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