Hyperchromatic Structural Color for Perceptually Enhanced Colorimetric Sensing by the Naked Eye

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Abstract: We report a novel colorimetric sensing paradigm using multi-chromatic light from an RGB laser combined with a structural color sensor for fast, ultra-sensitive, and spatio-temporally resolved detection of surface biomolecules by human eye or smartphone.

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Colorimetric sensing is a simple and low-cost diagnostic technique which enables rapid spatiotemporally resolved sensing to be performed via the naked eye or portable smartphone camera. Two general types of colorimetric sensors exist: (1) sensors that perturb an illuminant power spectral density P(λ)→P(λ)' (i.e. fluorophore or quantum dot), and (2) 'filter' based structural color sensors which modify the filter function of an illuminated sensing object R(λ)→R(λ)' (i.e. reflectance, absorption, etc.). Color perception can be mathematically expressed as a cross-correlation (Fig. 1) between the spectral power distribution of an illuminant P(λ) and color matching functions $\bar{x}(\lambda), \bar{y}(\lambda), or\ \bar{z}(\lambda)$, which represent the spectral sensitivity of each primary photoreceptor, weighed by the object filter function R(λ) [1]. In either sensing configuration, the fundamental aim of a colorimetric sensor (e.g. biosensor) is to provide a large perceptible color change, ΔE_{00}[2], per unit change in the sensor stimulus, e.g. the analyte surface adlayer thickness $\Delta\sigma$.

Label free biosensors, for example, can be constructed from type 2 colorimetric sensors which wavelength shift an optical filter in response to the analyte. For such a device we introduce a colorimetric sensitivity: $\Delta E_{00}/\Delta\sigma = (\Delta E_{00}/\Delta\lambda)(\Delta\lambda/\Delta\sigma) = S_1S_2$. The naked eye perceptual detection limit is $\Delta E_{00} \approx 2.3$, also known as the "just noticeable difference" (JND). Considering the JND, the limit of detection (LOD) by the naked eye becomes: LOD $\equiv \Delta\sigma = 2.3/(S_1S_2)$. Current colorimetric sensing techniques primarily focus on maximizing S_2 by utilizing unique materials or physical phenomena which leads to amplified $\Delta\lambda$. Porous silicon (pSi) for example has emerged as an attractive platform for biosensing because of its ability to offer one the highest S_2 values of any photonic sensing platform owing to its large surface area and tunable pore dimensions [3]. However, current colorimetric sensing schemes remain restricted by low S_1 values, thus not producing perceptible color change with low $\Delta\lambda$. For example, a broadband

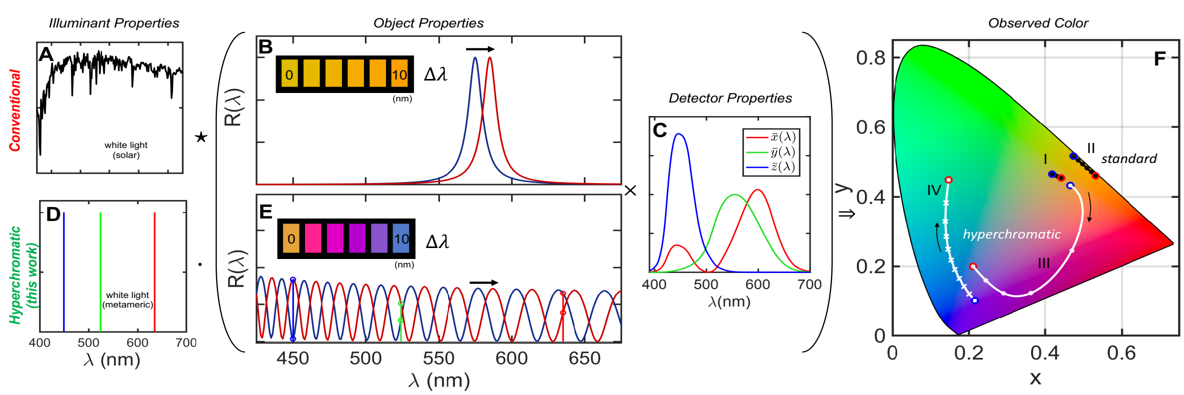

Figure 1. (A, B) Broadband illumination colorimetric sensing scheme with an optical filter (e.g. Lorentzian) with a wavelength shift and barely detectable color change (D, E) Hyperchromatic illumination with multi-laser (RGB) white light on a pSi thin film filter which shifts wavelengths and produces clearly perceptible color change (F) Chromaticity space color trajectories showing conventional sensors (I and II) with Q = 50 and 500 respectively, and example hyperchromatic sensors (III and IV) respectively. A spectral shift $\Delta\lambda = 10$ nm (from 575 nm) is modelled for (I, II, and III) while a shift $\Delta\lambda = 1$ nm is modelled for (IV).

illumination of a narrow band structural color filter only achieves $\Delta E_{00}/\Delta\lambda \sim 1\ nm^{-1}$. Narrow band illumination is another approach to amplify $\Delta E_{00}/\Delta\lambda$ and improve the LOD, however such sensors only utilize the luminance variations in ΔY direction [4-5] and ignores the Δx and Δy in the CIE xyY 3D color space $\Delta E_{xyY}=\sqrt{(C_1\Delta x^2 + C_2\Delta y^2 + C_3\Delta Y^2)}$. In our work, we introduce a sensing technique called "hyperchromatic structural color" (HSC), which employs metameric white light from a multicolor (RGB) laser in combination of a simple pSi thin film refractive index sensor (Fig. 1, bottom row). HSC enables theoretically unbounded amplification of S_1 and significantly enhanced color response as shown in simulations Fig. 1F.

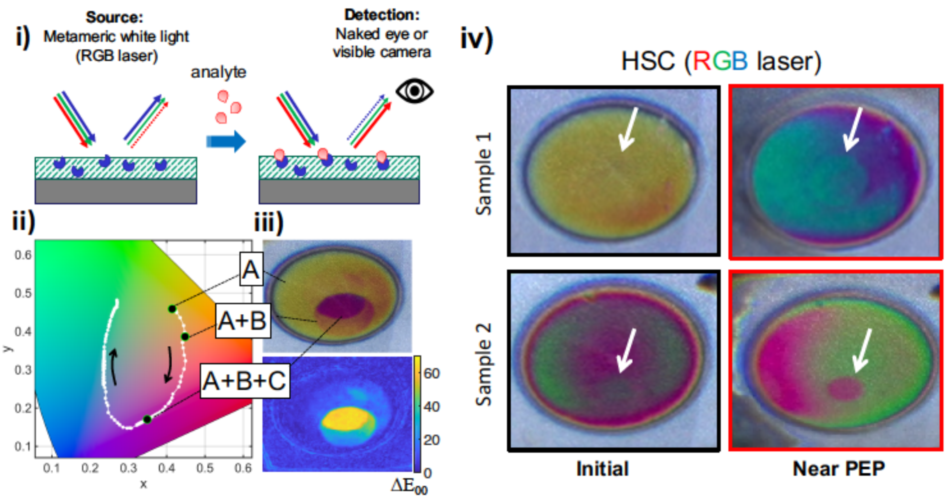

Figure 2. (i) Experimental scheme (ii) Color trajectory of the sample subjected to transient vapor deposition/evaporation and observed color due to small molecule attachment steps. (iii) Camera image of the HSC sensor after local surface functionalization. A = oxidized pSi surface, B = 3-APTES and C = Sulfo-NHS-Biotin. (iv) 2 samples initially (left) and near PEP (right) highlighting the perceptual enhancement through the clearly visible spot when crossing a PEP which is a key highlight of our technique.

We recently demonstrated HSC based colorimetric sensing using multi-chromatic illumination of structural color sensors based on mesoporous silicon thin-films[6]. After porous thin-film synthesis and surface oxidation, an RGB laser is used as the illuminant, while the color change in response to refractive index variations and/or small molecule attachment is characterized via a smartphone camera (iPhone 6). The initial color of the sensor can be swept across a trajectory via transient vapor deposition using simple human breath or a nebulizer. This dynamic variation in refractive index allows the sample to cross a perceptual enhancement point (PEP) where the perceptual sensitivity is significantly enhanced (i.e. >2-20x). Figure 2(iv) shows enhanced naked eye detection of immobilized sub-monolayer 3-APTES when a sample crosses the PEP (Fig. 2(iv) – right), whereas it was undetectable initially (Fig. 2(iv) – left). In Fig. 2(ii) and 2(iii) we further demonstrate spatially resolved sensing of small molecule attachment and specific surface functionalization. This image shows immobilized sulfo-NHS-Biotin (A+B+C) partially overlapping a 3-APTES (A+B) activated region on top of a sensor (A). Fig. 2(iii) illustrates a CIE map of the perceptual color difference ΔE_{00}. The large $\Delta E_{00} \sim 60$ is significantly greater than the JND=2.3 limit, which confirms the high sensitivity of the HSC technique.

In summary, we successfully demonstrate a novel colorimetric sensing technique that overcomes current colorimetric sensor limitations by achieving arbitrarily enhanced sensitivity via structural filter design that can be further amplified via the perceptual enhancements available in the chromaticity space. In combination to the high wavelength sensitivity of porous silicon, this platform offers a new benchmark for perceptual color change to small molecule attachments that can be spatiotemporally resolved using naked eye or smartphone camera.

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