Supplementary Information for

Hyperchromatic structural color for perceptually enhanced sensing by the naked eye

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Colorimetric Sensitivity: Bounded vs. Unbounded

A colorimetric response arises when an input sensor stimulus, $\Delta S$, perturbs the spectrum or intensity of light reaching the receiving photoreceptors. Such a task can be realized using structural color sensors, which filter the power spectral density $P(\lambda)$ of a stable illuminant. Perturbations in the structural color filter function $R(\lambda)$ can be described in relation to the sensor stimuli according to: $\Delta R(\lambda) = \Delta S \frac{\partial R(\lambda)}{\partial S}$. Therefore, colorimetric variations in CIE tristimulus values $(X,Y,Z)$ can be related to variations in sensor stimuli according to:

$$\frac{\Delta X}{\Delta S} = k \int_0^{+\infty} P(\lambda) \left( \frac{\partial R(\lambda)}{\partial S} \right) \bar{x}(\lambda) d\lambda$$

$$\frac{\Delta Y}{\Delta S} = k \int_0^{+\infty} P(\lambda) \left( \frac{\partial R(\lambda)}{\partial S} \right) \bar{y}(\lambda) d\lambda$$

$$\frac{\Delta Z}{\Delta S} = k \int_0^{+\infty} P(\lambda) \left( \frac{\partial R(\lambda)}{\partial S} \right) \bar{z}(\lambda) d\lambda$$

(S1)

where $k$ is a constant defined such that the luminance, $Y$, equals 100 for an appropriate white reference, and $\bar{x}(\lambda), \bar{y}(\lambda)$, and, $\bar{z}(\lambda)$ are color matching functions (Fig. 1(d) of main text) which describe the unique spectral characteristics of each primary photoreceptor (1–3). Note that the two dimensional chromaticity values $(x,y)$ in CIE $x\!y\!Y$ colorspace are determined directly from $(X,Y,Z)$ according to $x = X/(X+Y+Z)$ and $y = Y/(X+Y+Z)$. A generic measure of colorimetric sensitivity could be defined as the Euclidean color distance $\Delta E$ derived per unit variation in input stimulus $\Delta S$:

$$\frac{\Delta E}{\Delta S} = \sqrt{\left( \frac{\Delta X}{\Delta S} \right)^2 + \left( \frac{\Delta Y}{\Delta S} \right)^2 + \left( \frac{\Delta Z}{\Delta S} \right)^2}$$

(S2)

while the perceptual color change $\Delta E_{0.0}$ is derived per the CIE 2000 standardized color differenting equation which accounts for perceptual non-uniformity in the underlying CIE colorspace (4). To preserve generality, the variations in input stimulus $\Delta S$ can be considered any physical, chemical, mechanical, or other attribute which perturbs the structural color filter according to the function $\frac{\partial R(\lambda)}{\partial S}$ (e.g. temperature, chemical concentration, refractive index, etc.). The reason that $\frac{\partial E_{0.0}}{\partial \lambda}$ cannot be made arbitrarily high in the case of broadband illumination, can be seen from Eqs. (S1) and (S2). When illuminated with a broadband light source, the function $P(\lambda)$ is smooth and the Eq. (S1) integrals are always integrable and finite even if the function $\frac{\partial R(\lambda)}{\partial S}$ contains spikes or delta functions, which may be derived for example from arbitrarily high Q-factor spectral features. This implies that the colorimetric sensitivities $\frac{\partial E_{0.0}}{\partial S}$ and $\frac{\partial E_{0.0}}{\partial \lambda}$ are bounded when $P(\lambda)$ is smooth.

This limitation can be broken by using a linear combination of $N$ monochromatic lasers as the illuminant, where the function $P(\lambda)$ may be described as a discrete sum of Dirac delta functions placed at each laser wavelength: $P(\lambda) = \sum_{j=1}^{N} c_j \delta(\lambda - \lambda_j)$. In this situation, Eq. (S1) simplifies to a discrete sum which is no longer guaranteed to be finite and integrable:

$$\frac{\Delta X}{\Delta S} = k \sum_{j=1}^{N} c_j \left( \frac{\partial R(\lambda_j)}{\partial S} \right) \bar{x}(\lambda_j)$$

(S4)
Given that the $\frac{\partial R(\lambda)}{\partial S}$ terms may be arbitrarily high, the colorimetric sensitivity $\frac{\Delta k}{\Delta S}$ is now theoretically unbounded. If $N = 1$, then the sensor operates strictly based on luminance variations as in Fig. 1(b) (main text), while for $N > 1$ a “hyperchromatic structural color” (HSC) response can be achieved with the appropriate design as in Fig. 1(c) (main text).

**Hyperchromatic Structural Color with Thin-Film Interferometers** In the case of illumination with $N = 3$ lasers we assume the blue, green, and red frequencies are given by:

\[
\omega_b = \frac{2\pi c}{\lambda_b} \quad (S5)
\]
\[
\omega_g = \frac{2\pi c}{\lambda_g} \quad (S6)
\]
\[
\omega_r = \frac{2\pi c}{\lambda_r} \quad (S7)
\]

Where $c$ is the speed of light and $\lambda_b, \lambda_g, \lambda_r$ are the blue, green, and red wavelengths in free-space respectively. If we assume the lasers are approximately equally spaced in frequency by $\Delta \omega$, then we can write:

\[
\omega_r = \omega_b + 2\Delta \omega \quad (S8)
\]
\[
\omega_g \approx \omega_b + \Delta \omega \quad (S9)
\]

In this scenario, illumination of a thin-film interferometer will yield reflections at each frequency that are in phase when:

\[
\frac{\Delta \omega n_g}{c} 2D \cos(\phi_i) = m2\pi \quad (S10)
\]

Where $\phi_i$ is the internal angle in the film, which may be determined from Snell’s law, $\phi_i = \sin^{-1} \left( \frac{n_{ext} \sin(\theta_{ext})}{n_i} \right)$. $D$ is the film thickness, $n_g$ is the group index, and $m$ is a positive integer. Solving for the minimum thickness $D = D_0$ which satisfies Eq. (S10) we find:

\[
D_0 = \frac{\pi c}{n_g \Delta \omega \cos \phi_i} \quad (S11)
\]

We refer to integer multiples of this film thickness, $mD_0$, as “anti-magic” film thicknesses, as they result in suppression in the chromatic color response owing to all three color lasers modulating their intensity in phase. An example “anti-magic” colorimetric response is shown in the Figure Sq below. In this example the film thickness equals $D_0$ and $\phi_i = 0^\circ$, $n_g = 1.9$, and the color response is simulated for wavelength shifts in the range -20nm to +20nm @ 575 nm. The substrate is silicon and top cladding is air, and the laser wavelengths are $\lambda_b = 450 \text{ nm}$, $\lambda_g = 524 \text{ nm}$, and $\lambda_r = 635 \text{ nm}$.
Fig. S1. Achromatic color response from a thin-film interferometer designed at the “anti-magic” thickness $D_0$. (top left) trajectory through chromaticity space for +/- 20 nm wavelength shift variation, (top right) relative RGB laser intensities reflected by the optical filter (a.u.), (middle right) corresponding color variation, (bottom) reflectance of the interferometer at starting and end points of the +/-20 nm sweep.

An approximately three-phase configuration can be achieved when the reflections at each frequency are out of phase by $\pm \frac{2\pi}{3}$ such that:

$$\frac{\Delta \omega n_g}{c} 2D \cos(\phi_1) = 2\pi \left( m \pm \frac{1}{3} \right)$$  \hspace{1cm} (S12)

This yields the “magic” thicknesses for the three-phase configurations as:

$$D = \frac{\pi c}{n_g \Delta \omega \cos(\phi_1)} \left( m \pm \frac{1}{3} \right) = mD_0 \pm \frac{D_0}{3}$$  \hspace{1cm} (S13)

For film thicknesses $mD_0 + \frac{D_0}{3}$ the color trajectory through chromaticity space has a negative hue sensitivity such that $\frac{dn_{nh}}{d\lambda} < 0$. SFig. 2 below shows simulation results for examples where the film thickness is chosen to be $mD_0 + \frac{D_0}{3}$ in SFig. 2(A) and $mD_0 - \frac{D_0}{3}$ in SFig. 2(B) in the case $m = 2, \phi_1 = 0^\circ, n_g = 1.9$, for wavelength shifts ranging from -20nm to +20nm @ 575 nm. The substrate is silicon and top cladding is air, and the laser wavelengths are $\lambda_b = 450 \text{ nm}$, $\lambda_y = 524 \text{ nm}$, and $\lambda_r = 635 \text{ nm}$.
Fig. S2. Hyperchromatic color responses from thin-film interferometers designed at “magic” thicknesses. Thin-film thickness are selected to generate either RBG or RGB three-phase configurations with film thicknesses: (A) \(2D_0 + \frac{D_0}{3}\) and (B) \(2D_0 - \frac{D_0}{3}\). For each subplot A, B: (top left) trajectory through chromaticity space for +/- 20 nm wavelength shift variation, (top right) relative RGB laser intensities reflected by the optical filter (a.u.), (middle right) corresponding color variation, (bottom) reflectance of the interferometer at starting and end points of the +/-20 nm sweep.

By inspection we find that the “magic” film thicknesses for an illuminant comprised of a linear combination of \(N\) lasers, equally spaced in frequency by \(\Delta \omega\) is

\[
D = \frac{\pi c}{n g \Delta \omega \cos \phi} \left( m \pm \frac{1}{N} \right) = mD_0 \pm \frac{D_0}{N}
\]

(S14)

From this equation it is also clear that as the number of lasers \(N\) becomes large, the “magic” thickness converges toward the “anti-magic” thickness, the colorimetric response becomes increasingly achromatic and approximately equal to that derived using a broadband standard illuminant.
Fig. S3. Comparison of illumination methods and speckle artifacts. (Left) Illumination via standard 50 um core diameter multimode fiber (MMF) direct onto diffusing screen. (Middle) Illumination via Corning® Fibrance™ light diffusing optical fiber without fiber shaking (displacement ~2-5 cm, frequency ~100-200Hz), and (Right) with fiber shaking. Note: the residual features in the right most image originate primarily from the surface roughness/relief of the diffuser screen.
Fig. S4. Comparison of different illumination conditions for different fibers. (Top row) Corning® Fibrance™ light diffusing optical fiber with (left to right) static, fiber shaking, adjacent diffuser and diffuser touching fiber tip conditions. (Bottom row) Standard 50µm MMF with (left to right) static, fiber shaking, adjacent diffuser and diffuser touching fiber tip conditions.
Spectral characterization of recipe A and B

Fig. S5. Reflectance spectrum (a.u.) of several samples prepared using ‘recipe A’ and ‘recipe B’ (top) alongside showing their repeatable structural color properties (bottom).
Fig. S6. (A) Normal incidence reflectance (a.u.) spectra for ‘recipe A’ and ‘recipe B’ plotted on a dB scale. (B) Analysis of the theoretical and experimental free-spectral range (FSR) for each recipe at normal incidence. Inset reveals the FSR values at the green wavelength. (C) Theoretical reflectance (a.u.) spectra for ‘recipe B’ for various incident angles plotted on a dB scale showing no change in extinction ratio vs angle of incidence. (D) Theoretical free-spectral range (FSR) for each recipe as a function of incidence angle.
Spectral shift characterization for 3-APTES and streptavidin experiments

Fig. S7. (A) 3-APTES experiment: Wavelength shift $\Delta \lambda$ as a function of 3-APTES concentration (%) from multiple measurements from different samples (both ‘recipe A’ and ‘recipe B’). Errorbar represents 1 standard deviation. The observed 3-APTES wavelength shift is consistent with prior literature in porous silicon. (B) Biotin-streptavidin experiment: The change in hue as a function of wavelength shift $\Delta \lambda$, for the 1 min to 45 min streptavidin exposures depicted in Fig. 6 of main text.
**CIE color gamut: Naked eye vs. iPhone camera**

Fig. S8. The CIE color gamut accessible to the naked eye spans the entire RGB lasers gamut (blue), whereas the video taken on the iPhone is theoretically limited to the standard RGB (sRGB) color gamut owing to the data format of the video and subsequent analysis. The iPhone gamut was experimentally measured by individually illuminating red, green, and blue lasers.

As indicated above, the colorspace or chromaticity color gamut analyzed from iPhone videos and image is reduced compared to the intrinsic gamut of the RGB illumination scheme which is accessible to the human eye. iPhone images are analyzed in standard RGB (sRGB) format with data converted to CIE XYZ and/or CIELAB. For color transitions near the edge of the color gamut, iPhone analysis may underestimate the naked eye sensitivity and LOD. Optimization of the colorimetric response will naturally depend on the detector involved and their quantum efficiency curves, which exhibit variations between different camera models. In the present work, software analysis techniques strongly favor the use of sRGB analysis. Recent work has suggested that analysis of RAW data could be useful to overcome the limitations of sRGB (5). In principle, if the exact calibration curve or quantum efficiency of the RGB sub-pixels are known a priori, then a given colorimetric sensor can be designed/optimized using those sensitivity curves to maximize the detected color change with a color camera. For naked eye detection however, the color matching curves of Fig. 1d would be utilized (as in our case).
Comparative analysis of selected structural color sensors from recent literature

Fig. S9. Analysis of the colorimetric sensitivity to wavelength shifts from a structural color sensor. (left) Luminance type plasmonic Fano resonant sensor by Yanik et al. (6), (middle) chromatic type plasmonic nanocup array by Gartia et al. (7), and (right) luminance type porous silicon microcavity by Cao et al. (8)
**Video S1 (separate file).** Measurement of an unoxidized and hydrophobic sample’s response to vapor exposure.

**Video S2 (separate file).** Sensor response to refractive index changes induced by transient vapor deposition.

**Video S3 (separate file).** Vapor deposition demonstration on a Recipe B sample using a nebulizer.

**Video S4 (separate file).** Recipe A measurement corresponding to Fig3.

**Video S5 (separate file).** Recipe B measurement corresponding to Fig3.

**Video S6 (separate file).** Visualization of Manual Angle Scanning and Interrogation of a Sensor Chip with a Handheld RGB Module.

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### List of symbols

| Symbol | Description |
|--------|-------------|
| Q      | quality factor |
| λ      | wavelength |
| P(λ)   | power spectral density |
| R(λ)   | structural color filter function |
| ΔS     | input stimulus variation |
| X, Y, Z| CIE tristimulus values |
| Y      | luminance coordinate |
| k      | constant defining Y = 100 |
| \(\bar{x}(λ), \bar{y}(λ), \bar{z}(λ)\) | color matching functions |
| ΔE     | Euclidean color distance/difference |
| ΔE₀₀   | CIE2000 perceptual color difference |
| Δλ     | wavelength shift |
| JND    | just noticeable difference (e.g. ΔE₀₀ = 2.3) |
| cᵢ     | laser power coefficient |
| D      | thin film thickness |
| m      | integer, m = 1, 2, 3 ... |
| a      | scaling parameter (e.g. \(Dₘ/D₁\)) |
| N      | number of lasers |
| φᵢ     | internal angle |
| n      | refractive index |
| n₀     | group index |
| c      | speed of light |
| Δω     | frequency spacing between adjacent lasers |
| Δσ     | analyte mass surface density |