Methods for design and fabrication of bio-inspired nanostructures exhibiting structural coloration

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ABSTRACT

In recent years, structural color has burgeoned into a vibrant and dynamic field of study. Many structurally colored organisms rely on comparatively few materials to create a large diversity of optical responses and a broad array of compelling and functional features. Scientists and engineers often explore such systems as examples of sustainable, robust solutions to complex problems. By looking to existing hierarchical material systems in biological systems, we aim to determine guidelines for fabrication of material structures with pre-determined functionality and properties.

Here, we compare approaches for producing surfaces that reflect color and discuss tunable design parameters. Methods discussed include bottom up self assembly, abstracted lithographic replication of structures, and top down systematically designed surfaces. We consider existing techniques and levers available to control output, and present the components of an inverse design approach. We compare different methods on the basis of scalability, tunability, and achievable responses, and provide practical guidelines for producing bio-inspired surface structures.

Our proposed designs are constrained for realizable fabrication using additive direct laser writing techniques such as two-photon polymerization that are suitable for producing arbitrary structures with sub-wavelength resolution. These evaluated and characterized structures could eventually be adapted to roll to roll or imprint-based systems for scale-up and manufacturing on a commercial scale. Here we contribute to a broader vision of systematic materials design by exploring tools for generating color.

Keywords: structural color, bio-inspired design, simulation-based optimization, colloidal assembly, direct laser writing

1. INTRODUCTION AND MOTIVATION

The study of color in living organisms is one of the most intriguing and interdisciplinary fields today. Color can serve as a visual marker of an organism’s interaction with its surroundings, used for camouflage, attraction of mates, warning and signaling, and stress protection. As we gain the capability to produce and emulate color, we have uncovered more and more potential functions and use cases. As humans, we rely color as an indicator, as a means of communication and personal expression, and as aesthetic tool.

Structural color offers several advantages over traditional pigments. These colors are stable and robust, resistant to photobleaching, can rely on nontoxic materials, and can be tuned across a broad gamut of colors. Furthermore, as they derive their color primarily or entirely from the geometry and morphology, small alterations in the structure can yield profound spectral differences. Some of the most captivating aspects of natural structural color, like opalescence, iridescence, metallic sheen, and luster are difficult or impossible to achieve with most pigments. To fully take advantage of these benefits, we need precise control over the design of the geometry.

The mechanism of structural color is often based on periodic structures, which can be qualified as photonic crystals, based on a medium with a refractive index that varies in space periodically in structures such as thin films, particle arrays, gratings, bowls, etc. The morphology determines optical response and scatters incident illumination. Typical natural photonic crystals are comprised of chitin, keratin, cellulose, or collagen, which have refractive indices around 1.5-1.6.

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Hierarchical structures combining periodic features and randomness work together to produce the compelling optical responses visible in natural structures like the wings of the Morpho butterfly.\(^1\)

Examples of periodic photonic crystal structures, where different colors represent materials with different dielectric medium.\(^2\)

The hierarchical structures of butterfly wing scales, shown in this SEM image, produce fascinating effects. SEM images taken by B. Datta.

While natural systems exhibit rich properties from minimal materials, their fabrication is often self-directed and we often do not yet fully understand the mechanisms behind them. Conversely, synthetic analogs allow us to have a high level of control over functionality and development, but require specific conditions and complex fabrication. Thus, synthetic responses can be abstracted or simplistic. Successful development of scalable color is a laudable goal as structural color provides a fascinating, visually stunning, and robust interface, thus sparking an intense research interest in the photonic design principles found in nature. Applications are as far reaching as displays, textiles, sensors, and security features.

### 1.1 Existing approaches

In attempting to harness the spectacular functionality found in nature, scientists and engineers have developed a multitude of biomimetic and bio-inspired techniques, each with its own strengths and constraints. Drawing inspiration from creatures as varied as birds and opal shells, scientists and engineers have turned to self-assembly of colloidal structures as a cheap, simple way to mimic aspects of this coloration, often using materials like polystyrene or silica.\(^3, 4\) Colloidal assembly resolution is determined by the particle size, and the process can
be inexpensive, scalable, and can work with a large array of materials. Color in such structures stems from a combination of Bragg diffraction from constructive interference of light reflected at planes of the crystal lattice, and index contrast effects, typically characterized in a modified Bragg-Snell equation (see Equation 1 and Figure 5).^5

\[ \lambda = 2D(n_{eff}^2 - \cos^2 \theta)^{1/2} \]  

(1)

Figure 4. Left: 200 nm polystyrene particles assembled through evaporative assembly yielding iridescent surfaces, Right: 200 nm polystyrene and melanin particles assembled through evaporative assembly to yield amorphous structures that reflect angle-independent blue color. SEM images taken by B. Datta.^6

Self-assembly of spherical and non-spherical particles is an appealing approach as it can scalable, low cost, conducted under ambient and aqueous conditions, and versatile. There are many factors involved in the drying behavior of colloids which relate to self assembly and color visibility. We have access to many levers to tune structure formation, including particle composition, surface functionality, particle size and concentration, coating, solvent, substrate wettability and roughness, drying and deposition conditions, particle shape, and temperature, humidity, and pH of the environment. By manipulating these conditions, a host of fascinating visual effects can be produced.^6 There are also many tools with which to precisely design materials that can serve as substrates for colloidal self assembly. These surface properties will affect the dynamics of structural color production. In terms of bio-inspired design, these factors are levers, which can be tuned to yield a particular result. In this manner, we indirectly control the final structure. However, it is difficult to directly control assembly processes and these surfaces often contain numerous defects as they are scaled. Multiple components may be required to produce robust, angle-independent color, and chemical synthesis of tailored particles can be resource intensive.

Figure 5. The Bragg-Snell equation (equation 1 can be used to model the diffraction of light in a colloidal photonic crystal. The wavelength of light that is coherently scattered depends on the refractive index (n), the incident angle (\( \theta \)), and the periodicity (D).^5
Alternatively, many turn to top-down approaches, such as electron beam lithography. Electron beam lithography (EBL) allows for high precision, but it is slow and expensive and only works with certain materials. When employing EBL, researchers typically abstract natural structures towards multilayer stacks, ridge structure, or the classic “Christmas-tree” structure of the *Morpho* butterfly. EBL allows for features down to the nanometer scale, and processes have been well-developed. Typically, to generate color through EBL, researchers rely on multilayer stacks, which require sequential deposition, write, development, and etch steps. Thus, the process can be time-consuming. EBL works with a limited set of resists, but yields very precise structures.

In such multilayer arrangements, the spacing between ridges determines the color response, as described by Equation 2, where reflected color effects stems from the refractive index contrast between the material and air.

\[ 2(n_A d_A \cos \theta_A + n_B d_B \theta_B) = m\lambda \] (2)

Bottom-up assemblies can be scalable, but defect-prone. Top-down processes can be multi-step, material limited, and expensive. Each process has limits on scale, material, geometry, or cost and fabrication thus limits achievable spectral responses. Many commonly used fabrication techniques require a trade-off between precise structural control and scalability, and formation of complex geometries is still a challenge for easily scalable and cheaper processes. Efforts towards generation of structurally colored surfaces have relied on parametrization using forward models, brute force search algorithms that can be costly, and more recently, inverse design approaches that allow for more efficient searches. Recent literature towards inverse design of structural color surfaces frequently highlights geometries that are difficult or impossible to fabricate. Here, inverse design methods combined with printing techniques that allow for arbitrary three-dimensional forms may help bridge this gap.

In this paper, we explore methods for designing structures so that we can combine direct structural control with ease of fabrication. Computation and simulation allow for “cheap” experiments that quickly allow us to traverse a broad array of parameters and explore situations, experiments, and forms that do not yet exist. The method we use imposes limitations on how we can search for structures and what we can physically produce. Combined optimization and inverse design move us away from experimental limits and allows us to approach theoretical limits, especially in cases where solutions are non-intuitive and and analytical solutions are difficult to achieve. This allows us to approach the bounds of light-matter interaction. As we have gained further computational tools, instrumentation, and fabrication abilities, we can move beyond replication and begin to generate structures that do not yet exist in nature. Expanding the space of possible structures allows for more intriguing and varied optical responses. Here we ask, how do we build structures to give us specific spectral responses? How to we access the greatest number of colors and enable truly scalable structural color? In this paper, we outline preliminary methods for an inverse design approach combining simulation and optimization.
2. PROBLEM FORMULATION AND METHODS

As one potential approach for combining flexible fabrication methods with control over output, we explore an
iterative inverse design method by optimizing towards a target spectral response in a physically realizable manner.
This approach allows for direct control in which the response is tuned via structure and material properties. We
specifically focus on single component systems, though some prior work uses multi-material systems.

To quantify the physical interactions that occur in these photonic structures, researchers often describe
the angle-dependent reflection of light from a surface through the bidirectional reflectance distribution function.\(^8\)
In defining the bidirectional reflectance distribution function (BRDF), \(f_r(\omega_i, \omega_r)\) is a function that defines how
light is reflected off a surface. It is used often in optics, computer graphics, and in computer vision. It represents
a ratio of reflected radiance exiting in the outgoing direction \(\omega_r\) to the irradiance incident on the surface from
\(\omega_i\). Each \(\omega\) is represented by \(\phi\) and \(\theta\). The appearance of surfaces depends on illumination conditions, detection
settings, the surface structure, and the material properties of the surface. Formally, a given BRDF is wavelength
dependent, and to account for effects such as iridescence or luminescence the dependence on wavelength must be
made explicit, or a separate BRDF must be calculated at each wavelength of interest.\(^9\) Note that in the typical
case where all optical elements are linear, the function will obey \(f_r(\lambda_i, \omega_i, \lambda_r, \omega_r) = 0\) except when \(\lambda_i = \lambda_r\) that
is, it will only emit light at wavelength equal to the incoming light.

Simple or abstract systems, such as alternating index multilayer stacks or thin-films with interference ef-
fcts, provide very effective cases of matching theoretical optical response with observation. For these simpler
structures, dimensional spaces are limited, so parameters can be adjusted to have predictions match observation
with relative ease. In contrast, complex structures and 3D systems require more complex modeling (typically
FEM or FDTD-based).\(^10\) In many cases, simulation starts with perfectly periodic, idealized structures to reduce
computational load. However, natural systems do not develop in this manner, and imperfections provide crucial
design features. This complexity and disorder can complicate theoretical models, but provide much richer effects.
Similarly, representation of refractive indices is also idealized and based on estimates, further removing the model
from observable phenomena.\(^10\)

To implement our approach, our problem statement is as follows: If we specify a response, what is a plausible
structure that could yield this? Here our input is a target response out of all possible spectral responses
\(f_r(\lambda, \omega_i, \omega_r, x)\) and our output is structure selected out of the space of all possible structures \(M(x, y, z)\).

![Figure 7](image-url)

**Figure 7.** Components of the inverse design process: 1) Initial height map, 2) Reflectance distribution function (RDF)
found using a forward model, 3) Target reflectance distribution function, and 4) unknown target structure.

2.1 Set-Up and Simulation

We begin by defining a modeling domain, a design domain, and a target domain, and apply a numerical or
physical model. While in prior work (explained in Section 3), we relied on Scalar Diffraction Theory as a model,
here we employ Maxwell’s equations and a full vectorial model applied using the Finite Difference Time Domain
(FDTD) method. Using the Finite Difference Time Domain method allows us to evaluate the electromagnetic
patterns around a structure in the far field and measure scattering by evaluating the field amplitude on a specific
grid.

On a high level, we set up a simulation space, and run an optimization routine that calls this. To implement
our proposed simulation-based optimization, we employ the following components: a design area and geometry,
boundary conditions, an input source or incident field, a forward model for simulating interaction, a near to far
field conversion, a color conversion, an objective function and error calculation step, a randomization factor, and
potential post-processing steps. Incorporating randomness suppresses iridescent effects as scattered fields add
incoherently, which is necessary for many applications of structural color.

![Flowchart](image.png)

**Figure 8.** Simulation-based optimization allows us to iteratively design a structure based on a desired response. The
simulation module allows you to test the structure and understand the behavior of light while interacting with the
geometry, and the optimization module searches the space of available structures to find the best fit.

First, we specify a design area and associated geometry for a starting structure. Due to the complexity of
running 3D simulations, initial attempts often begin with a 2D version of the structure. Once a reasonable
geometry has been established, a field or input source is injected into the simulation. Our samples are designed
to reflect color under ambient conditions, so we approximate a light source based on daylight or broadband
reflection. Natural light is incoherent and unpolarized. To approximate this, two simulations are run with
orthogonal linear polarizations. These results can then be averaged. We introduce an incident plane wave
towards the structure. Once the design area and light source have been selected, a forward model is used to
simulate the BRDF or spectral response generated by the structure.

We use forward models to simulate the behavior of light while interacting with our generated surfaces. We can
examine the complex phase modulation of a plane wave incident upon this surface, in which a height distribution
creates a phase lag \(2(h_{\text{initial}} - h(x))\lambda\). One approach is scalar Diffraction Theory (SDT), used to simulate the
interaction of light based on near field diffraction and far field effects, shown in Figure 9. Here we look at an
incoming beam with some wavelength interacting with a collection of scatterers in three dimensions, and then
evaluate the far field response some distance far away from these scatterers. Huygen’s principle posits that every
point on a wavefront can be a source for secondary wavelets, and these spherical wavelets combine to form the
wavefront envelope. Fresnel added that these wavelets then interfere, accounting for diffraction effects. When
combined with the Born approximation, this allows us to ignore multiple scatterers and instead treat scatterers
together, providing a simple place to start. SDT is thus simple to formulate and implement, but neglects many
effects.

Another commonly used approach is Finite Difference Time Domain method (FDTD), a fully vectorial 3D
Maxwell solving technique, introduced by Taflove. For FDTD calculations, the field is determined over a
discrete structure in space, defined by Yee Cell dimensions (see Figure 10). In this technique, we iterate through
Maxwell’s equations in small time steps, coupled with boundary conditions. Calculations are evaluated on a grid
staggered in time and space. This method relies on a structured grid, but it is versatile, accurate, and applicable
to large-scale simulations. FDTD is very flexible and generalizable to many problems in electrodynamics: it allows
us to probe light-matter interactions that enable the fascinating optical effects we see from complex biophotonic
structures. FDTD calculations are very computationally costly and may require parallelization.
Figure 9. Simplified Schematic of SDT

Figure 10. Illustration of how the finite-difference time-domain method in computational electromagnetism discretizes the space, interleaving the fields components for higher precision. For a system with translation symmetry along an axis, the TE/TM problems can be decoupled and solved separately. a) is a two-dimensional case with the magnetic field along the axis (perpendicular to the screen); b) is likewise a case with the electric field along the axis. In a general case, the Yee grid on figure c) is used. CC BY-SA 4.0 from FDominec

We can then examine the far field response. First, we calculate the near-field scattering off of the generated structure by examining the radiation in a desired direction (in this case the reflected light). We examine the discrete fourier transform fields near the structure, and compute the far field. The far field is typically at a distance many times larger than the source wavelength.¹⁵

Next, we require a metric to move from recorded intensity to observed color based on the illumination of the structure by unpolarized light located infinitely far away. The reflected spectrum is then converted to color coordinates by applying a color-matching function, using the CIE 1931 tristimulus values converted to an RGB color space based on a D65 daylight approximation. Appearance is not perceived strictly in terms of intensity, rather viewing angle has a significant impact on perceived color.¹⁶

Figure 11. The basis for color-matching functions using XYZ tristimulus values from the 1931 CIE standard colorimetric table.¹⁷

Simulation objects must be assigned material properties based on the medium, dielectric properties, and dispersion. Defining the geometric objects imparts dielectric properties within the simulation. Geometries can include binary phase gratings, two dimensional profiles, three dimensional free form structures, etc.

For this instantiation, surface features sit atop a glass substrate, so the design area is comprised of a structure region above a substrate region. Light is introduced to the cell at an incident plane above the structure and
propagates down toward the structure. We specify an observation plane at which we record reflected light. For this set up, we seek to only record the scattered and reflected light produced from the interaction of the incident field and the structure. All light should be scattered, reflected, or absorbed here, and should not reach the bottom of the cell. To prevent unwanted reflection off the side walls, we introduce an absorbing boundary condition above and below the structure, known as a perfectly matched layer. With this geometry, we can record the intensities at the source and above the structure and calculate spectral reflectance. We can further introduce periodic boundary conditions on the side of the cell to incorporate the effect of a larger structure. Given the

![Diagram of simulation geometry](image)

Figure 12. Schematic of simulation geometry established for this example problem inside a unit cell.

fabrication requirement, all structures must be comprised of units constrained by the minimum feature size achievable for the processing method. As a starting point, by limiting this system to a 2.5 dimensional height map we must also impose the constrain that all features are connected (each element sits atop another).

2.2 Optimization

Our general optimization process is set up as follows: in an unknown parameter space, we aim to define and evaluate an objective function, which we then minimize or maximize. In order to do this we:

1. Formulate an objective function
2. Add constraints and tolerances
3. Limit to realizable parameters
4. Select an appropriate optimization scheme or algorithm
5. Set a termination condition
6. Evaluate the system and calculate the objective function

The applied forward model calculates optical response to dielectric structures, and we can optimize based on phase modulation or desired response. Based on variations of a surface profile, gradient-based optimization can be used to create visible color in specific angular intervals. Thus, we optimize a material layout with some imposed constraints and boundaries with the goal of maximizing performance. As the optimization proceeds, the gradient is calculated using the objective function, and the structure is modified to step towards minimizing or maximizing the objective function. There are many ways to evaluate the objective function: in some cases gradient-free approaches can be effective, but for designs with a large number of variables and parameters,
gradient-based approaches are commonly applied. To speed up the search process, we can start with a pre-
simulated set of structures, or we can begin with a random dielectric distribution.

When determining our objective function, there are many considerations, and this function needs to handle ambiguity. We can specify an exact target BRDF, but this will lead us to one specific structure. However, many structures may yield visually similar responses if they have similar spatial frequencies, even if they do not appear similar. Alternatively, desired color can be specified as an angle or angular range in reference to the RGB color space. We can also set up a maxmin problem to emphasize different color vectors in different directions, where we want to maximize color in a prescribed direction. In some cases, a term may be minimized to suppress effects such as backward propagation, or colors outside of the target color.\textsuperscript{16,18,19}

However, we might want to weight certain aspects of the response more highly (i.e. is there a range of angles at which we really want to see blue, and perhaps do not care if we see other colors outside of that range?). We can also weight our objective function to emphasize constraints or balance requirements. Weights are assigned to emphasize constraints versus the objective function: we can either prioritize easy fabrication or heavily constrain the designs to our desired spectral response.

As a post-processing step, filtering steps can be added for smoothing and binarization. A filter radius can apply a soft length scale constraint. Geometric robustness can be applied: designs with features that are slightly larger and slightly smaller than the optimized design are tested to account for fabrication error and tolerances. Thresholding levels can be altered to binarize the design. The initial design and compared to these altered design, and optimization stops when the difference in response is minimal. Connectivity constraints may also be needed to ensure realizable designs. Prior research suggests that certain colors are more difficult to obtain or require a greater height differential, as low pass or high pass filters are easier to achieve that stop band or pass band structures.\textsuperscript{16}

Researchers have proposed an alternative adjoint method as a simpler approach than repeated recalculations of electromagnetic responses. A model is created to quantify the change in field based on alteration of structure (and the resulting change in spatial permittivity), where the relevant design parameters are the permittivity of the underlying structure. This approach relies on the computation of an objective function response with respect to the permittivity on a discrete spatial grid, or the sensitivity that specifies a change in the objective based on a change in material properties over a specified small volume. Thus, the sensitivity defines a relationship between changing material properties and resulting electromagnetic response. Two calculations are then performed: 1) a forward calculation to compute objective function and 2) an adjoint calculation.\textsuperscript{20–22} Modifying the objective function then results in modification of the underlying dielectric structure. The adjoint method is thus faster and simpler than recomputing the electromagnetic response of an entirely new structure for each iteration.\textsuperscript{20,21}

3. PRIOR AND RELATED WORK

Previous work has demonstrated the utility of inverse design methodologies in the computational formulation of nanostructures tailored for specific spectral responses,\textsuperscript{16,18,19,22} generally tailored around a single spectral band. Many of these inverse design methods output structures that are difficult or unrealistic to fabricate, do not work with fabrication resolution limits, or do not account for multiple complex structural features that result in desired optical effects (such as disorder leading to wide angle responses). In our previous work, we depicted a design methodology based around computational inverse design for the formulation of nanostructures exhibiting composite structural coloration in a variety of disjoint spectral bands.\textsuperscript{23}

In our prior optimization process, we compare the forward model of a structure to a given reflectance distribution function, which was then optimized in phase space. In this investigation, we relied on abstractions of wide angle diffusion and structural color, but further examination is needed to compare the actual \textit{Morpho} with a multi-layer stack to determine if other optical properties are necessary to achieve the full optical functionality of the butterfly.\textsuperscript{23}

We started with the existing \textit{Morpho} structure and examine the structural elements that contribute to desired optical effects. Then, we simplified the structure down to an abstracted form for the purposes of optimization - in this instance arbitrary height maps. We performed a spectral transform on this abstract or simplified structure, and used this process to compute a near field response from the interaction of light with the surface. This
near field response was then transferred to a far field response as the viewing perspective is comparatively far. A RDF was calculated from this spectral transform. The structure was perturbed and altered slightly, a new RDF calculated, and the output compared to our initial “target” response. Based on the distance from the objective, the structure was continuously altered. We then incorporated disorder, evaluated the final response, and incorporated physical fabrication constraints.\textsuperscript{23}

For this initial attempt, we relied on a more simplified Scalar Diffraction Theory approach to replicate some aspects of Bragg behavior. This model is widely used for calculating diffraction and surface scattering for applications such as determining reflections emanating from rough surfaces, as it relies on simple mathematical expressions. Thus, it allows for rapid calculations that enable repetitive simulations. Scalar Diffraction Theory provides computationally simple calculations and thus an accessible starting point for our inquiry, but it has certain limitations due to the level of abstraction.

Simulated annealing, shown in Figure 13, was used to run the optimization process as it works to minimize the distance from the target function by simulating atoms undergoing cooling. The algorithm calculates the error of a structure, flips a pixel at random, and recalculates the error. We specified a rate of cooling that dictates the rate of perturbation as iterations occur.

![Figure 13. Flow diagram of simulated annealing process. An initial pixel is edited at random. If the error is lower, the change is accepted. The algorithm evaluates the Boltzmann probability, accepts or rejects the change, and determines if the ultimate error is low enough to end the process or continue iterations.\textsuperscript{23}](image.png)

In Figure 16 we see the results of a simulation run over 25,000 iterations.\textsuperscript{23} The target function in Figure 16a) defines the desired wavelengths and angular distribution: in this case a distribution of wavelengths between 460-480 nm, centered at 473 nm, with an angular spread of 5\textdegree and a center angle of 1\textdegree. The optimized function, b), shows the resulting spectral response. Further iterations would lead to a more accurate resulting RDF and resulting structure height map. Different grey levels in this map represent different heights between 0 and 5 \textmu m.

![Figure 14. a) Input target RDF defined for our simulations, intended to produce a blue color, b) optical properties (RDF) determined by the iterative solver using simulated annealing, c) generated structure and resulting height map\textsuperscript{23}](image.png)
4. FABRICATION

There are many fabrication methods used in this field, each with limits on scale, material, geometry, or cost. Existing methods include multi-step deposition, etching, and assembly processes.\textsuperscript{24–26} In comparison to existing fabrication methods for Morpho-inspired structures, such as interference lithography, sputtering, atomic layer deposition, or electron beam lithography,\textsuperscript{25} direct laser writing methods allow for flexible, three-dimensional, volumetric feature patterning on multiple length scales.

| Technique                  | Resolution |
|----------------------------|------------|
| Replica Molding            | nm         |
| Electron Beam Lithography  | nm         |
| Embossing                  | nm         |
| BCP assembly               | nm - 100 nm|
| Layer by Layer             | nm- µm     |
| Laser ablation             | nm - µm    |
| Colloidal Processing       | nm - µm    |
| Multiphoton Absorption     | nm - µm    |
| Direct Write               | 100 nm- µm |
| Photolithography           | µm         |
| Microcontact Printing      | µm         |
| Laser deposition           | µm         |
| 3D Printing (traditional)  | µm - mm    |

Table 1. There are many fabrication options, with different limitations and opportunities\textsuperscript{27–30}

4.1 Two-photon polymerization

Fabrication of bioinspired materials can be extremely challenging due to the intricate nature of these structures. Previous researchers have worked to replicate the structure or functionality of Morpho structures through a combination of deposition-based, lithographic, or combined methods. To develop flexible fabrication methods to analyze color formation based on hierarchical structures, we look to direct write techniques that enable realization of arbitrarily generated structures.

A commercial option for two-photon processing is the Photonics Professional by Nanoscribe GmbH system, which can achieve features down to 100 nm. Here, fabrication was performed using a Nanoscribe printer to conduct two-photon polymerization. In contrast to other lithography methods, two-photon polymerization offers flexibility due to the maskless fabrication of arbitrary structure shapes and its simple production process. Typically, two-photon polymerization processes rely on photosensitive resins, specifically acrylic-based materials.

Figure 15. Grating Written Using Two-Photon Polymerization
For this system, a piezoelectric motor is used to move the laser. Multiple configurations can be used, but a commonly used mode is the Dip-in Laser Lithography (DiLL) mode where the microscope objective is directly dipped into the photoresist. The laser power is tuned to alter voxel size, down to one micron in z height. Fused silica is the most commonly used substrate for Nanoscribe prints, with a refractive index of $n = 1.46$. Methacrylate-based IP-Dip negative tone resist (Nanoscribe GmbH) is used: a material that is transparent in the visible spectrum. After the free radical polymerization reaction, IP-Dip goes from an index of refraction of 1.52 to 1.55. To focus properly, a refractive index of at least 0.05 is needed between the substrate and the resist. The beam operates at 780 nm, with a pulse duration of 100 fs and a repetition rate of 80 MHz. Multiple objectives can be used, but here we used a 63X objective with NA 1.4. After the write process, the resist is developed and all but the solidified region is washed away using Propylene glycol monomethyl ether acetate (BTS-220 by Baker).

![Image](image1.jpg)

Figure 16. In previous work, diffusers were designed using a Gerchberg Saxton algorithm to approximate disorder. Shown here are A) Simulated Disorder Function for Uncorrelated Noise Function and B) an SEM image of the Fabricated Disorder Function, showing that this is a viable fabrication method for our designs. While these samples demonstrate the foundation needed to develop the proposed method, further work is needed to optimize dose and scan speed for each of these optical structure types. SEM images taken by B. Datta.

We also work with a Pharos DPSS Yb:KGW Femtosecond Laser femtosecond laser that operates at 1030 nm (with harmonics at 515 and 324), 80 MHz, and 300 fs. The laser has built-in control for intensity, repetition rate, and operating wavelength. Within our current setup, we can tune five primary parameters to control the resolution and accuracy of laser writes that enable a variety of processes: i) The spot size due to the numerical aperture of the objective lens, 2) the light intensity, 3) the exposure time / repetition rate, 4) the wavelength of the femtosecond pulses, and 5) material selection. We use a 25W Pharos with a pulse duration under 290 fs to accommodate a wide range of materials and enable multiple processes. We use an Aerotech nano-positioning stage to translate the sample and control write area. Stage speed and positioning, combined with repetition rate, allow us to achieve specific exposure times. We will draw comparisons between the commercial Nanoscribe system and our Pharos setup throughout the process. Because the two lasers operate at different wavelengths and repetition rates, between the two systems we have the opportunity to explore a range of resists and other materials with which we can attempt to create structural color.

4.2 Characterization

The resulting structures can then be characterized both computationally and physically, allowing the acquisition of spectral and spatial information. For our studies, three primary techniques are employed: scanning electron microscopy of fabricated samples, spectrophotometry and integrating sphere photometry, and macroscale optical and photographic recording. SEM has become an integral tool for revealing surface morphology and roughness measurements. For our purposes, SEM probing allows for confirmation of correct fabrication of the designed structure, an initial understanding of any fabrication errors, and a basic measurement of feature size and spatial profile. Samples may be coated with 10 nm of gold to prevent charging artifacts.
The samples proposed here are intended to be perceivable by human observers, so optical microscopy and macroscale imaging can be useful to confirm the generation of color viewable at a distance. Sample orientation can be shifted to understand angular dependence.

To quantitatively measure color production and angular response in our samples, we employ angle-resolved reflectance and integrating sphere spectrometry using a Cary 7000 Universal Measurement Spectrophotometer UV/Vis/NIR for reflectance measurements. Angle and polarization dependent reflectance spectra can be acquired with angle-resolved spectrometry. Light from a broadband source (such as a halogen lamp) is focused onto a sample and scattered by surface structures and received by a photodetector or spectrometer. The incident light and sample can be rotated, thus the experimental values here are incident and reflected wavelength, angle of incidence and detection, and resulting intensities. The resulting BRDF can be read based on incident intensity, incident angle, and sample rotation. A reference standard is used to deconvolve the effect of the illumination source and instrument effects.

Integrating sphere measurements allow for measurement of total reflected light based on control of the incident intensity and wavelength. This method measures the light captured over a hemisphere of scattered light based on a broadband source. In some tests, using a laser light source or monochromator is used to understand wavelength dependent scattering.

By combining these three approaches, a full picture of the spectral response of designed and fabricated samples can be painted.

5. CONCLUSION AND DISCUSSION

Structural color is an incredibly appealing technology and design tool. Color serves as an intuitive interface for indicators and sensors, both for purely aesthetic expression and for signalling for environmental conditions, mechanical and structural changes. Structural shifts result in visible color fluctuations, so applications can range from humidity and temperature sensing to indicating of pending infrastructural failure to camouflage inspired by cephalopods. The sheen and intensity of these physical structures is captivating and inspiring.

Historically, was difficult to obtain the fabrication and computational resources to truly harness the power of structural color. Researchers then relied on direct replication of existing structures through methods like templating, or abstraction of structures by reducing complex elements to motifs like the “Christmas trees” of the Morpho butterfly. As more and more processes have been developed, we can move towards potentially surpassing the functionality of nature. In this paper we discussed fabrication processes and material components in contrast with computational inverse design. Here we presented a method for approaching the design of color-generating surfaces paired with versatile fabrication techniques. We further discussed the practical constraints and feasible fabrication methods and background for making these computational structures a reality. The iterative inverse design process we outline can be used to not only replicate the optical functionality of classic structures like the Morpho, but also towards more complex or less well-explored spectral responses. The structures can then be fabricated and characterized with the techniques enumerated here to compare experimental and simulated behavior.

This approach paves the way for scalable surface design. As mentioned above, the proposed fabrication processes provide an accessible, cost-efficient method for prototyping quickly based on optimized structures, before processes are moved to roll to roll or imprint systems. By starting with a 2.5 dimensional height map, we can potentially utilize scalable approaches like nanoimprint lithography. Similarly, grating structures can be replicated using molding and casting. Alternatively, the design process explained here could be used to design substructures with predetermined optical responses, which can then be tiled into a globally optimized system. One option is to produce small area voxels of 10-20 microns (based on the coherence length of sunlight) and then design an algorithm to combine these into super-pixels (metasurface literature refers to these as meta-atoms). There is a trade-off here as well: if there are more predefined pixels, there are more options to iterate over in a superpixel, but there are also more achievable responses. What happens at the boundaries of these pixels? Can we make pixels big enough to avoid pixel-pixel interaction? How many pixels do we need in a superpixel? Future work should examine the role of tiled motifs to represent the disorder factor present in natural systems. Using a motif would allow us to focus on a small region and repeat this unit over the entire surface, simplifying calculations. With larger structures, the coherence length of light may have a serious impact on output. While
this paper focuses on reflective elements, tiles could be designed for absorption and transmission as well. Similar approaches have been applied towards metamaterials in recent years. There is much to explore about tile to tile interactions and large area effects. As an additional approach, if enough data can be collected from existing natural structures or simulated results, machine learning algorithms can be trained to predict viable photonic structures. Researchers have begun to replace physics engines with data driven neural networks, using these tools to conduct thousands of virtual experiments and optimize accordingly. Researchers have begun to harness “bioinspired algorithmic-driven design” to translate evolutionary insights into synthetic evolution and discover new materials.33

To move towards more sustainable and nontoxic color systems with many applications, we propose the use of biodegradable and biopolymer-based print materials to fabricate these structures, such as cellulose or chitosan. Presently, with many such materials it is difficult to achieve the highest resolution level.

To fully realize the vision shared here, computational costs must be reduced. We further need to examine the trade-off between fabrication constraints that allows for ease of processing balanced with intensity and accessible portions of the color gamut. How do we incorporate fabrication constraints in a way that is useful and does not limit achievable structures? How do we design structures that are fabricable without making it overly challenging to get the desired color? How do we define an objective function that is both specific enough to yield desirable control while flexible enough to converge easily and allow for multiple structure options? How do we move towards fully three-dimensional structures? We have yet to fully harness the full potential of this field, but we hope to contribute towards further advancement.

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