Large-Scale and Wide-Gamut Coloration at the Diffraction Limit in Flexible, Self-Assembled Hierarchical Nanomaterials

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Unveiling physical phenomena that generate controllable structural coloration is at the center of significant research efforts due to the platform potential for the next generation of printing, sensing, displays, wearable optoelectronics components, and smart fabrics. Colors based on e-beam facilities possess high resolutions above 100k dots per inch (DPI), but limit manufacturing scales up to 4.37 cm², while requiring rigid substrates that are not flexible. State-of-art scalable techniques, on the contrary, provide either narrow gamuts or small resolutions. A common issue of current methods is also a heterogeneous resolution, which typically changes with the color printed. Here, a structural coloration platform with broad gamuts exceeding the red, green, and blue (RGB) spectrum in inexpensive, thermally resistant, flexible, and metallic-free structures at constant 101 600 DPI (at the diffraction limit), obtained via mass-production manufacturing is demonstrated. This platform exploits a previously unexplored physical mechanism, which leverages the interplay between strong scattering modes and optical resonances excited in fully 3D dielectric nanostructures with suitably engineered longitudinal profiles. The colors obtained with this technology are scalable to any area, demonstrated up to the single wafer (4 in.). These results open real-world applications of inexpensive, high-resolution, large-scale structural colors with broad chromatic spectra.

1. Introduction

The study of structural colors stimulates large interests across different scientific areas ranging from holographic data storage,[1–5] to light filtering,[6–13] high-resolution printing,[14–19] security,[20–22] and integrated opto-electronics components.[23] Contrary to pigments and dyes that fade away with time, structural colors can persist for hundreds of million years,[24] opening to permanently replace toxic dyes with an inexpensive technology that could also enable new pathways toward smart fabrics and artificial skins.[25–28]

For structural coloration to be competitive with conventional pigment-based techniques and reach maturity for real-world applications, it needs to address four main areas: i) wide colors gamuts, ii) low manufacturing costs, iii) large-scale printing, and iv) high printing resolutions.[15,16,29–56] While advances in single points (i)–(iv) have been reported, there exist no present technology that can concurrently address all of them.

Presently, the highest resolution of 256k dots per inch (DPI) is with free-electron dielectric meta-surfaces on millimeter-scales.[45] Nanoplasmonic structures reach scales up to centimeter-sized samples with resolutions around 100k DPI.[42,47,57,58] Dielectric materials can achieve similar resolutions but suffer from metallic counterparts’ scalability issues.[31,44,46] A common issue of current methods is also a heterogeneous resolution, which typically changes with the color printed. Here, a structural coloration platform with broad gamuts exceeding the red, green, and blue (RGB) spectrum in inexpensive, thermally resistant, flexible, and metallic-free structures at constant 101 600 DPI (at the diffraction limit), obtained via mass-production manufacturing is demonstrated. This platform exploits a previously unexplored physical mechanism, which leverages the interplay between strong scattering modes and optical resonances excited in fully 3D dielectric nanostructures with suitably engineered longitudinal profiles. The colors obtained with this technology are scalable to any area, demonstrated up to the single wafer (4 in.).

In all these works, the mechanism of color generation relies mainly on resonant optical structures with classical shapes such as, for example, spheres, cylinders, cubes, or other longitudinally invariant forms with a constant profile under the dimension orthogonal to the sample surface. These structures demand a trade-off between scalability and flexibility. Wide gamuts require nanostructures with a large number of degrees of freedom implemented via e-beam lithography, constraining manufacturing scalability and imposing heterogeneous resolutions.[16] Scalable manufacturing techniques,[16,50,52–56] on the contrary, do not yet offer nanostructures with sufficiently high complexity, and are unable to address large color gamuts and high resolutions (Figure S1, Supporting Information).
Here, we address these problems by studying a new mechanism of structural color generation, which exploits complex light–matter interactions occurring in hierarchical, fully 3D dielectric nanostructures with varying profiles along all dimensions. The manufacturing of these nanostructures combines self-assembly, scalability, and industrial technology for mass production, with a suitably engineered process of plasma etching. To the best of the authors’ knowledge, no prior work reported the use of self-assembly to realize such complex 3D shapes. The structural coloration obtained with this approach results in wide gamuts, supporting all primary colors and exceeding the red, green, and blue (RGB) spectrum, at constant 101600 DPI resolution for every color printed, on both single colors 4 in. wafers and large-scale flexible substrates. The proposed technique is complementary metal–oxide–semiconductor (CMOS) compatible and supports integration with flexible electronics and wearable devices.

2. Results

Figure 1 summarizes the main fabrication steps of the technique proposed in this work. It begins with the self-assembly of a closed-packed monolayer film of polystyrene spheres (PS) on silicon (Si), typically grown on an insulating platform, either a rigid wafer such as glass, or flexible support such as Kapton film (Figure 1a). Self-assembly uses a custom setup made in our lab (details in Experimental Section), which allows fine-tuning of both speed and density of nanospheres on the Si surface via a syringe pump (Figure 1a). The pump promotes PS self-assembly in close-packing through capillary forces between adjacent spheres, allowing the formation of a homogeneous film over all the surfaces we wish to color. The nanospheres film area obtained with the self-assembly is scalable and limited only from the substrate’s container size. Self-assembly is also intrinsically fast, requiring only 3 minutes to cover the entire surface of a 4 in. wafer. Figure S2, Supporting Information, shows: a) optical and b) scanning electron microscopy (SEM) images of a large-area monolayer homogeneous film of PS with close hexagonal packing.

After self-assembly, reactive ion etching (RIE) processes the sample to create complex hierarchical shapes at the bottom of the nanospheres (Figure 1b). Plasma etching depends on a manifold of five different parameters: the gas flow (GF), the radio frequency (RF), the set pressure (SP), the inductively coupled plasma (ICP), and the etching time (ET). The controlled variation of these parameters engineers nontrivial, fully 3D geometrical shapes possessing complex hierarchical structures with repeatable features over all the surface of the sample (Figure 1c,d). These complex nanostructures yield brilliant, high-fidelity colors on both single wafers and flexible materials, with any desired artwork shape via successive steps of RIE (Figure 1e). Figure S3, Supporting Information, shows an example SEM image and reflectivity spectrum of nanostructures implemented in flexible Kapton. Figure S4, Supporting Information, illustrates the various stages of the manufacturing process in detail for flexible substrates. The first stage is growing a Si layer on top of Kapton by plasma-enhanced chemical vapor deposition (PECVD) (Figure S4a, Supporting Information). We then spin-coat AZ-ECI 3027 resist, complete the first exposure and development (Figure S4b, Supporting Information), followed by PS self-assembly (Figure S4c, Supporting Information), plasma etching, and resist removal (Figure S4d, Supporting Information). We then perform photolithography alignment with the second mask, resist exposure and development (Figure S4e, Supporting Information), followed by a second PS self-assembly (Figure S4f, Supporting Information), plasma etching, and resist removal (Figure S4g, Supporting Information) to obtain the final, two-color structure. Figure S5, Supporting Information, shows SEM images (a,b) and reflectivity spectra (c,d) of two areas of the sample showing different colors.

Figure S6, Supporting Information, illustrates the fabrication stages of Figure S4, Supporting Information, in the case of a rigid sample. Figure S7, Supporting Information, shows SEM images and reflectivity spectra of nanostructures showing the two different colors on the sample.

We investigate the mechanisms of structural color generation from the experimental and theoretical study of a large set of samples assembled with PS of 200 nm diameter. In performing these experiments, we vary the plasma gas flow of sulfur hexafluoride (SF₆), fluoro hydrocarbon (CHF₃), and oxygen (O₂) between 10 standard cubic centimeters per minute (sccm) to 50 sccm, the RF power from 25 to 150 W, the ICP power between 100 W and 1700 W, the SP from 10 mTorr to 50 mTorr, and the ET between 10 s and 3 min. We create a set of 144 samples in which we change one parameter at a time within the ranges mentioned above. We then measure the colors arising from each sample with a spectrum analyzer, converting the sample reflectivity into a CIE 1931 xy color space, and acquire SEM images of the morphology of each sample (see Experimental Section).

Figure 2a plots the coordinates xy of the obtained colors in a CIE 1931 chromaticity diagram. The color observed in the sample covers a large portion (around 80%) of the standard RGB region, also exceeding the green and blue areas. Figure 2b,c illustrates the experimental color palette of a subset of the samples in Figure 2a. The colors form a complete rainbow, from blue to red. Images of each sample in Figure 2c show that colors are uniform and homogeneous over the entire surface. Figures S8 and S9, Supporting Information, present reflectivity spectra and SEM images of the samples in Figure 2b,c. Figure 2d shows the primary colors appearance when changing observation angles from 0° up to 60°. The colors are not iridescent and stable, with no appreciable variation. Figure S10, Supporting Information, presents reflectivity spectra of the samples in Figure 2d. Figure 2e,f reports SEM images of the nanostructures supporting (e) the primary RGB structural colors, and the structures resulting from variation of single parameters (CHF₃, O₂, SF₆ gas flows, SP, ICP, and RF) in the RIE etching process. The corresponding marker (circle, asterisk, cube, cross, star, and triangle) in the CIE diagram of Figure 2a reports the colors associated with the variation of each RIE parameter (Figure S11, Supporting Information). The SEM images in (e,f) show that controlling each etching parameter engineers a wide variety of structures with complex 3D morphology, ranging from nanodisks with parallel and non-convex walls to hierarchical structures with different scales of features. Figure S12, Supporting
Information, displays SEM top views of the morphology of the corresponding sample, which changes from disks to polyhedral and more complex shapes.

The manufacturing technique of Figure 1 overcomes both the limitations of conventional lithography and current wet-chemistry solutions, processing a new family of 3D structures with reproducible features that support broad chromatic spectra. Complex nanostructures result from the interplay between the plasma etching in Si and the nanospheres assembled on the sample. In this process, the plasma ingredients and the ion bombardment rate control the ratio between physical (anisotropic) and chemical (isotropic) etching, triggering competing mechanisms that generate broad varieties of morphology.

The experimental results of Figure 2 show that in the 5D manifold of plasma parameters, CHF$_3$, O$_2$, and the radio frequency RF achieve the most significant morphology change. Correspondingly, the colors associated with these structures show significant chromatic variations in the CIE diagram of Figure 2a. The mechanism for coarser morphology change in the SEM images of Figure 2f for CHF$_3$ and O$_2$ rely on the

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**Figure 1.** Manufacturing pipeline of structural colors. a) Image of self-assembly setup of PS. b) Rendering image of close-packing assembled PS. d) SEM images of nanostructures with different morphology after RIE. e) Large-scale artwork examples on rigid and flexible (Kapton) substrates. The scale bar for the images in the first row of (e) is 2 cm. The scale bar for the vase patterns in the second row of (e) is 1 cm, and for the letters pattern in the second row of (e) is 5 mm.
competition between CHF$_3$, which has a strong effect in protecting the walls of Si structures during the etching process, and O$_2$, which speeds up the chemical etching of PS. The substantial morphology change sustained by the RF, conversely, occurs because RF regulates the plasma amount and ion bombardment, allowing to control of both aspects of etching (physical and chemical) in longitudinal and horizontal nanostructuring.

We theoretically study the optical response of these complex nanostructures by combining finite-difference time-domain (FDTD) simulations and analytic theory. We consider the structures observed in the three primary colors displayed in Figure 2d, represented by pillars with different depth and non-parallel, non-convex walls originated from asymmetrical etching (Figure 2e). The results obtained from these examples (Figure 3) are then straightforwardly generalized to interpret the behavior of all complex structures in Figure 2f. We studied the reflectivity spectra (Figure 3a) originated from two separate classes of deformations: i) nanostructures composed by pillars with constant diameters $d = 200$ nm and varying etching depth $0 \leq h \leq 200$ nm (Figure 3b), and ii) longitudinally deformed pillars with constant depth $h = 200$ nm and varying inner waist $w$ (Figure 3c). FDTD computed reflectivity spectra (Figure 3a) show the formation of two different regimes of light–matter interactions, with a smooth cross-over when 3D deformations in Figure 3c begin to appear.

For pillars with varying etching depth and parallel walls (Figure 3a,b), the material response maintains a power-law decaying profile that progressively shifts toward lower values the maximum reflectivity response. Such reflectivity response is similar to that of a Rayleigh scatterer and generates a blue color (Figure 3d,e, primary blue sample). In this specific regime, the material response is analogous to an effective index material with homogeneous refractive index $n(\omega) = n_{\text{Si}}(\omega) + n_{\text{eff}}$, being $n_{\text{Si}}(\omega)$ the bulk refractive index of the Si substrate and $n_{\text{eff}}$ a constant refractive index modeling the effect of the progressive removal of Si material during etching. To demonstrate this

Figure 2. Experimental classification of structural colors versus 3D nanostructures morphology. a) CIE 1931 chromaticity $xy$ coordinates of experimental samples. b) Color palette obtained from a representative set of samples. c) Sample image details. d) Optical images at different angles within 60° of primary color samples possessing red, green, and blue colors. e) SEM images of related nanostructures (scale bar: 100 nm). f) SEM images of samples nanostructure morphology by changing one parameter (flow of SF$_6$, CHF$_3$, and O$_2$, RF, SP, and ICP) at a time in the RIE process (scale bar is 50 nm). (a) shows the color corresponding to each marker in (f). The black triangle in (a) represents the gamut of RGB primary colors.
Figure 3. Theoretical analysis of mechanisms of color formation via interactions between scattering modes and resonances. a) Reflectivity spectra of pillars with diameter $d = 200$ nm and varying etching depth $h$ (b) and longitudinally modified pillars with $d = h = 200$ nm and varying waist $w$ (c). d) Spectra of (a) for $h = 12.5$ nm (red) and $h = 125$–nm (yellow) versus effective index theory (orange and green). e) Spectra of (a) for $w = 130$ nm (blue) and $w = 60$ nm (purple). f) FDTD computed density of states and e) TDCMT model predictions. g) TDCMT-computed resonant frequency $\omega$ and decay constant $\gamma$ of modes in the DOS of (f). The size of each marker in (g) is proportional to the quality factor $Q = \omega/2\gamma$ of the resonance.
statement quantitatively, we calculate the material reflectivity \( |R(\omega)|^2 \) via standard multilayer theory \( |R(\omega)|^2 = \frac{1 - n(\omega)^2}{1 + n(\omega)^2} \) by using an effective index model \( n(\omega) \), and compare it against exact FDTD predictions (Figure 3d). The two models (i.e., exact FDTD and effective index theory) match with good agreement, demonstrating the effective index behavior of the nanostructures. Intuitively, the effective index behavior originates because, in closely packed nanospheres, the amount of Si material removed during etching is a small fraction contained in a tiny region of space. This effect induces a simple light–matter interaction, which creates an effective medium homogenized over all the sample’s surface.

This condition breaks when we apply a longitudinal deformation to the structure (Figure 3a,c). In this situation, we observe the formation of resonances in the material response, manifested in the generation of sharp peaks in the reflectivity spectrum that cannot be explained with an effective index material (Figure 3a,e). In this regime, the material response becomes more complex and equivalent to that of a feed-forward neural network, which can assume in principle any desired form if the geometry of each nanostructure is suitably controlled.\(^{[60]}\)

We study the behavior of the system via time-domain coupled-mode-theory (TDCMT).\(^{[61,62]}\) which provides an accurate and intuitive description of the material response by separating scattering from resonant contributions. In this approach, the reflection spectrum \( R(\omega) \) is expressed as \( R(\omega) = R_0(\omega) - K \times a(\omega) \), with \( R_0 \) the scattering response observed with no resonance, \( K \) an array of coupling coefficients, and \( a = [a_1, ..., a_n] \) a network of resonances. Each resonance carries an electromagnetic energy contribution that appear in frequency as a Lorentzian linewidth \( n(\omega)^2 - 1/(\omega - \omega_0)^2 + \gamma^2 \), with \( \omega_0 \) the resonant frequency and \( \gamma \) the decay constant of the resonance.

A network of resonances \( a \) with diverse frequencies \( \omega_0 \) and lifetimes \( 1/\gamma \) create rich modulation profiles in the reflectivity spectrum \( |R(\omega)|^2 \), as we observe in Figure 3e. We computed the resonances network that generates the reflectivity profiles of Figure 3e from FDTD calculated density of states (DOS), with the methodology described in ref.\(^{[62]}\). Specifically, DOS spectra (Figure 3f) are expanded DOS = \( \sum \Delta(\omega_0, a)|a_0(\omega)|^2 \) as the energy contribution of the network modes, with \( a_0(\omega) \) computed via rational fitting of the DOS.

The prediction of TDCMT matches with almost perfect agreement FDTD calculations (Figure 3f). Figure 3g plots the resonant frequency and decaying constant of each mode in the two networks sustaining the reflectivity spectra of Figure 3e. The plot shows a complex network dynamics for diverse longitudinal modulations, with resonances splitting up, shifting, and merging as \( \omega \) changes value. These results show that fully 3D nanostructures encompass a composite scenario of material responses, complementing the one attained by the effective medium of Figure 3a and resulting in large varieties of spectral response attainable.

Figure 4 investigates this point quantitatively by studying the experimental reflectivity spectra (Figure 4a) that generate the colors in Figure 2a, corresponding to the RIE parameters described in Figure 2f. Figure 4b reports SEM images of the structures sustaining the spectral responses of Figure 4a), while Figure 4c displays in detail each reflectivity spectrum. These experimental results exhibit a complex interplay between scattering and resonances, characterized by both sharp and broad linewidths at multiple resonant frequencies, explaining the wide spectrum of chromaticity observed in the samples of Figure 2a. In agreement with the FDTD and effective index theory analysis, thin structures with parallel walls (Figure 4b,c) tend to behave as quasi-Rayleigh scatterers with power-law \( -\lambda^a \) reflectivity versus wavelength \( \lambda \), yielding different varieties of blue-sky colors in Figure 2a. Conversely, structures with non-convex walls support the progressive formation of sharp resonances. These create multifrequency notch light filters with color gamuts in the red-green area (Figure 2a), which is the typical coloration found in natural insects possessing more ordered (i.e., resonant) textured nanostructures.\(^{[63]}\)

Nanostructures possessing more complex hierarchical features in panel (b,c) support the formation of broader resonances at various frequencies, triggering other varieties of color responses in Figure 2a. Mixing up scattering and resonant effects in a non-trivial fashion is a crucial aspect of this technology, which allows the observation of all primary colors, ranging from blue induced by scattering-like, effective medium responses to red-green sustained by resonant light–matter interactions.

To experimentally assess the DPI achieved by this technology, we follow the standard procedure discussed by Kumar et al.\(^{[64]}\) The idea is to print patterns larger than the unit resonator used to create colors and assess the smallest spatial features that it can clearly distinguish with a brightfield optical microscope. The size of this structure defines the smallest characteristic pitch and the corresponding resolution in DPI. In our work, we employ a microscope configuration composed of a 100× objective with numerical aperture NA = 0.9 to distinguish patterns of nanogrooves in a ZEP 520A resist. We set the width of the grooves to 250 nm, which is sufficient to accommodate inside one nanoparticle of diameter \( d = 200 \) nm. We then self-assemble the PS inside the ZEP 520A (Figure S13a, Supporting Information), apply RIE etching, remove residual nanospheres, and assess the final nanostructure patterns by the SEM and optical microscopy (Figure S13b,c, Supporting Information). Due to the thickness of the resist and the fact that the sidewalls are not perfectly at 90° but inevitably oblique, the SEM shows multiple nanoparticles assembled on the groove sidewalls (Figure S13a, Supporting Information). Only one is touching the Si wafer of these nanoparticles, while the ZEP 520A resist matrix incorporates the others. The ZEP 520A protects sidewall nanoparticles during the RIE, and does not create nanoresonators on the Si substrate. In the final stage, when the ZEP 520A clears away, it also removes sidewall nanoparticles. High-resolution SEM image (Figure S13c, Supporting Information) confirms this analysis by showing the implementation of single nanoresonator patterns inside the groove.

To visualize this process in more detail, we also created a second mask, fabricating two different adjacent structures (Figure S14, Supporting Information). These experiments illustrate that adjacent PS are etched with different sharp conditions and resulting geometries.

The microscopy image in Figure S13b, Supporting Information, shows clear, distinguishable lines of 250 nm width. Inside each line, we see blurred images of 200-nm diameter nanoresonators, which are hard to detect even at this magnification.
We therefore provide an estimate of the DPI from the resolution of the line patterns of 250 nm, which are clearly distinguishable in the images, obtaining a DPI = 101600. By creating different colors from structures with diverse 3D profiles and constant unit-cell spacing, colors manifest from nanostructures with constant distance thereby resulting in a constant DPI resolution for every color printed.

Figure 5 provides examples of complex artworks printing. Figure 5a,b shows the original images, while Figure 5c,d illustrates printing results at 101600 DPI. We carry out printing with successive steps of RIE on different portions of each image, transforming it into an array of photolithography masks, one for each color. With these masks, we expose one color region at a time, self-assemble PS of 200 nm diameter on the substrate, and perform plasma etching with the recipe for the colors displayed in Figure 2a. We then lift off residual PS by toluene solvents, followed by washing of ethanol and water. Despite a slight difference observed in the blue color, we observe good fidelity in color reproduced in each image.

Figure 5e,f illustrates top and high-magnification SEM view of fabricated nanostructures in Figure 5c,d. SEM images in Figure 5e correspond to purple and dark blue areas of Figure 5c, while Figure 5f maps the area of the red and brown colors of Figure 5d. Figure 5g,h show the nanostructures at the boundary of the patterns in Figure 5e,f, respectively. The high-magnification SEM view of different nanostructures supporting these colors in Figure 5i–l and Figure S15, Supporting Information, shows good repeatable features across the sample, generating the uniform coloration observed in printed images in Figure 5c,d. Figure 5c,d show that the adjacent structures
are etched well and precisely controlled. Figure S16, Supporting Information, shows the reflectivity response of nanostructures in Figure 5c,d. As a third printing example, we design the letters of our group name (Figure S17, Supporting Information), and print them at 101600 DPI on a 1.70 cm × 0.15 cm sample with four different colors for every two letters (Figure S17a, Supporting Information). We print letters “PR”, “IM”, “AL”, “IG”, and “HT” in green, light green, gray, orange, and pink colors, respectively. Figure S17b–f, Supporting Information, displays the SEM image corresponding to each letter, while Figure S17g–k, Supporting Information, presents details of top-view of the associated nanostructures.

3. Conclusions

We present a structural coloring technology that simultaneously addresses scalability, low-cost, high-resolution printing, and wide color gamuts. This platform exploits self-assembly and the surface physics governed by plasma etching to create fully 3D complex nanostructures supporting competing interactions between scattering modes and resonances, generating brilliant color at constant 101600 DPI in both rigid wafers and flexible materials.

The self-assembly procedure implemented in this work requires only 3 min to cover the entire area of a 4 in. wafer and costs 0.077 USD for a printing area of 81 cm². The self-assembly of approximately 8000 pieces of 4 in. wafer employs only a tiny quantity of PS, diluted at 10% in a solution of 100 mL. Only 1–2 min of plasma etching is required to complete the final colors at 101600 DPI. The entire manufacturing costs at 101600 DPI range between 0.21 and 0.34 USD per wafer, assuming an RIE cost of approximately 8 USD per hour in our university. While the RIE cost is substantially smaller in an industrial facility, the calculated manufacturing cost of this technology is already competitive with traditional printers. The price of printing high-resolution color artwork above 600 DPI lies between 0.1 and 0.6 USD per page. For color inkjet printers, the prices at 300 DPI are around 0.2 USD per page.

While being competitive in terms of cost, the technique proposed in this work enables significantly higher printing resolutions at 101600 DPI that capture higher-quality image details. Another advantage lies in silicon, a thermally stable material that offers robust performances for long-term applications, such as in, for example, anti-counterfeiting or the industry of car paintings. The structural coloring procedure discussed in this work is also CMOS compatible, opening the integration of structural colors at high resolutions, large scales, and contained costs for successive generations of flexible electronic components, such as displays, sensors, smartphones, or camera modules.
The rich plasma-induced morphology observed in Figure 4b also suggests that it could be possible to extend the color gamut achievable with this technique beyond the results of Figure 2. In the experiments reported in this work, we explored only a tiny fraction of the effect of the parameters in the RIE process, studying only a change along a single direction in 5D manifold space, employing a single family of 200 nm radius nanospheres.

The sharp resonances illustrated in Figure 4 of few nm linewidth are competitive with plasmonic resonances,[65] and also suggests that it could be possible to extend the color gamut also for the manipulation of light’s properties at the nanoscale.

4. Experimental Section

Materials: Polystyrene latex particles (PS200NM, 10% w/v) were purchased from MAGSPHERE Inc. Ethanol, toluene, and sodium dodecyl sulfate solutions (SDS, 10% in H2O) were acquired from Sigma-Aldrich Inc. Si wafers were obtained from University wafer Inc., while AZ ECI 3027 resist and AZ 726 MIF developer from MicroChemicals Aldrich Inc. Si wafers were obtained from University wafer Inc., while Az ECI 3027 resist and AZ 726 MIF developer from MicroChemicals. Deionized water (Milli-Q Advantage A10) with a resistance of 18 MΩ cm was used in the process, the CHF3, O2, and SF6 gas flows were adjusted from 10 to 50 sccm, self-assembled PS on Si was then inserted into the RIE chamber (Oxford Instruments, Plasmalab 100 - ICP 380) for controlled etching. In the etching process, the CHF3, O2, and SF6 gas flows were adjusted from 10 to 50 sccm, SP from 10 to 50 mTorr, ICP power from 100 to 1700 W, RF parameters from 25 W to 150 W, and ET between 10 s and 3 min. After etching, the residual PS was lifted off by toluene and the samples washed with ethanol and pure water. Likely, the structure within the nanogrooves of 250 nm width was fabricated. First, the Si substrate was spin-coated with 600 nm thickness ZEP 520A resist and the ZEP 520A nanogrooves fabricated on the Si substrate with EBL. Then, PS was self-assembled, RIE etching applied, and residual nanospheres and ZEP 520A resist finally removed.

Fabrication of Multicolor Patterns: The Si substrate was spin-coated with 4.0 μm AZ ECI 3027 resist, followed by soft-baking at 100 °C for 60 s. Next, a photolithography machine (EUV, EUV 6200) with an alignment mask was used and the substrate exposed with vacuum contact mode. The exposed substrate was immersed in AZ 726 MIF solutions, developing the resist for 60 s. After subsequent oxygen plasma treatment, self-assembly and RIE etching were performed, as explained in the previous section. This step was replicated for the implementation of multiple patterns for different colors.

Sample Characterization: The nanostructures were placed onto a 3D translation stage under an optical microscope (Carl Zeiss, Merlin). A UV-vis spectrometer with an integration sphere (Ocean Optics) was used to characterize the reflectance of the samples in the wavelength range of 200 to 1000 nm. Digital photographs and optical microscopy images of the samples were recorded with a digital CMOS camera (Canon EOS 700D) and a microscope (Nikon Instruments Inc., ECLIPSE L200N).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

N.L. and A.F. initiated, managed, and planned the overall project. N.L. and F.X. completed the fabrication process as well as optical measurements. N.L., M.B., and V.M performed the fabrication of photolithography mask. F.G. finished the deposition of amorphous Si on Kapton substrate. N.L. characterized SEM images for the samples. M.E. did the FDTD simulations. A.F. and M.E. completed TDCMT data analysis. All authors contributed to data analysis and manuscript refinement and preparation.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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