

Nanorod metamaterials for high-resolution responsive color definition

An Ping,^a Haibin Ni,^{a,*} Toluwalase A. Isogun[©],^a Alexey V. Krasavin,^b Ying Shi,^a Bo Ni,^a Jianhua Chang,^a and Anatoly V. Zayats^{b,*}

^aNanjing University of Information Science & Technology, School of Electronics and Information Engineering, Jiangsu Key Laboratory of Meteorological Observation and Information Processing, Nanjing, China

^bKing's College London, Department of Physics and London Centre for Nanotechnology, London, United Kingdom

Abstract. Nanostructured materials have attracted considerable attention as a versatile platform for achieving robust artificial color patterning with ultrahigh resolution as opposed to conventional pigments and dyes. We present a strategy for creating efficient structural colors by employing vertically aligned gold-core/silver-shell nanorod metamaterials. The developed approach enables broad structural-color tuning and maintains stable reflected colors over a wide range of incident angles. The metamaterials are fabricated by a template-assisted electrodeposition method using self-organized anodic aluminum oxide nanopores, which is compatible with large-area production. We further demonstrate applications in refractive index and humidity sensing, which are important for anti-counterfeiting, environmental monitoring, and other responsive color applications.

Keywords: structural color; responsive sensing; nanorod metamaterials.

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1 Introduction

Color definition and high-resolution printing are widely embedded in modern daily life. However, most printing or dyeing technologies, which are presently used, face problems of limited durability and environmental pollution, whereas wetting or carbonization of the pigments leads to errors in color reproduction. In addition, the imaging resolution of traditional laser or inkjet printers is typically 1200 to 5000 dots per inch (dpi), which falls short of meeting the requirements of high-definition applications. At the same time, the use of resonant spectral properties of metallic nanostructures related to the excitation of surface plasmons has shown great potential for achieving high-resolution color definition.^{1–3} Utilizing the unique property of the plasmonic nanostructures to confine light to the subwavelength dimensions, it is possible to reach higher dpi characteristics⁴ for advanced anti-counterfeiting,⁵ sensitive detection,⁶ and other high-resolution applications.

Engineering plasmonic resonances through tuning the geometrical parameters of individual nanoparticles, such as nanodisks,^{7–9} nanorods,¹⁰ nanoholes,^{11,12} and nanocavities,^{13,14} enables selective absorption or reflection of light. Thus, wide-angle color reproduction can be achieved using localized plasmon resonances.¹⁵ At the same time, due to the diffraction effects for the inter-particle distances above the light wavelength or electromagnetic coupling at subwavelength spacings, it can be challenging to realize color definition solely based on individual resonances.^{16,17} Thus, to increase the overall optical response, especially in applications where the color patterning should be visible with the naked eye, an implemented pixel can contain a substantial number of resonant nanostructures.

In parallel with structural-color generation based on individual nanostructures, periodic metallic or dielectric nanostructures supporting collective optical modes provide an alternative route to structural colors.^{18–23} Although periodic nanostructures can provide a similarly wide spectral range, they are generally associated with lower dpi resolution because collective optical modes usually require larger patterned areas. At the same time, it is possible to develop a method,

*Address all correspondence to Haibin Ni, nihaibin@nuist.edu.cn; Anatoly V. Zayats, a.zayats@kcl.ac.uk

which combines the best of these two approaches and provides high-density pixel arrays producing bright, wide-angle colors. Metamaterials and metasurfaces, i.e., artificial materials nanostructured in 3D and 2D, respectively, at a subwavelength scale or in a randomized fashion to realize artificial optical materials, present very attractive concepts for the realization of the structural color due to the absence of diffractive effects and the possibility to fully engineer their spectral response by the design of the nanostructuring. Particularly, metamaterials based on aligned arrays of metallic nanorods have shown outstanding performance for polarization management,²⁴ spectral control of fluorescence,²⁵ tunneling emission,²⁶ as well as sensing applications,^{27,28} presenting an interesting platform for color design, including the realization of responsive functionalities.

Responsive structural color, which can be changed by external stimuli, drastically extends the application area of structural-color definition. It can be used in sensing applications, on the one hand, to detect the presence of biological or chemical species and, on the other hand, to produce an actively and dynamically switched color response. This approach is widely used in various applications, including color definition in displays, sensing, and information storage. Particularly, swelling/shrinking of smart photonic crystal materials,^{29–31} vapor exposure,^{32–34} magnetic field,^{35,36} stress,^{37,38} and other factors has been shown to induce the desired spectral changes. At the same time, fabrication of high-resolution structural color materials, including those with responsive dynamic functionalities,

requires cutting-edge manufacturing technologies, such as confined shearing,³⁹ standing-wave carving,⁴⁰ two-photon polymerization, and 3D printing,^{41,42} which in all cases increases the cost of large-scale fabrication. In this respect, self-assembly techniques present particular interest due to the possibility of inexpensive scaling up of the processes to meet the demands of mass production.⁴³

Here, we developed a gold-core/silver-shell hetero-metal nanorod metamaterial (HNM) through a template-assisted electrochemical fabrication method based on self-organized nanopores in anodic aluminum oxide (AAO), enabling high-resolution and wide-angle structural-color generation. Taking advantage of the interplay between localized plasmonic resonances of individual nanorods and their collective optical modes produced due to strong inter-rod electromagnetic coupling, efficient and controllable structural-color generation spanning broad CMY and RGB trajectories is demonstrated. Furthermore, the possibility of easy access of external analytes to the inter-rod region, together with high sensitivity of the electromagnetic coupling of the nanorods to the refractive index changes in this area, provides a robust mechanism for the realization of responsive structural color.⁴⁴ Such functionality was demonstrated by dynamically tuning the optical response of the nanostructure through changes in its surrounding fluidic environment. Operating in either an active or a passive regime, the developed technological platform can be applied to high-resolution display, biochemical sensing, anti-counterfeiting, and high-definition printing.

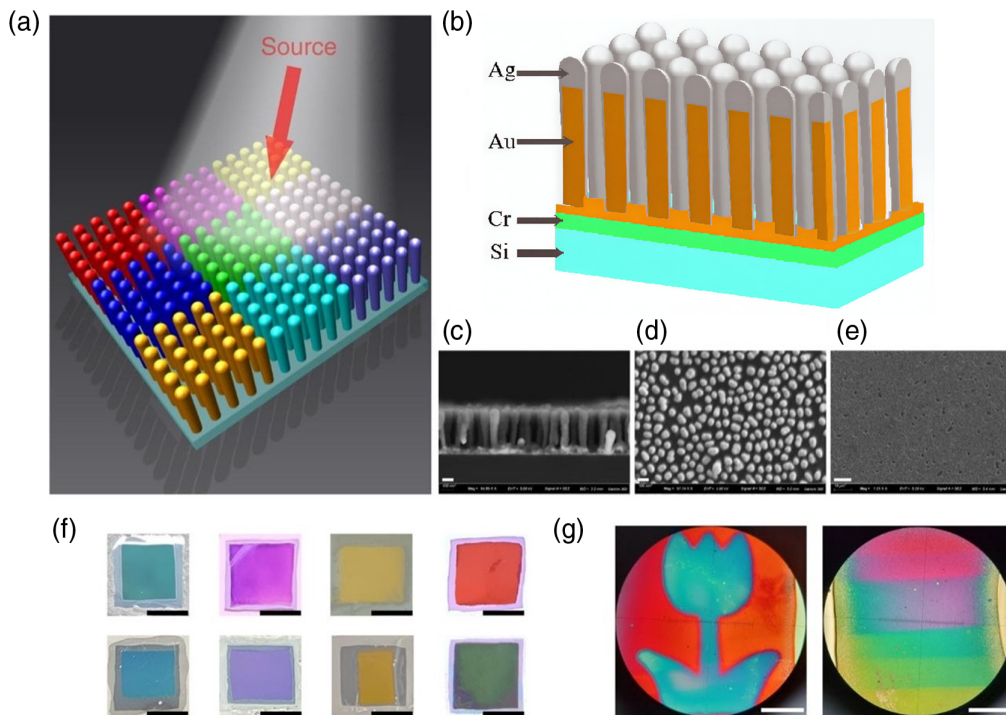


Fig. 1 (a) Schematic illustration of structural-color generation based on HNMs with different geometrical parameters. (b) Structural design of the HNMs. (c) Side-view SEM image of a representative HNM; scale bar: 100 nm. (d) Top-view SEM image of a representative HNM; scale bar: 100 nm. (e) Low-magnification SEM image of an HNM; scale bar: 10 μ m. (f) Multicolor patterning based on HNMs; scale bar: 1 mm. (g) Proof-of-concept region-selective color patterning on a single substrate by area-selective Ag deposition through an aluminum-foil mask; scale bars: 5 mm.

2 Metamaterial Design and Principle of Color Definition

2.1 Design and Fabrication

The design of the HNMs for high-resolution and wide-angle color definition in reflection is schematically illustrated in Figs. 1(a) and 1(b). The HNMs consist of closely packed arrays of vertically aligned Au-core/Ag-shell nanorods with a randomized in-plane distribution and a subwavelength average inter-rod spacing of ~ 100 nm. They were fabricated by a template-assisted electrodeposition method based on self-organized AAO nanopores⁴⁶ that is well suited for large-area production (Fig. 2). Here, "self-organization" refers to the spontaneous formation of a quasi-ordered nanopore array during anodization of the Al film. Driven by electric-field-assisted dissolution and compressive stress at the alumina/metal interface, cylindrical pores appear and propagate vertically through the Al layer without lithographic pre-patterning, which results in a quasi-ordered hexagonal arrangement with a controlled average inter-pore spacing. Specifically, Cr, Au, and Al films were first sequentially deposited onto a smooth Si substrate by magnetron sputtering. The 5 nm Au film served as the working electrode for subsequent electrodeposition, whereas the 10 nm Cr film acted as an adhesion layer. The Al film was then anodized in 0.3 mol/L oxalic acid at 40 V and 0°C to 1°C to form AAO with vertically aligned cylindrical pores and an average inter-pore spacing of ~ 100 nm. Gold nanorods were subsequently grown inside the pores by electrodeposition using the underlying Au electrode. The plating solution consisted of HAuCl_4 (0.05 mol/L), Na_2SO_3 (0.42 mol/L), and $\text{Na}_2\text{S}_2\text{O}_3$ (0.42 mol/L). The nanorod height was controlled by the electrodeposition time, with its maximum value determined by the initial Al thickness. After wet etching of the template with NaOH to form a free-standing nanorod array, Ag was deposited onto the Au nanorods by magnetron sputtering to obtain the HNMs. To minimize Ag oxidation, all measurements in this work were performed immediately after the Ag deposition (see Sec. S1 in the [Supplementary Material](#)). Representative scanning electron microscope (SEM) images of the fabricated samples are shown in Figs. 1(c)–1(e). The color variation obtained by changing the fabrication parameters is shown in Fig. 1(f). As

illustrated in Fig. 1(g), spatially distinct colors were produced on a single substrate by selectively depositing Ag in predefined regions using an aluminum-foil mask, thereby enabling area-selective modulation of the nanorod geometry. This multistep strategy provides a feasible route toward pixelated structural-color patterning.

2.2 Principle of Color Definition

The optical behavior of a metamaterial is defined by both the optical response of the constituting nanostructures (called meta-atoms) and the coupling between these components. In the absence of diffractive effects, light perceives the metamaterial as a uniform medium with dielectric permittivity defined by the above effects, which can be calculated using effective-medium theories (EMTs). From this perspective, plasmonic nanorod metamaterials are artificial optical materials possessing a record-high level of anisotropy.⁴⁵ Furthermore, their anisotropic optical properties can be tuned by varying geometrical and material parameters at the fabrication stage. Reflection of light from a nanorod metamaterial layer presents an interplay of EMT spectral features related to the excitation of the transverse plasmonic resonances of the nanorods or epsilon-near-zero behavior and Fabry-Pérot (F-P) or guided mode resonances of the metamaterial layer.⁴⁶ Engineering of these phenomena with the hetero-metallic realization of these metamaterials—HNMs—provides an efficient means for the realization of structural-color definition.

The principle of metamaterial color definition was first investigated by finite-difference time-domain simulations. The optical constants of Au and Ag, Cr, and Si were taken from Refs. 47, 48, and 49, respectively. The simulation results are presented in Fig. 3. As the base structure for the realization of the HNMs, gold nanorod arrays with typical geometrical parameters of diameter $d_{\text{Au}} = 50$ nm, height $h_{\text{Au}} = 250$ nm, and inter-rod spacing of the order of 100 nm were chosen. Although simulation of randomized nanorod arrays is computationally prohibitive, it can be utilized that their optical response within the EMT is identical to that of square arrays with appropriately chosen subwavelength spacing to match the metal filling factors.⁴⁵ In the latter case, it is possible to fully calculate the metamaterial optical response by simulation of a metamaterial unit cell with

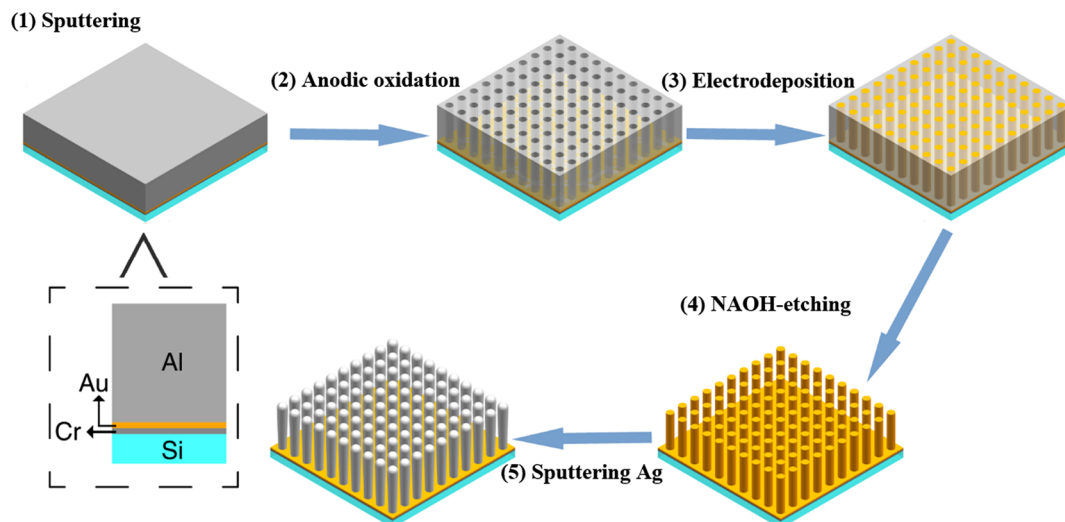


Fig. 2 Schematic of the fabrication workflow of Au-core/Ag-shell nanorod metamaterials.

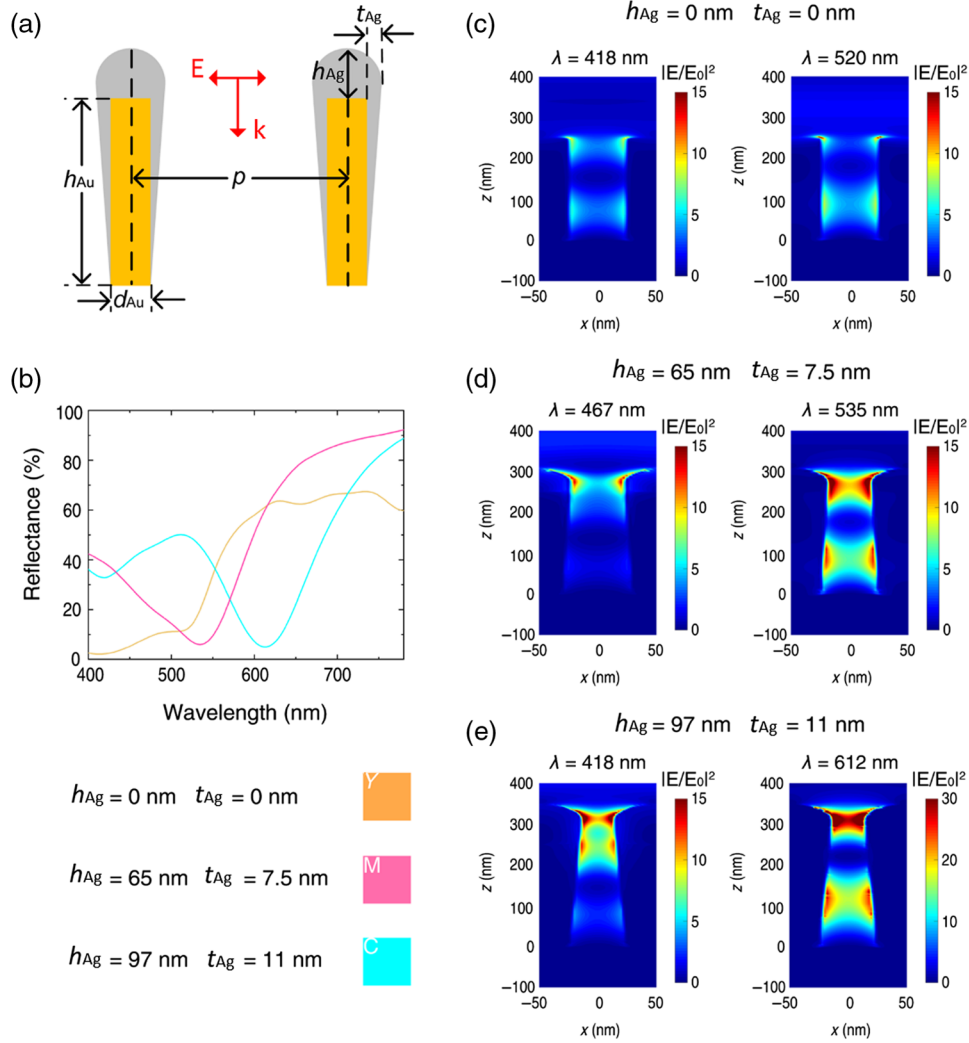


Fig. 3 (a) Definition of geometric parameters for modeling of HNMs. (b) Numerically simulated reflection spectra at normal incidence for the indicated shell geometrical parameters corresponding to yellow, magenta, and cyan structural colors. Electromagnetic field distributions corresponding to the spectral minima in (b) for (c) yellow, (d) magenta, and (e) cyan structural colors. The geometrical parameters of the initial nanorod metamaterial are $h_{Au} = 250$ nm nanorod height, $d_{Au} = 50$ nm diameter, and $p = 100$ nm periodicity.

periodic boundary conditions set on its sides, and this is the approach adopted here. The Ag shell with a variable geometry corresponding to various deposition conditions was described by a set of geometrical parameters: a maximum thickness at the top of the nanorod h_{Ag} and a maximum thickness to the side of the nanorod $t_{Ag} = (d_{Ag} - d_{Au})/2$, where d_{Ag} is the diameter of a hemispherical tip of the HNM nanorods and d_{Au} is the diameter of their Au cores [Fig. 3(a)]. Numerical simulations show that varying the geometrical parameters of the Ag shell substantially modifies the HNM reflection spectrum, enabling reflected structural colors that span a broad CMY trajectory [Fig. 3(b)]. These parameters are controllable at the fabrication stage.

For an uncoated HNM ($h_{Au} = 250$ nm, $d_{Au} = 50$ nm) shown by the yellow curve in Fig. 3(b), the field maps corresponding to the reflection minima for normally incident x -polarized plane-wave illumination at 418 and 520 nm exhibit features of both the transverse plasmonic resonance of the nanorods, evidenced by field enhancement at the nanorod tips

[Fig. 3(c)], and a second-order F-P resonance, evidenced by the two-lobe standing-wave pattern along the nanorod length. Thus, the minima are produced by hybridization of these HNM plasmonic resonances, the 520-nm one mostly matching the transverse plasmonic resonance of gold nanorods, and the 418-nm one mostly produced by the F-P resonance.

The combination of these minima produces a broad low-reflectivity region below 550 nm, which, when mapped onto the CMY palette,¹⁴ defines a yellow color. With the addition of a Ag shell, the resonances experience opposite spectral shifts. The transverse plasmonic resonance is blue-shifted to 467 nm, as shown in Figs. 3(b) and 3(d), due to much more negative values of the real part of Ag permittivity. At the same time, the F-P resonance is red-shifted in accordance with the trend for the effective permittivity that the EMT gives for Ag-based nanorods. Overall, this results in a pronounced reflectivity minimum in the green region of the spectrum, resulting in a magenta color, as shown in Fig. 3(b). For thicker Ag layers, the observed trends continue,

as shown in Figs. 3(b)–3(e), producing a less pronounced transverse plasmonic resonance minimum at 418 nm (partly hybridized with a higher-order F-P mode) and a well-defined deep second-order F-P resonance at 612 nm. This results in the subtraction of the red part of the spectrum from the reflected signal and therefore produces a cyan color [Fig. 3(b)].

2.3 Influence of Geometric Parameters on Coloring

To further analyze the possibility of color engineering, numerical simulations of HNMs with varied geometrical parameters were performed. Figures 4(a)–4(c) show the effects of changing d_{Au} , h_{Au} , and p on the reflection spectra for gold nanorods without a silver shell, taking $h_{Au} = 250$ nm, $d_{Au} = 50$ nm, and $p = 100$ nm as the initial parameters. In a simple physical picture, increasing the nanorod diameter d_{Au} narrows the inter-rod gap, which strengthens inter-rod coupling and enhances the local electric field. This leads to higher fields inside the rods and, therefore, increases the overall metamaterial absorption. More

precisely, from the point of view of EMT, this increases the metal filling factor, which increases the effective-medium absorption, simultaneously extending it into the red part of the spectrum. In addition, the increase in the filling factor leads to the rise of the real part of the effective refractive index, which leads to a red shift of the F-P resonance. This exact behavior was observed in the numerical simulations [Fig. 4(a)]. In contrast, the increase of the nanorod height h_{Au} does not affect the nanorod coupling but changes the thickness of the metamaterial layer and, therefore, the spectral positions of the F-P resonances, shifting them to longer wavelengths [Fig. 4(b)]. Furthermore, when h_{Au} reaches 350 nm, a new reflection dip corresponding to an F-P resonance of the next order appears at the wavelength of 400 nm, demonstrating the same red-shift rate as the previous one. With the increase of the inter-rod spacing, the metal filling factor of the metamaterial decreases, and according to the considerations above, the associated trend is opposite to the one observed in Figs. 4(a) and 4(c). The corresponding optical behavior for the Ag-coated HNMs is presented in

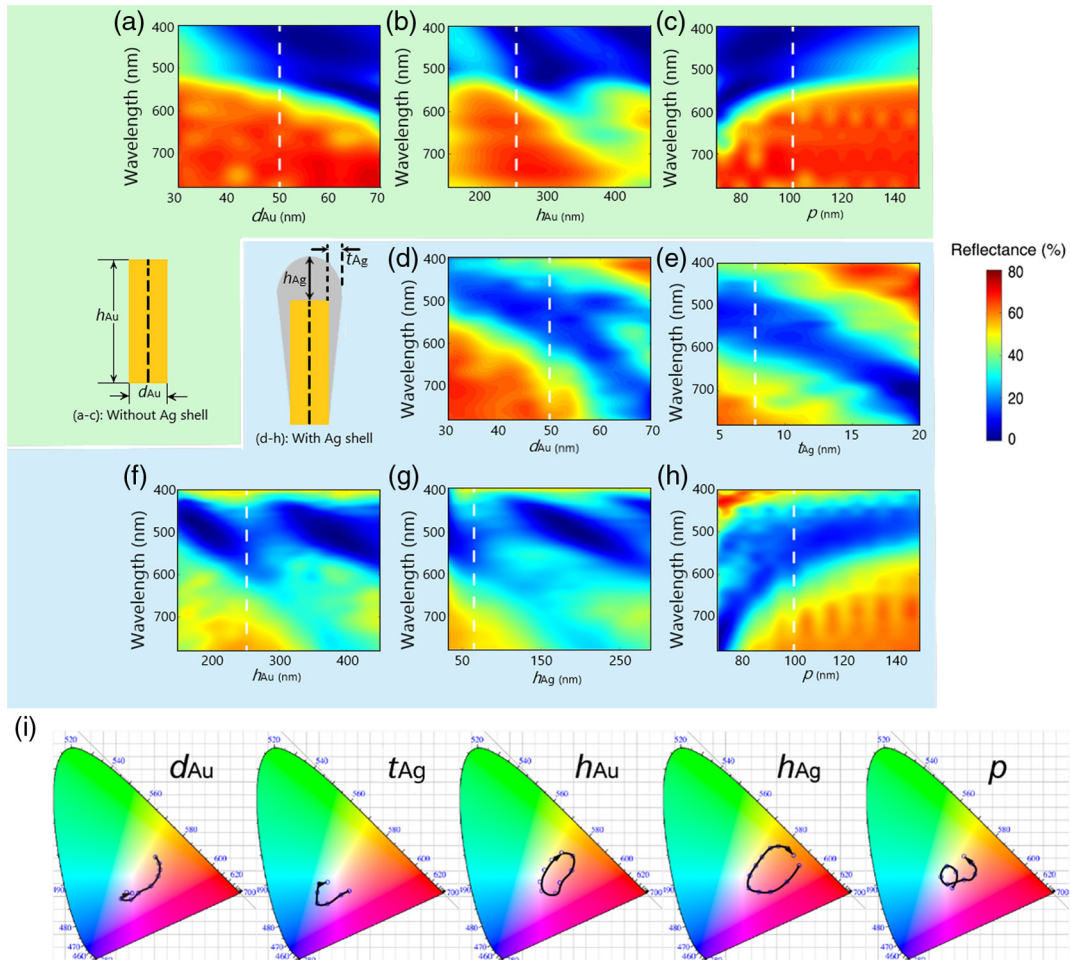


Fig. 4 (a)–(c) Numerically simulated dependence of the reflectance spectra at normal incidence on (a) diameter d_{Au} , (b) height h_{Au} , and (c) periodicity p of uncoated gold nanorods. Unless otherwise stated, all other parameters are fixed at $d_{Au} = 50$ nm, $h_{Au} = 250$ nm, and $p = 100$ nm; the spectra of the initial metamaterial are indicated by white dashed lines. (d)–(h) d_{Au} -, t_{Ag} -, h_{Au} -, h_{Ag} -, and p -dependent reflectance spectra at normal incidence for HNMs with a silver shell. Unless otherwise stated, the fixed parameters are $d_{Au} = 50$ nm, $h_{Au} = 250$ nm, $t_{Ag} = 7.5$ nm, $h_{Ag} = 65$ nm, and $p = 100$ nm; the spectra of this HNM are indicated by white dashed lines. (i) Gamut path diagrams for the HNMs with structural parameter variations presented in panels (d)–(h).

Figs. 4(d)–4(h). The trends in the graphs can be explained within the framework discussed above but have more pronounced F-P features compared with the uncoated rods. To guide the engineering of the structural color in the experiments, Fig. 4(i) shows the resulting reflected color for the variations of HNM geometrical parameters presented in Figs. 4(d)–4(h) using the CIE 1931 xy color space chromaticity diagram. The results indicate that through the structural design of the nanostructure, the color can be continuously tuned across all chromatic directions and with different saturation levels.

3 Structural Color Definition Using HNMs

3.1 Realization of CMY Color Palette Using HNMs

Samples with initial parameters of $h_{Au} = 250$ nm, $d_{Au} = 50$ nm, and an average spacing of ~ 100 nm were selected for structural-color generation, whereas the individual color of each sample was tuned by varying the Ag magnetron sputtering time. Figure 5(a) shows CCD images of the colors obtained with increasing the Ag-deposition time. As confirmed by the corresponding SEM images in Fig. 5(b), longer sputtering simultaneously increases the top cap height and side-shell thickness, leading to increases in h_{Ag} and d_{Ag} . In particular, the side-shell thickness t_{Ag} , estimated from the average maximum nanorod width, increased from 2.5 to 17.5 nm, whereas the average overall nanorod height increased from 260 to 387 nm, corresponding to an increase in h_{Ag} from 10 to 137 nm. As a result, the reflected color evolves continuously from light yellow through orange, magenta, purple,

indigo, and cyan to green, covering a broad CMY trajectory. The corresponding path on the CIE 1931 xy color space diagram is presented in Fig. 5(c). The appearance of green at the end of the trajectory is attributed to the emergence of a higher-order F-P resonance with the increase of the HNM height, which produces two pronounced reflection minima within the visible range and leaves a dominant reflection in the green spectral region. In principle, RGB structural colors could also be achieved by further increasing h_{Au} . However, fabrication tests showed that nanorods with $h_{Au} \approx 600$ nm are prone to collapse, which compromises color reproducibility. The reflectance of a representative magenta HNM was further measured as a function of incident angle for both TM- and TE-polarized illumination, as shown in Fig. 5(d). The corresponding colors remain nearly unchanged up to 55 deg, confirming the potential of HNMs for wide-angle color definition. From the in-plane localization length of the metamaterial plasmonic modes, estimated from the measured spectral widths, the achievable pixel size is ~ 0.5 μ m, corresponding to an estimated resolution of $\sim 50,000$ dpi.

3.2 Material Dependence

To show the advantages of the implemented hetero-metallic design, its performance was compared with that of single-metal counterparts. Particularly, Figs. 6(a) and 6(b) show the reflectance spectra and the corresponding structural colors obtained for Au-core/Au-shell and Ag-core/Ag-shell combinations for varied shell thicknesses. One can see that due to strong inherent

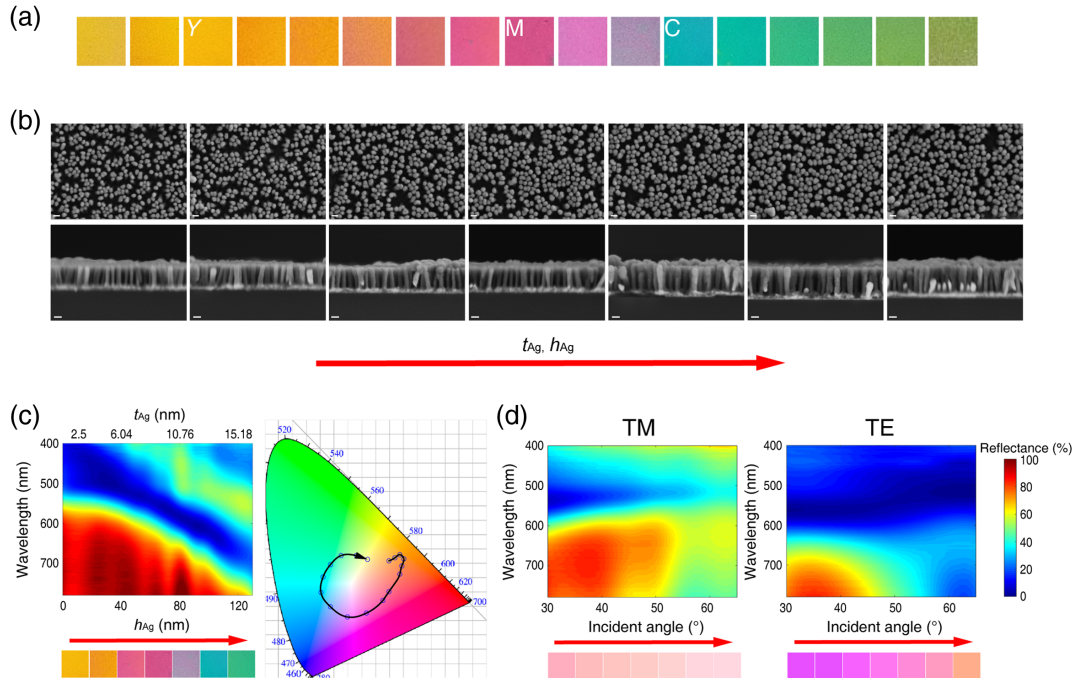


Fig. 5 (a) CCD images showing color variation with the increase of the Ag-deposition time. (b) SEM images of selected samples showing the corresponding geometrical evolution; scale bar: 100 nm. (c) Experimentally measured reflectance at normal incidence for HNMs with increasing Ag-shell dimensions, with the corresponding reflected colors shown below the map and the gamut path shown on the right. (d) Experimentally measured angular dependence of HNM reflectance for TE- and TM-polarized illumination, with the corresponding reflected colors shown below the maps. The initial nanorod metamaterial has $h_{Au} = 250$ nm, $d_{Au} = 50$ nm, and an average spacing of ~ 100 nm.

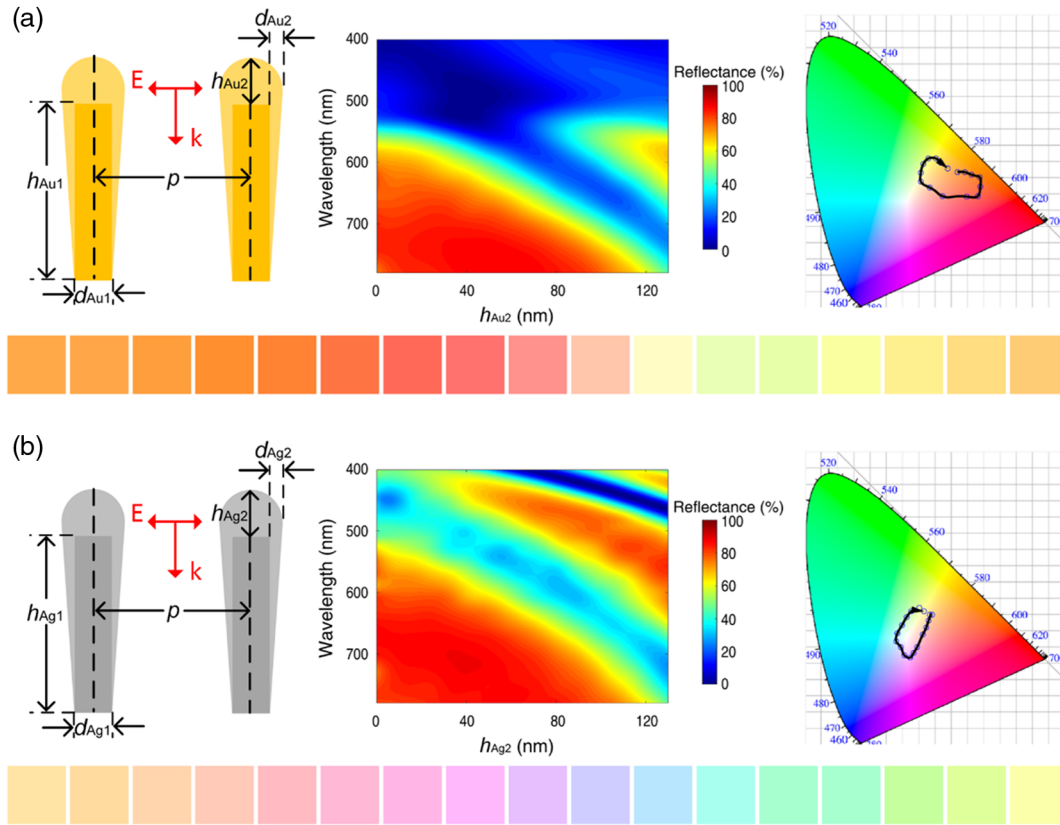


Fig. 6 Numerically simulated dependence of the normal incidence reflectance spectra on the height of the sputtered gold shell h_{Au2} for (a) Au-core/Au-shell metamaterials and (b) Ag-core/Ag-shell metamaterials, with the corresponding colors and the path on the CIE 1931 xy diagram. The geometrical parameters of the initial nanorod metamaterial are $h_{Au} = 250$ nm height, $d_{Au} = 50$ nm diameter, and $p = 100$ nm periodicity.

absorption in the 400 to 500 nm spectral region, it is practically impossible to achieve the reflected colors in the blue-green part of the visible spectrum with a solely gold metamaterial, which therefore cannot cover the entire visible color gamut. The small compensating advantage of this structure is that it produces more pronounced reflection minima, which results in purer other colors. The reflection spectrum of Ag-core/Ag-shell HNMs presented in Fig. 6(b) indicates limitations in achieving high color purity with pure Ag metamaterials due to their high reflectivity at the minimum, resulting in weaker color saturation. This design remains attractive because of its wide color coverage and lower material cost. This confirms the distinct advantage of the original Au-core/Ag-shell design for the realization of a broad and deep CMY color gamut [cf. color gamuts in Fig. 5(c) with those in Fig. 6]. The Au-core/Ag-shell HNM not only exhibits low reflectivity at the reflection dips, leading to well-defined saturated colors, but also supports reflected structural colors spanning a broad CMY trajectory.

4 Responsive Colors with Nanorod Metamaterials

The facile access of external materials, particularly liquids, to the inter-rod regions of a nanorod metamaterial, together with the high sensitivity of its optical response to such changes,^{27,28} offers a versatile route toward responsive structural color.

Specifically, the color response of the HNM can be engineered by gradually adding dielectric material between the nanorods, whereas its sensitivity to the refractive index of the inter-rod material can be used for sensing applications.²⁷

4.1 Realization of Color Palette with Gradual Addition of Inter-Rod Materials

The above advantages lead to another straightforward route for structural-color definition by controllable deposition of another material into the inter-rod regions [Fig. 7(a)]. Particularly, taking a gold nanorod metamaterial ($h_{Au} = 250$ nm, $d_{Au} = 50$ nm, and ~ 100 nm spacing) as the initial structure, a silica gel layer was deposited into it via spin-coating [Fig. 7(b)]. The spin-coating process involved sequential deposition steps, adding approximately a 15 nm layer each time. The resulting color evolution of the samples is presented in Fig. 7(a). Slightly specular coloration of the sample is caused by large gel particles occasionally present in the sample. Generally, the color in this case is produced by the interplay between the excitation of nanorod transverse plasmonic resonances in air in the top metamaterial section together with the corresponding resonance in the silica gel-filled region in the bottom section and F-P metamaterial layer resonances, all affected by the change in h_{gel} . At very small silica gel thicknesses, a low-reflection region covers all the wavelengths below 600 nm [Fig. 7(c)], which produces a red color. With

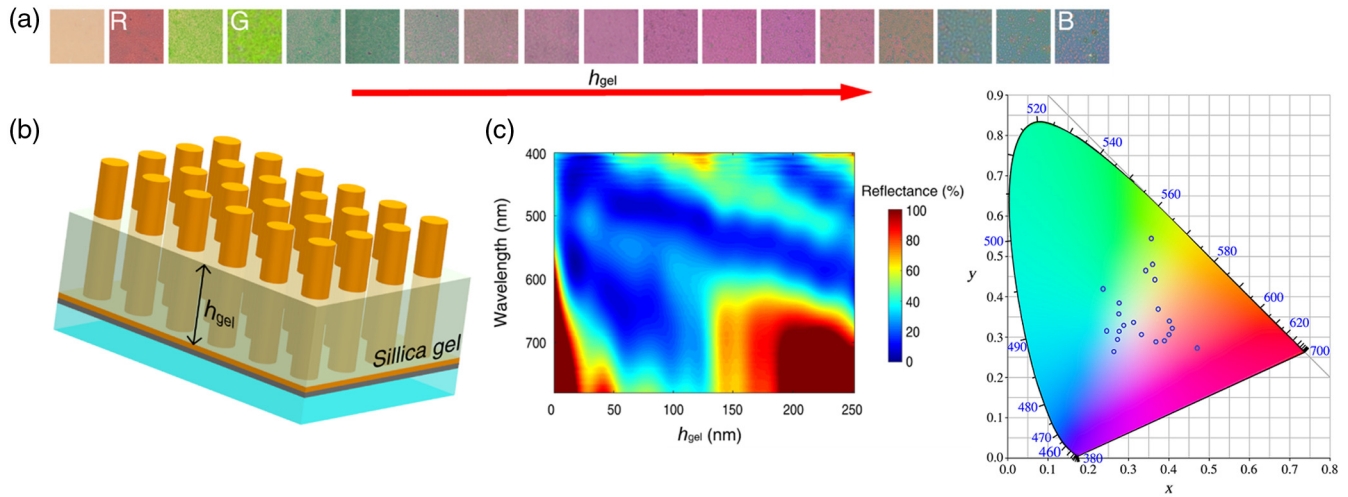


Fig. 7 (a) CCD image of the nanorod metamaterial with the silica gel height h_{gel} increased in ~ 15 nm increments. (b) Schematic diagram of a nanorod metamaterial with a deposited silica gel layer. (c) Experimentally measured dependence of the reflectance spectra on the silica gel thickness h_{gel} for the initial gold nanorod metamaterial with $h_{\text{Au}} = 250$ nm, $d_{\text{Au}} = 50$ nm, and an average spacing of ~ 100 nm, and the corresponding CIE 1931 xy chromaticity diagram is shown on the right.

the increase of h_{gel} to the values just below 50 nm, this region covers the entire visible region, but a small maximum corresponding to the reflection of a green color between two F-P resonances appears. Around 150 nm thickness, there is suppressed reflection for the wavelengths between 500 and 600 nm, which gives a magenta color. Finally, at a thickness of ~ 250 nm, low reflection covers the entire spectrum above 450 nm, resulting in a blue metamaterial color. It can be seen that dielectric loading by silica gel enables responsive structural colors spanning a broad RGB trajectory [Figs. 7(a) and 7(c)].

4.2 Refractive Index Sensing

The performance of nanorod metamaterials for color-marking of the refractive index of the surrounding media was also explored. Particularly, CCD images of an HNM immersed in media with different refractive indices are shown in Fig. 8(a). The initial color of the HNM in the air was purple. When the medium changed to methanol, the color changed to light

yellow. With the increase of the refractive index of the surrounding medium in just a few percent steps, two reflection dips experiencing a gradual red shift appear in the spectrum. This leads to a change in color to orange, with the saturation level marking the refractive index change, which can be easily observed with the naked eye. Using numerical simulations, the potential of HNMs for obtaining a more vivid response to the refractive index changes was further demonstrated. Particularly, for the optimized design ($h_{\text{Au}} = 250$ nm, $d_{\text{Au}} = 50$ nm, $h_{\text{Ag}} = 65$ nm, $t_{\text{Ag}} = 7.5$ nm, and $p = 100$ nm), media with refractive-index differences of only a few percent can be individually distinguished with high-contrast coloration, ranging from magenta through blue and cyan to green.

4.3 Humidity Sensing

The metamaterial color sensitivity to the changes of the refractive index can be further exploited for monitoring the relative humidity. For this purpose, an HNM was functionalized

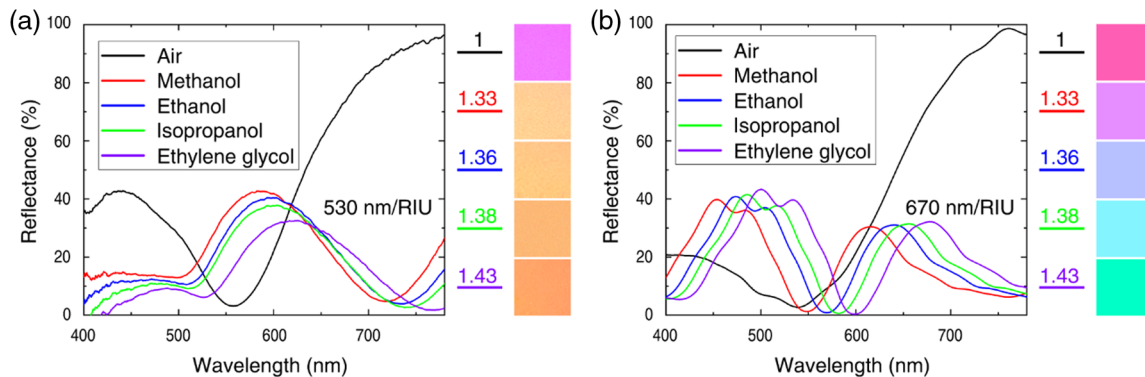


Fig. 8 (a) Experimental results for color-marking of the surrounding-medium refractive index using an HNM ($h_{\text{Au}} = 250$ nm, $d_{\text{Au}} = 50$ nm, $h_{\text{Ag}} = 73$ nm, $t_{\text{Ag}} = 8.5$ nm, and an average inter-rod spacing of ~ 100 nm). (b) Simulation results for the optimized HNM geometry.

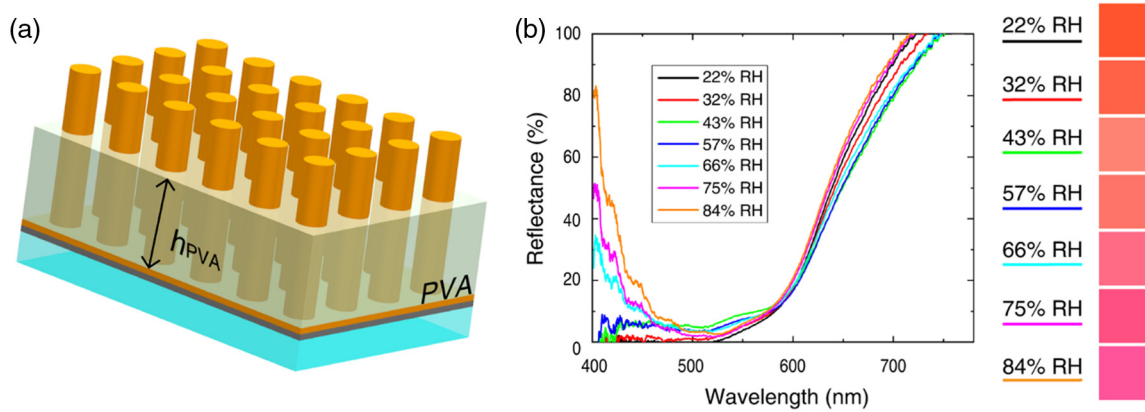


Fig. 9 (a) Schematic diagram of an HNM, filled with PVA. (b) Experimentally measured reflection spectra of the PVA-filled HNM ($h_{Au} = 250$ nm, $d_{Au} = 50$ nm, $h_{Ag} = 0$ nm, $t_{Ag} = 0$ nm, and ~ 100 nm spacing) for various levels of environmental humidity, together with the resulting color change presented on the right.

with polyvinyl alcohol (PVA), forming a layer with an ~ 150 nm thickness at the base of the metamaterial [Fig. 9(a)]. PVA swells upon water-vapor absorption, which leads to both structural and refractive index changes in the inter-rod space. As a result, the modification of the metamaterial color due to the changes in the relative humidity can be seen with the naked eye [Fig. 9(b)]. The variation of the reflectivity is particularly pronounced in the violet part of the spectrum, which, using an added color filter (e.g., cutting off wavelengths above 550 nm), could further enhance visual color discrimination and improve the distinction between individual humidity states. Finally, the experimentally measured color marking was reproducible with a response time of less than 10 s, which ensures a stable and fast operation of the sensor.

5 Discussion

The Ag-coated Au nanorod metamaterials demonstrated here provide a versatile platform for structural-color engineering. Their optical response is governed by the interplay between plasmonic and F-P-type resonances and can therefore be tuned through the structural parameters of the nanorods, including the Au-core diameter and height, the Ag shell thickness and cap height, the inter-rod spacing, and the dielectric loading within the inter-rod region. In this work, CMY structural colors were achieved through geometrical control of the nanorod architecture, whereas additional responsive color tuning was realized by modifying the surrounding dielectric environment. Even for a single set of initial nanorod parameters ($p = 100$ nm, $h_{Au} = 250$ nm, and $d_{Au} = 50$ nm), the deposited-Ag series experimentally produced structural colors occupying 38% of the sRGB gamut and 28% of the Adobe RGB gamut by changing the thickness parameters of the deposited Ag [Fig. 5(c), see also Sec. S2 and Fig. S1(a) in the [Supplementary Material](#)], including representative colors from the CMY palette and extending the color space toward the green region. As experimentally shown by silica gel loading of the initial metamaterial without the Ag shell, deposition of an inter-rod dielectric can further expand the accessible color range by shifting the spectral response over a broad region of the CIE color space [Fig. 7(c)]. The color-space extension achievable by silica-gel deposition into Ag-covered metamaterial structures was estimated numerically, showing a large increase in the color coverage to more than

70% of sRGB and 52% of Adobe RGB gamuts [see Fig. S1(b) in the [Supplementary Material](#)]. Both Ag deposition on the nanorods and dielectric filling between the nanorods can, in principle, be implemented in an area-selective manner for spatially resolved color patterning, whereas additional tuning of p , h_{Au} , and d_{Au} of the initial nanorod metamaterial can further improve color management.

Although the experiments presented here were mostly performed on uniform-color samples, the fabrication strategy is, in principle, compatible with pixelated color patterning on a single substrate. Distinct color regions could be produced by defining local areas using lithographic masking and selectively varying the nanorod geometry through sequential deposition or etching steps.¹⁴ The region-selective Ag-deposition approach using a hard mask presented in Fig. 1(g) provides a proof-of-concept demonstration of this local color-tuning capability. Local dielectric filling may provide an additional route for the color adjustment. Because the coloration is determined by subwavelength structural parameters rather than diffractive pixel geometries, the HNM approach has the potential to support high-resolution pixelated structural color with broad angular tolerance. Further development will require improved control of multistep alignment, protection of previously defined regions during subsequent processing, and enhanced long-term stabilization of Ag-containing nanostructures, as discussed in Sec. S3 in the [Supplementary Material](#).

6 Conclusion

We have developed a plasmonic nanorod metamaterial platform for structural-color generation and responsive optical functionality. The structures are fabricated by a template-assisted electrodeposition method based on self-organized AAO nanopores, which is readily scalable to large-area production. By employing a hetero-metallic Au-core/Ag-shell nanorod architecture, we realized high-resolution, wide-angle structural colors spanning a broad CMY trajectory. In addition, responsive RGB color tuning was achieved by dielectric loading with silica gel, whereas the strong dependence of the optical response on the surrounding environment enabled refractive-index and humidity sensing through readily distinguishable color changes. These results highlight the potential of nanorod

metamaterials as a versatile platform for high-resolution color patterning, anti-counterfeiting, optical encoding, and environmental or chemical sensing.

Disclosures

Anatoly V. Zayats holds equity in Metasenz Ltd commercialising sensing applications of nanorod metamaterials. All other authors declare no conflicts of interest. Anatoly V. Zayats is co-editor-in-chief of *Advanced Photonics Nexus*. To maintain transparency and uphold the highest standards of editorial integrity, the peer-review process for this paper was managed independently by an editor who oversaw the review and editorial decision-making process.

Code and Data Availability

Data underlying the results presented in this paper are not publicly available at this time but may be obtained from the authors upon reasonable request.

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An Ping received his MS degree from Nanjing University of Information Science and Technology, China. He is currently a PhD candidate at the School of Electronic Science and Engineering, Southeast University, China. His research interests include micro-/nano-photonics.

Haibin Ni is an associate professor at the School of Electronics and Information Engineering, Nanjing University of Information Science and Technology, China. He received his PhD from Nanjing Normal University,

Nanjing, China, in 2014. His research interests focus on micro-/nano-photonics sensing and fiber-optic sensors, including plasmonic micro/nano-structures, microstructured fiber platforms, and multiparameter sensing for environmental and biomedical applications.

Toluwalase A. Isogun is currently a PhD candidate with the School of Electronics and Information Engineering, Nanjing University of Information Science and Technology, China. His research interests include nanophotonics and optical engineering.

Alexey V. Krasavin received his BSc (with honors) and MSc (with honors) degrees from Moscow Institute of Physics and Technology, Russia. In 2006, he was awarded a PhD in physics from the University of Southampton and joined Queen’s University Belfast as a Research Fellow. Since 2010, he has worked at King’s College London. His research interests include active manipulation of light at the nanoscale, nonlinear plasmonic-assisted effects, plasmonic-enhanced fluorescence, and nonlocal and quantum phenomena.

Ying Shi is an undergraduate student at the School of Electronics and Information Engineering, Nanjing University of Information Science and Technology, China.

Bo Ni is a lecturer at the School of Electronics and Information Engineering, Nanjing University of Information Science and Technology, China. He received his PhD in microelectronics and solid-state electronics from the University of Chinese Academy of Sciences (Shanghai Institute of Technical Physics). His research interests focus on micro-/nano-photonics and related optoelectronic devices.

Jianhua Chang received his PhD from Southeast University, Nanjing, China, in 2005. He is a professor and PhD supervisor at Nanjing University of Information Science and Technology, China. His research interests include optoelectronic sensors, ultrafast lasers, and optoelectronic hybrid integration.

Anatoly V. Zayats is a chair in experimental physics and the head of the Photonics & Nanotechnology at the Department of Physics, King’s College London, United Kingdom. He is also a co-director of the London Centre for Nanotechnology and the London Institute for Advanced Light Technologies. His research interests include nanophotonics and plasmonics, metamaterials and metasurfaces, electromagnetic field topology and optical spin-orbit coupling, and nonlinear and ultrafast optics.