The iridescence of disordered resonant metasurfaces

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Abstract: Due to the intrinsic limitations of pigment coloration, the generation of bright, largely tunable, and angle-insensitive colors with nanostructured surfaces has received considerable interest. However, coatings that exhibit diffuse color changes with the viewing and illumination directions are also important as they provide extra degrees of freedom to create attractive visual effects. Here, we present metasurfaces composed of a non-close packed assembly of metallic nanoparticles deposited on a reflective substrate coated with a low-index spacer. This geometry, which combines plasmonic and Fabry-Perot resonances, offers uncommon iridescences, differing from those classically observed with natural nanostructures or thin-film interferences. We highlight a remarkable iridescence with only two distinct colors and theoretically investigate its origin with an intuitive and accurate model that unveils the rich physical mechanisms at play. The interpretation paves the way towards the design of easy-to-make and universal building blocks with a large resilience to fabrication imperfections, and great potential for innovative coatings and fine-art applications.

Significance statement: Natural or engineered iridescent surfaces are known to offer outstanding color effects that change in hue or intensity with the viewing or illumination geometry. They drive attention in diverse research fields and inform the design of cosmetics, advanced coatings and paints. Here, we exploit the rich palette of optical resonances offered by metasurfaces made of high-index nanoparticles randomly deposited on a reflective substrate. The metasurfaces create unconventional iridescences not found in nature. We report on a particular iridescence that produces only two distinct colors for all illumination and observation directions.

Introduction

Nature offers us beautiful colors and visual appearances produced by the interaction of light with micro- and nano-scale structures [1]. The most resplendent appearances of butterfly wings or bird plumages often come from the iridescence of melanosome forms organized in thin layers [2]. The micro and nanoscale complexity not only inform biologists studying structural color biodiversity, but also inspire engineers designing nanophotonic systems to achieve angle-insensitive structural colors or prescribed angular color response [3,4,5].

Artificial optical metasurfaces composed of monolayers of Mie or plasmonic nanoresonators have recently attracted considerable attention for various applications, including color generation [3,4,5]. Be they disordered [6,7,8,9,10], as in Fig. 1, or minutely organized [11,12,13], they offer many degrees of freedom that are not encountered in nature. At the nanoscale, a plethora of high-index materials and shapes can be used to tailor the resonances of the individual constituent metaatoms. In addition, when the array lies on a reflective substrate, mode hybridization occurs between the nanoresonators and their mirror images, leading to considerable changes of the spectral and spatial properties of the modes [14,15,16]. At the mesoscale, a combination of short- and long-range electromagnetic interactions...
results in complicated nonlocal responses that may involve many nanoresonators \[17,18,19,20,21\]. Since these man-made metasurfaces rely on high-index nanostructures that are not found in nature, one is entitled to wonder whether they may offer iridescence \[22,23\] or visual appearance \[24,25\] so far unseen in the biological world.

In this work, we study the iridescence of disordered metasurfaces made by large silver nanoparticles deposited on a reflective substrate coated with a submicrometric dielectric spacer (Figs. 1a-b). The metasurfaces rely on a cornerstone geometry of nanophotonics, often referred to as nanoparticles on reflective substrates, which are easy to fabricate, have a small geometrical cross section, and offer manifold optical resonances passively or dynamically tunable by varying the film thickness or the permittivity \[6,15,28,29,30,31,32\].

The color variations of the metasurfaces might be a bit reminiscent of the classical iridescence obtained with thin-film interference. However, their physical origin is completely different. The iridescence is not only observed in the specular direction but in every direction (Fig. 1c), hence the name diffuse iridescence. It is driven by nanoscale resonances (Fig. 1d), rather than thin-film interferences. Additionally, the colors and their variation are markedly different from the classical rainbow-colored iridescence observed, for instance, by reflection with thin oil films on water or by diffraction with photonic crystals. We notably report an unconventional visual effect, in which only two colors are observed, irrespective of the viewing and illumination directions.

The visual observations are supported by quantitative measurements of the bidirectional reflectance distribution function (BRDF) and by a semi-analytical model that highlights the main nanoscale mechanisms. We show that not all the resonances of the individual nanoparticles hybridize (Fig. 1d) despite the presence of the reflective substrate, implying that some resonances have the same frequency irrespective of the spacer thickness. The model also predicts that the frequencies of the BRDF spectral peaks that govern the metasurface colors are not determined by the resonance frequencies. It also explains why the colors are quite resilient to the inevitable polydispersity in size and shape of the nanoparticles, an important property that considerably lowers fabrication costs for large-scale applications.

**Figure 1.** Diffuse iridescence of disordered arrays of \(~ 100 \text{ nm} \) side silver nanocubes (AgNCs) on high refractive index Si substrates, coated with a sub-micrometric SiO\(_2\) layer of height \(h\). a, Schematic profile view of the sample configuration. b, Scanning electron microscope (SEM)
Two-color diffuse iridescence

The metasurfaces are fabricated by dip-coating a SiO$_2$/Si wafer with a colloidal monolayer of silver nanocubes (see Methods). For the study, we have gathered experimental results for a series of samples obtained with moderate silver nanocube densities ($\rho = 0.2$ to 8 nanoparticles per $\mu$m$^2$) and SiO$_2$ layer thicknesses, from $h = 0$ to $h = 700$ nm with a $\approx 100$ nm step. The nanoparticle density has little impact on the appearance, admittedly reinforcing the diffuse brightness but leaving unchanged the hue. Hereafter, we focus on the samples with an intermediate density $\rho = 2$ $\mu$m$^{-2}$.

Under a full sunlight illumination, all the samples (except for the reference sample with the nanocubes directly on the silicon wafer, $h = 0$ nm) exhibit iridescence with distinctive and vivid colors that vary as the samples are rotated. To quantify and evaluate the color variation, the metasurfaces are characterized in a controlled environment with a collimated solar simulator and the metasurface appearance is recorded with the camera of a smartphone fixed on a motorized stage (see Methods). Figure 2a shows two stripes of photographs recorded for the samples with thicknesses $h = 320$ and 640 nm. The Supplementary Note 1 further documents the color gamut observed for other thicknesses.

In general, the dependence of the diffuse color with the viewing and lighting directions is gradual and involves several hues, see for instance the upper stripe of photographs in Fig. 2a or Supplementary Fig. S1.1. From the very first observations, we have been intrigued by the metasurface with a spacer thickness $\bar{h} = 640$ nm. This metasurface stands out strikingly due to its iridescence mostly composed of two colors only, green and violet, the intermediate blue hue appearing only transitorily as we rotate the sample. The uncommon effect is easily seen from the lower series of photographs in Fig. 2a, which is recorded for normal incidence.

The iridescences of both metasurfaces are further documented in Fig. 2b, in which the colors extracted from the photographs recorded by the camera are displayed for six angles of incidence $\theta_i$ and for $|\theta| < 80^\circ$. We note several remarkable features for the metasurface with $h = 640$ nm. First, the green and violet colors largely dominate the metasurface response. The blue color is fleetingly observed as a rapid transition between green and violet. Second, one notices that the color, initially green around the normal, does not change up to angles of $\theta \approx 45^\circ$, for which the metasurface color abruptly changes into violet, before becoming again green for even larger (almost grazing) viewing angles. Yet, another remarkable transition occurs for fixed viewing angles, this time as the angle of incidence increases and reaches $\theta_i \approx 45^\circ$. For instance, when it is seen from above around the normal ($\theta = 0$), the metasurface, initially green, suddenly turns violet for $\theta_i \approx 45^\circ$, before becoming again green for large incidences ($\theta_i \approx 70^\circ$).
Figure 2. Direct visual demonstration of the two-color iridescence phenomenon with a solar simulator. 

a, Series of photographs of two metasurfaces with $h = 320$ nm (top, multicolor iridescence) and $h = 640$ nm (bottom, two-color iridescence) taken by varying the viewing angle at normal incidence. 
b, Extended visualization of the two metasurfaces at several angles of incidence ($\theta_i = 0^\circ \rightarrow 70^\circ$) and viewing angles ($\theta = -75^\circ \rightarrow 80^\circ$). The colors are extracted from the central part of the metasurface in steps of $\Delta\theta = 1^\circ$ and black zones are due to the detector support blocking the incident light. Note that, since the area occupied by the angular sectors for small $\theta_i$'s is greater than that corresponding to large $\theta_i$'s, the weight of the colors at the largest $\theta_i$'s are underrepresented in the hand-fan.

One may be tempted to see these color transitions as classical iridescence resulting from thin-film interferences combined with a diffuse reflection added for instance by roughening the film surfaces. This vision is quite erroneous for several reasons. First, the light diffusion feeds the entire half space above the metasurface, owing to the deep subwavelength scale of the nanocubes, in contrast to the diffusion produced by a rough film that occurs around the specular direction. Secondly, and more importantly, the diffuse colors and their gradual variations have very little to do with those produced by the specular iridescence of the same thin SiO$_2$ layer. This point is highlighted in Supplementary Note 2 by comparing the diffuse iridescence gamut with the specular iridescence computed and measured on the same sample in a zone without nanoparticles. Thin-film interference is indeed involved in the diffuse iridescence mechanism, but the latter possesses extra degrees of freedom, the nanoparticle resonances, which play a key role (Supplementary Note 3).

Two-color iridescence is not uncommon. For instance, the wing color of the celebrated Morpho butterfly, which is blue when the viewing angle is normal or slightly inclined, changes into violet rather suddenly when the angle becomes large enough, while maintaining the lighting direction perpendicular to the wing veins [34]. The uniqueness of the present phenomenon stems from the large hue difference, $\Delta h_{ab} \approx 150^\circ$ in the HSV/HSL encodings of RGB [33], between the two colors, green and violet, therein largely neglecting the blue and cyan parts of the spectrum. Yet, it is quite astonishing that the large difference is maintained almost irrespectively of the viewing and lighting directions, especially in view of the continuous color variation produced by film interferences as these directions vary. The distinct hues can produce a particularly beautiful visual effect for curved metasurfaces. Owing to the curvature, the normal to the metasurface is no longer fixed. Therefore, we expect to observe a non-uniform
appearance with a two-color patchwork of prevailing violet and green zones that alternate depending on the local normal of the metasurface. As predicted in [26], variations of the viewing direction will result in a dynamic change of the patchwork, in which the colored zones gently deform and glide on the curved surface (Supplementary Note 4).

The resonance modes of plasmonic nanoresonators on reflective substrates

At low and moderate densities, in-plane electromagnetic interactions between the nanocubes are supposedly weak. In this perspective commonly referred to as the independent scattering approximation in random-media theory [35], the light scattered off the metasurfaces can be approximately determined by multiplying the response of every individual nanocube by the density of nanocubes [26].

The analysis of the angular and spectral properties of nanoparticles on reflective substrates is traditionally assessed with many independent computations performed at a fixed frequency and by varying the frequency in the spectral range of interest. The approach, albeit accurate, hides the essence of the physical mechanisms at play, i.e. the nanoparticle resonances and their hybridization. Thus, hereafter, we develop a semi-analytical model that explicitly considers the quasinormal modes (QNMs) [36] of the individual nanocubes.

Figure 3a displays the complex frequencies $\tilde{\omega}$ ($\text{Im}(\tilde{\omega})$ is encoded with colors) of a silver nanocube as the spacer thickness is varied. The nanocube is assumed to have a 100 nm size as estimated by averaging particles imaged in several transmission electron microscopy (TEM) micrographs. As we first dedicate the analysis to the iridescence for normal incidence, only the QNMs with a symmetry plane ($Oxz$ or $Oyz$) are considered. The insets display a few QNM radiation diagrams computed at the real QNM resonant frequencies for normalized QNMs. The QNMs are computed and normalized with the freeware MAN (Modal Analysis of Nanoresonators) [37], see Methods.

Two types of resonances with contrasted behaviors are found. The first one presents eigenfrequencies that notably vary across the visible spectral range as $h$ varies. In contrast, and perhaps surprisingly, we also find a second type in the blue part of the spectrum with eigenfrequencies that are nearly independent of $h$. As explained below, the second type of resonance has a frequency fixed by the particle size and shape, while the other corresponds to a ‘plasmonic dimer’ [29,30,31] formed by the nanocube and its mirror-image in the silicon substrate.

To trace back the origin of the two types of modes, we first consider the QNMs of a silver nanocube laying directly on a SiO$_2$ semi-infinite substrate (we refer to this geometry without silicon as $h = \infty$ hereafter). We find two QNMs, either with dominant dipolar or quadrupolar characters. Their near fields are shown in the maps on the left sides of Fig. 3b and Fig. 3c. Comparisons with the actual QNM field distributions of the silver nanocube on the SiO$_2$/Si substrate are also shown in the same figure for three different values of $h$. Specifically, we find that the first- and second-type resonances result from electric-dipolar (ED) and electric-quadrupolar (EQ) modes.

It is well known that substrate-mediated hybridizations of dipolar and higher-order plasmons of nanoparticles laying on high-index substrates significantly change the resonant frequency and radiative decay of localized plasmons by forming bonding and antibonding states [14,18,29,30,31]. In this case, we may intuitively see the metasurface as a bilayer, in which a dense network of in-layer and inter-layer electromagnetic interactions takes place. When the separation distance between the nanoparticles and their mirror image becomes comparable to the wavelength, the hybridization does not rely on static (evanescent) fields, but rather on propagating waves (right inset in Fig. 1d). The hybridized modes...
then acquire a strong photonic character with a significant field in the silica layer, see Fig. 3c. They are Fabry-Perot modes [15,31,32] formed by the bouncing of light, back and forth between the silicon substrate and the resonant nanoparticle (or between the nanoparticle and its virtual mirror image in the bilayer picture). As a matter of fact, all the QNMs of Fig. 3a, which line up in a series of parallel branches as \( h \) varies, are Fabry-Perot resonances. The number of nodes inside the thin layer is constant within a branch and varies from branch to branch (Fig. 3c).

It remains to be understood why the frequencies of the second-type resonances do not significantly vary with \( h \), but rather oscillate around the frequency of the EQ mode, which is shown with the red vertical line in Fig. 3a. We hypothesize that it is due to the quadrupolar nature of the resonance. In Fig. 3d, we compare the scattering diagrams of the ED and EQ modes for \( h = \infty \). In clear contrast with the ED mode, the EQ mode radiates much less energy towards the SiO\(_2\) substrate (\( z < 0 \) half-plane). Additionally, it preferentially radiates light at \( \approx \pm 45^\circ \) from the normal in the silica layer, with a very weak radiation in the normal \( z \)-direction. Though the hybridization relies on the QNM field radiated at wavelength-scale (not far field) distances, we think that the difference in the radiation diagrams intuitively explains why the ED mode strongly hybridizes, while the quadrupolar mode is reluctant to form Fabry-Perot resonances with the substrate.

**Figure 3.** a, Eigenfrequencies of the dominant QNMs for a \((100\times100\times100 \text{ nm}^3)\) Ag nanocube on a Si substrate coated with a silica film of thickness \( h \). The color of the dot represents the quality factor \( Q \). The scattering diagrams of several normalized QNMs are also displayed in the insets. The solid vertical lines correspond to the eigenfrequencies of the dipolar (ED) (black) and quadrupolar (EQ) (red) modes of the same nanocube on a SiO\(_2\) substrate (\( h = \infty \)). b-c, Near-field distributions of the quadrupolar (b) and dipolar (c) modes for three values of \( h \) labeled as i, ii and iii in a. The maps show the real part of the QNM electric field \( x \)-component, \( \tilde{E}_x \), in the \( xz \)-plane. The fields are computed and normalized with the freeware MAN [37]. d, Scattering diagrams of the normalized dipolar and quadrupolar QNMs for \( h = \infty \).

The six insets in Fig. 3a show the far-field radiation diagrams of a few normalized QNMs, see Methods. The diagrams feature various dominant lobes that drive the change of the metasurface color as the
viewing angle $\theta$ varies. Irrespective of whether the QNM is hybridized or localized on the nanocube, the dominant scattering directions of the diagrams change significantly as $h$ varies, even for QNMs belonging to the same Fabry-Perot branch. The precise mechanisms that lead to the formation of the lobes are comprehensively analyzed in the Supplementary Note 3. The latter shows that the dominant scattering directions can be analytically predicted with simple thin-film interference arguments. For the localized EQ resonance, the interference occurs between the light scattered off the Ag nanocube, either directly in air or after reflection on the substrate (Fig. S3.1). In contrast, for the hybridized FP resonance, the dominant scattering directions are determined by constructive interference between the light scattered by the nanocube and its virtual mirror image (Fig. S3.3).

**BRDF measurements**

To better assess the origin of the diffuse iridescence phenomenon, we consider the metasurface BRDF, $f_r$, a high-dimensional radiometric function useful in the assessment of material visual appearance. Essentially, the BRDF relates the radiance $L_r$ of a surface in a particular direction ($\theta, \phi$) to the irradiance $E_i$ impinging on it with polar and azimuthal incident angles ($\theta_i, \phi_i$) at a certain wavelength $\lambda$, i.e., $f_r = L_r(\theta, \phi, \lambda)/E_i(\theta_i, \phi_i, \lambda)$ [38].

For the BRDF measurements, we illuminate the samples with a supercontinuum laser beam and record the spectrally- and angularly-resolved response with a gonio-scatterometer (see Methods). The BRDFs are then normalized by the nanocube density, $\rho \approx 2 \mu m^{-2}$. Figures 4a-c show the BRDF intensity maps for three angles of incidence. The horizontal black strips correspond to detection angles for which the incident light is blocked by the detector support. The maps carry several noticeable features. First, they are quasi-symmetric with respect to the surface normal, rather than to the specular direction (black strips) as would be the case for the iridescence of a rough thin film, for instance. This is likely due to the deep subwavelength size of the nanocubes that act as Lambertian diffusers. Second, the maps show distinctive peaks that vary in form and number as the incidence or viewing angles vary. Note that, voluntarily, we do not associate the peaks with resonances since this association is unjustified in the present case, as will be clarified in the next section.

For the normal incidence case (Fig. 4a), the BRDF map is composed of an intense peak, at 550 nm for $\theta = 0$, a blue-violet peak at $\lambda \approx 430$ nm, and a series of less intense peaks at large viewing angles, $|\theta| > 50^\circ$. The intense peak is responsible for the green hue observed at small viewing and illumination angles in the rightmost hand fan of Fig. 2b. As the illumination angle increases (see Fig. 4b-c), the main trends are a blue shift of all the peaks and a splitting of the intense and initially green peak into two smaller peaks, symmetrically centered around $\theta = 0^\circ$. These trends are particularly visible in the Supplementary Fig. S5.1a that displays a progressive series of additional BRDF maps measured for other angles of incidence. The trends are comprehensively explained in the Supplementary Note 5 with the help of the semi-analytical model developed in the next Section. The model unveils the available dials, permitting variation of the hue and controlling the dominant lobes of the scattered light. In brief, the model attributes the blue shift to classical interferences in the SiO$_2$ film, which modulate the intensity of the driving field incident onto the nanocube and shift its maxima. It also attributes the splitting to a peculiar property imposed by the hybridized modes. In fact, the modes are effectively excited whenever the direction $\theta_i$ of the incident plane wave coincides with their preferential and natural scattering direction $\theta$ which corresponds to the lobe maxima in the radiation diagrams of Fig. 3a, for example. This explains why the split angularly increases as $\theta_i$ increases and why split peaks coincide with the horizontal black strips for which $\pm \theta \approx \theta_i$. 

Figure 4. Measured BRDFs of the two-color metasurface as a function of the wavelength and viewing polar angle $\theta$ for several incidences: a, $\theta_i = 0^\circ$; b, $\theta_i = 30^\circ$; c, $\theta_i = 50^\circ$. The measurements are performed $10^\circ$ above the plane of incidence. The BRDFs are normalized by the nanocube density, $\rho = 2 \ \mu m^{-2}$. d, The chromaticity diagrams show the loci of the colors achieved at three angles of incidence as the viewing angle varies from 0 (light gray) to 70$^\circ$ (dark gray). The chromaticity coordinates are extracted from the calibrated real photographs of the metasurface illuminated by the solar simulator (Fig. 2b).

The BRDF maps are rather complex. To confirm and quantitatively assess their dominant green and violet hues, we calculate their chromaticity coordinates, $x$ and $y$. These coordinates are widely used to link reflection or transmission spectra with the physiologically perceived colors in human vision. In the chromaticity diagram, the reference white is located at $x = y = 1/3$. The direction and distance from that point express the chroma and saturation of the color, respectively [39]. The curves in the insets of Fig. 4d represent the color trajectories of the metasurfaces as the viewing angle varies from 0$^\circ$ to 70$^\circ$ with a 10$^\circ$ step, each angle $\theta$ being marked with a point. The trajectories do not make a loop through the blue zone, but rather straightly cross the white zone, therein convincingly supporting the two-color nature with a transitory blue hue.

The physical mechanisms at play in the diffuse iridescence

We have now a clear overview of the resonances at play for all thicknesses and the evolution of the multipeak BRDFs with the incidence angle. The question arises, how does every individual QNM contribute and, in the present context, how is it possible that several resonances (they are four for $h = 640 \ \text{nm}$) result in only two dominant colors. To answer these questions, we provide a step-by-step reconstruction of the BRDF, considering the contribution of every QNM one by one. Figure 5 summarizes the relevant information.

We first consider the differential scattering cross-section of a single 100-nm Ag nanocube for $h = 640 \ \text{nm}$, see the upper map of Fig. 5a obtained with full-wave computation performed with COMSOL. The BRDF experimental data of Fig. 4a are shown again in the lower map of Fig. 5a, for comparison.
Note that, due to the $\theta \rightarrow -\theta$ symmetry at normal incidence, only the measurements for $\theta = 0^\circ \rightarrow 70^\circ$ are shown. The agreement is more than qualitative, especially if one considers that the single nanocube computation completely neglects the nanocube polydispersity and the electromagnetic interaction between nanocubes.

Encouraged by the agreement, we further study how the most relevant QNMs contribute to the scattering cross-section map. Figure 5b displays a series of reconstructions of the cross-section maps obtained by progressively increasing the number of QNMs retained in the expansion of the scattered field [36,37]. Additionally, for the sake of clarity, the QNM eigenfrequencies are highlighted with dashed-white vertical lines and black arrows. Only the EQ QNM is considered for the upper map; we indeed obtain an intense violet peak at $2\pi c / \text{Re}(\tilde{\omega}_{\text{EQ}}) = 433 \text{ nm}$. Adding the Fabry-Perot mode $\text{FP}_1 \ (2\pi c / \text{Re}(\tilde{\omega}_1) = 455 \text{ nm})$ in the next maps lowers the prominence of the violet peak and brings a second weak peak at a much longer wavelength $\approx 560 \text{ nm}$. As we introduce the two last QNMs, labelled $\text{FP}_2 \ (2\pi c / \text{Re}(\tilde{\omega}_2) = 490 \text{ nm}, \text{ baby blue})$ and $\text{FP}_3 \ (2\pi c / \text{Re}(\tilde{\omega}_3) = 560 \text{ nm}, \text{ green-yellow})$ in the two lower maps, we end up with a reconstruction that is quite similar to the numerical data of Fig. 5a.

Conventionally, one expects a one-to-one correspondence between resonance frequencies and the peak frequencies. The evolution of the cross-section maps clearly contradicts this well-established intuition, as exemplified by the long-wavelength peak brought by $\text{FP}_1$ in the reconstruction, or, even more strikingly, by the absence of any peak at the $\text{FP}_2$ resonance frequency.

**Figure 5.** Backscattering cross-section spectra as a function of viewing angle $\theta$ for a single nanocube and $h = 640 \text{ nm}$. a, Full-wave numerical results obtained with COMSOL (no free parameter in the model) are compared with BRDF measurements normalized by the nanocube density. b, Reconstructed scattering cross-section using 1,2,3 and 4 QNMs. The eigenfrequencies of the EQ, $\text{FP}_1$, $\text{FP}_2$, and $\text{FP}_3$ modes are indicated with black arrows and dashed-white lines. c, Plots of a Lorentzian function $L_2(\omega)$ (blue) centered at the resonance frequency $\tilde{\omega}_2$ of the $\text{FP}_2$ mode, the volume overlap integral $I_2(\omega)$ (orange) between the driving and the QNM $\text{FP}_2$ fields and the absolute value of the modal excitation coefficient $\alpha_2 = L_2 I_2$ (green). The maxima of $L_2$ and $I_2$ are indicated by blue and orange dotted lines. The reconstruction is performed using the reconstruction toolbox of the freeware MAN [37].
This can be understood by considering the QNM expansion of the field $E_{3}(r, \omega)$ scattered by a resonator upon excitation by a driving field $E_b(\omega), E_{3}(r, \omega) = \sum_m \alpha_m(\omega) \tilde{E}_m(r)$ [36], and further focusing on the QNM excitation strength $\alpha_m$. The latter is maximal when the driving and QNM fields well match spatially and spectrally: $\alpha_m(\omega) = (\varepsilon_{Ag} - 1)I_m(\omega)L_m(\omega)$ [36], with $L_m(\omega) = \frac{\omega}{\omega_m - \omega}$ a Lorentzian function and $I_m(\omega) = \iint_{V_c} E_b(r, \omega) \cdot \tilde{E}_m d^2r$ an overlap between $E_b(r, \omega)$ and the normalized QNM electric field $\tilde{E}_m(r)$, which is performed over the volume $V_c$ of the nanocube. Note that, insignificantly for the present purpose, a more accurate formula has been used to compute the $\alpha_m$’s and reconstruct the field in Fig. 5b (see Methods).

Figure 5c illustrates the interplay of $L_m(\omega)$ and $I_m(\omega)$ in the formation of the scattering cross-section peaks for the striking example of the FP$_2$ resonance. For nanoresonators on highly reflective substrates, the driving field intensity is an almost stationary pattern with alternating intensity maxima or minima as the silica thickness or the driving frequency $\omega$ are varied. The sinusoidal pattern distorts the Lorentzian response $L_m(\omega)$. When the maxima of $L_m$ and $I_m$ coincide, the product $L_m(\omega)I_m(\omega)$ results in a reinforcement of the resonance peak. However, it might also happen that the maximum of $L_m(\omega)$ coincides with a minimum of $I_m(\omega)$. Then, the excitation strength exhibits a camel-like response, in which the resonance peak splits in two side peaks (Fig. 5c).

Resilience to fabrication defects

Metasurfaces generally face substantial challenges towards large-scale production for the consumer market. They are often not robust to fabrication imperfections and require expensive, slow, and size-limited fabrication techniques [40-42]. For instance, for color generation with Mie or plasmonic resonances, small size or shape variations of the constituent nanoparticles lead to significant color changes [2,43]. Despite significant size or shape dispersions and occasional particle aggregation, see the statistical analysis of the top inset in Fig. 6, quantitative and qualitative agreement (Figs. 5a and S4.1) is achieved between the measurements and our theoretical predictions based on a monodisperse approximation. This suggests that the present samples are exceptionally resilient to fabrication imperfections.

To intuitively understand the reason for the resilience, we again use QNM theory and study the variations of the BRDF peak frequencies induced by changes of the nanocube size. Both terms, $L_m(\omega)$ and $I_m(\omega)$, have to be considered according to the previous Section. The second term brings great stability: its minima or maxima are independent of the nanoparticle size, shape, or even aggregation. It solely depends on the low-index film thickness that is well controlled. The first term, $L_m(\omega) = \frac{\omega}{\omega_m - \omega}$, is universally encountered in all resonant systems and is a priori not expected to offer a distinctive resilience for the present metasurfaces in comparison to others. In fact, hybridization makes the variations of $\omega_m$ less sensitive to imperfections. To see this, we consider the dominant ED mode and compare two geometries. Figure 6a is obtained for a reference case (no hybridization), in which the nanocube directly sits on a semi-infinite SiO$_2$ substrate. Consistent with earlier works on plasmonic color generation [2,4], both the real and imaginary parts of the ED eigenfrequency $\lambda_{ED}$ largely vary. Notably, $\text{Re}(\lambda_{ED})$ spans over almost the entire visible spectral domain, $\text{Re}(\Delta\lambda_{ED}) \approx 200$ nm. Comparatively, much smaller variations are obtained for each Fabry-Perot mode, FP$_1$, FP$_2$ or FP$_3$ of the hybridized case ($h = 640$ nm), the maximal variation, $\text{Re}(\Delta\lambda_3) = 60$ nm, being obtained for FP$_3$ (Fig. 6b).
Figure 6. Resilience of the hybridized QNMs to size dispersion. Top inset, Size and shape distributions of the nanocubes. On the left side, the fitted normal distribution yields an average nanocube edge length of $90 \pm 8$ nm. The table on the right side shows the distribution of the different shapes of particles in the solution. a, Trajectory of the computed complex eigenfrequencies for the reference non-hybridized case, $h = \infty$ as the AgNC size $(s \times a, a = 100$ nm) is varied. b, Same computation for the three FP modes for $h = 640$ nm. In a-b, the color of the star marks represents the size factor $s$.

The role of hybridization in the resilience of the complex frequency against size dispersion can be understood with general arguments based on non-Hermitian cavity perturbation theory. The latter stipulates that the size-dependent eigenfrequency change $\Delta \tilde{\omega}$ is proportional to the square of the normalized QNM electric field $\tilde{\mathbf{E}}(\mathbf{r})$ inside the perturbation volume $\Delta V$, $\Delta \tilde{\omega} \propto \iiint_{\Delta V} \tilde{\mathbf{E}}(\mathbf{r}) \cdot \tilde{\mathbf{E}}(\mathbf{r}) \, d\mathbf{r}$ [44]. For non-hybridized plasmonic nanoparticles, $\tilde{\mathbf{E}}(\mathbf{r})$ is intensely localized on the particle (Fig. 3b) and $|\Delta \tilde{\omega}|$ is large, as we all experience with plasmonic sensors. In contrast, FP modes bear both a plasmonic and a photonic character with a normalized field that is distributed not only in the vicinity of the Ag nanocube but also inside the SiO$_2$ layer (Fig. 3c). This is a general property of hybridized plasmons, which inevitably results in a significant increase of the mode volume and a lowering of the sensitivity to imperfections.

Conclusion

We have characterized the diffuse iridescence of disordered monolayers of resonant nanoparticles laying on a reflective substrate coated with a low-index spacer. Owing to the excitation of nanoscale resonances, the angular color response of the metasurfaces differs from those encountered in nature with low-index nanostructured materials. In particular, we have identified a specific geometry that displays a remarkable angular color-dependence, in which only two distinct colors are observed for all directions.

The metasurfaces considered in the present study constitute a generic structure of nanophotonics with various intrinsic advantages and applications [30-33]. The large set of available degrees of freedom...
allows for tuning the metasurface properties at various scales. Conveniently, our fabrication approach based on bottom-up self-assembly techniques is relatively simple and can be easily adapted to large-scale surface coatings at low manufacturing costs.

An important fundamental outcome of the work is the clarification of the origin of the optical resonances and their impact on the color and direction of the scattered light. Notably, we have shown that the metasurfaces possess both hybridized Fabry-Perot-like and non-hybridized resonances. Furthermore, the resonances do not necessarily result in a BRDF peak at the resonance frequency, implying that several resonances with distinct frequencies may be combined to produce the same color. We expect this understanding to inspire and motivate further metasurface designs with prescribed angular color responses so far difficult to predict.

The study also shows and explains the considerable resilience of the diffuse iridescent effect to fabrication defects. Fabrication flexibility is essential for real applications, as it may result in a strong reduction of manufacturing costs. This reinforces our expectation that the present metasurfaces can find genuine applications for security holograms or various stunning coatings for luxury goods.

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Competing interests
The authors declare the following competing interests: Patent deposited on the control of visual appearance with disordered metasurfaces [Applicants: Université de Bordeaux, Centre National de la Recherche Scientifique (CNRS), Institut d’Optique Théorique et Appliquée, and Université Paris-Saclay; Inventors: K.V., R.P., X.G. and P.L.; filing date: February 1st, 2021; Application number: FR 2100948.]

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nm in edge length, are synthesized via a seed mediated growth protocol [47]. In a second step, a
dielectric thin-film of controlled thickness is produced through a sol-gel reaction and deposited on
a silicon wafer using dip-coating technique. A \( h = 100 \pm 10 \) nm SiO\(_2\) layer is reproducibly deposited.
By repeating this process, a series of SiO\(_2\)/Si substrates is fabricated in the range of \( h \approx 105 - 710 \) nm.
Finally, the silver nanocubes are deposited by dip-coating. The nanocube density is controlled by

Methods

Fabrication. Samples are fabricated using a multi-step bottom-up approach that involves colloidal
synthesis, metal oxide thin film formation and nanoparticles deposition. First, silver nanocubes, 100
nm in edge length, are synthesized via a seed mediated growth protocol [44, 46]. In a second step, a
dielectric thin-film of controlled thickness is produced through a sol-gel reaction and deposited on
a silicon wafer using dip-coating technique. A \( h = 100 \pm 10 \) nm SiO\(_2\) layer is reproducibly deposited.
By repeating this process, a series of SiO\(_2\)/Si substrates is fabricated in the range of \( h \approx 105 - 710 \) nm.
Finally, the silver nanocubes are deposited by dip-coating. The nanocube density is controlled by
changing the concentration of the cubes in suspension, changing the dispersive medium, or by increasing the number of deposition cycles by dip-coating.

**Characterization.** All the measurements are performed with an in-house goniospectrophotometric setup, which uses a supercontinuum source or a solar simulator for the illumination and a cell-phone camera or a spectrometer for the detection. Two concentric stepper motor rotation stages (Newport, URS75 and URS150) and a vertical arm control the incidence and scattering (viewing) angles, $\theta_i$ and $(\theta, \phi)$, respectively.

More specifically, for the BRDF measurements, we use an unpolarized centimeter-scale expanded supercontinuum laser beam (Leukos, Rock 400). A short-pass filter (Schott, KG-1) restricts the incident spectrum to the visible range. The backscattered light is collected slightly above the plane of incidence by a 1 mm-diameter optical fiber connected to a spectrometer (Ocean Insight, HDX). The incident laser radiant flux is measured with the same setup and with the fiber detector facing the focused laser beam. In the Supplementary Note 6, the accuracy of the BRDF measurements is assessed with a diffuse reflectance reference sample with a known BRDF.

For the characterization of the color variation with the viewing angle in Fig. 2a, the metasurfaces are illuminated with a directional white light illumination provided by a collimated solar simulator (ASAHI SPECTRA, HAL-320) and the metasurface appearance is recorded with a smartphone camera (iPhone 11, 12 MP Wide camera, $f/1.8$ aperture) at fixed exposure times for each series. Images are captured with the default white balance and encoded in the sRGB color space which meet the color accuracy requirements of the present work and ensure standard color reproduction across different displays.

**QNM computation.** The QNM analysis takes benefit from significant progress made during the last decade [36]. To compute the resonances of the Ag nanocubes, we use the QNMEig solver [49] of the freeware MAN (Modal Analysis of Nanoresonators) [37]. The computation precisely considers the spectral dispersion of silver with a bi-pole Drude model and silicon with four pairs of Lorentz poles [50]. The refractive index of the silica layer is assumed to be equal to 1.47. The COMSOL model can be downloaded from the MANMODELS folder.

The radiation diagrams of Fig. 3 are computed in air at the real QNM resonant frequencies, $\text{Re}(\tilde{\omega})$, with the near-to-far-field transform freeware RETOP [51]. They are obtained from the near-field maps of the normalized QNMs [37], which allows for a direct comparison of the resonance radiative strengths.

The QNM reconstruction of the BRDF (Fig. 5) is obtained with the reconstruction toolbox of MAN [37] by using the expressions of the excitation coefficient that are provided in Eq. 6 in [49].