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Flexible, Angle-Independent, Structural Color Reflectors Inspired by Morpho Butterfly Wings

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Multilayer interference underlies many startling colors in nature. Of the many examples of such structural colors,[1,2] perhaps one of the most well-known example is the genus *Morpho* butterflies[3–6] from Central and South America, whose colors range from the pale, gossamer blue of *Morpho godarti* to the deep, liquid-like blue of *Morpho rhetenor,* and have such a high reflectance that they are reportedly visible over kilometers and even from low-flying aircraft.[7,8] Furthermore, *Morpho* butterflies are rather unique in that their color appears to remain bluish over a wide range of viewing angles, contrary to what is often observed from other natural examples of structural colors such as soap bubbles, beetles,[9,10] and birds' feathers[11,12] that show rainbow-like, shimmering iridescence.

These qualities have attracted a great amount of research, as understanding and ultimately recreating such brilliant, angle-independent structural colors would not only be of great scientific interest, but also could have a great impact in a wide range of applications such as reflective displays, packaging, and advertising. By now, there is a general consensus that the overall color of *Morpho* butterflies, on the most basic level, arises from interference within the periodic, multilayered ridges on the scales that cover the surface of their wings.[13–17] These ridges all have similar shapes, and are placed on the scales with enough order such that a high packing density can be obtained, leading to the high reflectivity.[16,17] At the same time, the exact spatial locations of the ridges, both horizontal (along the surface of the scale) and vertical (perpendicular to the surface) are disordered on the subwavelength scale such that each ridge contributes individually to interference instead of forming a continuous multilayer. This, together with the narrow width of the ridges, random variations in the exact shape of each ridge, and pigment in the scales, causes the *Morpho* butterfly wings to exhibit not only interference,[18,19] but also diffraction,[20] scattering, and even pigment-induced absorption,[13] which all work together to produce the paradox of brilliant, yet angle-independent iridescence of *Morpho* butterflies.

Unfortunately, reproducing such a complex structure that can exhibit all the necessary properties in a man-made structure has so far been challenging, partly due to many orthogonal requirements. For instance, the reflecting elements must be subwavelength sized, yet need to be produced on a large scale; they must be sufficiently ordered to produce the desired color and reflectivity, yet be disordered enough on the subwavelength scale, in both shape and location, to remove the directionality and sharp reflectance peaks associated with multilayered interference. Thus, previous attempts used simplified structures that contained only a binary disorder in height instead of a continuous disorder[21,22] that demonstrated these basic principles. Better structures have been reported but, as they used butterfly wings themselves as templates for atomic layer deposition[23] or created templates using ion-beam chemical deposition,[24] they cannot be used for any practical, large-scale applications. In most cases, the samples fabricated were small, and while qualitative comparisons of the reflectivity with actual *Morpho* butterflies have been reported,[25] quantitative comparisons of absolute reflectance values have not yet been reported. Furthermore, the samples were fabricated on a rigid substrate, which severely limits the scope of possible applications.

Yet the *Morpho* butterflies manage to create such complex structures spontaneously through self-assembly, without any directed construction.[17,26] Inspired by this fact, we have developed a process using the combination of a silica microsphere base layer and directional deposition of a dielectric multilayer to produce such a structure. We find that the fabricated thin film not only reproduces the bright, saturated color of *Morpho* butterflies, but also provides better color and brightness stability over wider viewing angles and directions. Expanding on this structure, we move beyond the limitations of actual butterfly

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wings by creating a flexible thin-film color reflector that, unlike real *Morpho* wings, can be bent and folded freely and yet retains its *Morpho*-mimetic photonic properties.

We start with spin-coating a random mixture of silica microspheres with diameters ranging from ≈200 to 400 nm on a Si wafer to form a loosely packed monolayer. A 300 nm thin film of Cr is then sputter-deposited to provide a uniform, dark background in order to reduce the back-reflection of transmitted light, for higher color purity.[27] In the case of actual *Morpho* butterflies, melanin-containing scales and base layers have been reported to play a comparable role.[13,28,29] Subsequently, 8 pairs of TiO_2 and SiO_2 layers were sputter-deposited. The deposition pressure was intentionally kept low at 0.3 mT such that the molecular mean free path was longer than the sputter-target to substrate distance of 12 cm, leading to directional growth and suppression of conformal step coverage and associated reduction of surface roughness during the deposition process. Finally, the entire sample was spin-coated with polydimethylsiloxane (PDMS). During the deposition, the sample was not heated intentionally, but becomes hot during the deposition process (see Supporting Information (SI), Figure S1 for details).

The detailed structure of the deposited thin film is compared with that of an actual *Morpho didius* butterfly in **Figure 1**. Figure 1a shows a cross-section scanning electron microscope (SEM) image of the densely packed, multilayered ridges on the scales of *Morpho didius* that generate its color. While similar in shape, the ridges also show the disorder necessary to create the angle-independent iridescence: the nonplanar shape of the lamellae that form the multilayer;[21–22] variations in detailed shape among the ridges, and;[20] the random variation in the vertical offset of the ridges that disrupts the intrascale planarity of reflecting multilayers, as shown in more detail in Figure 1b.[18,19,30,31] On a slightly larger scale, Figure 1c shows that the ridges run parallel along the length of the scale, thus giving rise to the anisotropic color stability[28] and polarization dependence.[13] Finally, as Figure 1d shows, the overall wing surface is quite rough on the macroscopic scale due to its scaly construction and the curved shape of each scale.[12,32] Consequently, the wing shows many localized glints rather than a uniform, specular reflection, which further contributes to the angle-independent iridescence and glitter. Figure 1e–h show the corresponding SEM images of a fabricated thin film prior to PDMS spin-coating. The multilayered structure necessary for color generation is shown in Figure 1e. Yet as Figure 1f,g show in more detail, the shape and the size of the underlying microspheres are preserved due to the directional, nonconformal nature of deposition. Consequently, the film consists of close-packed columns that have the same periodicity of SiO_2 and TiO_2 layers, but different width and curvature. Furthermore, the variation in the diameter of the underlying microspheres is directly translated into a variation in the spatial location of each column such that the vertical offset of the multilayer reflecting columns varies randomly and continuously across the film, even between two neighboring columns, and the columns form a Voronoi diagram of random points when seen from the top. Finally, as Figure 1h shows, the film is not specular; it is quite rough on the macroscopic scale, with ridges that are similar in size to scales of *Morpho* butterflies seen in Figure 1d. We note that no extra steps were taken to create such ridges. During the deposition, the film remains macroscopically flat. However, since the entire film is deposited on a base layer of silica microspheres that are bound only loosely to the Si substrate, the film buckles and partially delaminates from the substrate during the post-deposition cooling step, forming the observed ridges. No such ridges form if the silica microspheres are fixed to the Si substrate by high-temperature annealing prior to the multilayer deposition (data not shown).

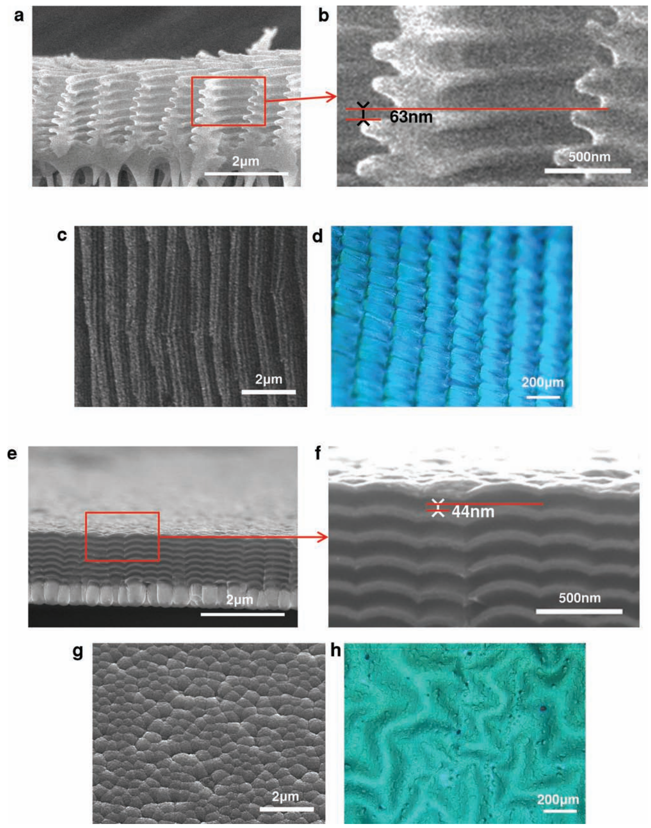

Figure 1. Structural comparison between butterflies and fabricated films. a) Cross-sectional SEM image of the multilayered ridges on the dorsal ground scale of a *Morpho Didius* butterfly. The red rectangle indicates the region shown in more detail in (b). b) A close-up view of the ridges, showing a vertical off-set of 63 nm between two neighboring ridges. c) Top-view of the dorsal ground scale at a lower magnification. The ridges are parallel, and run the length of the scale. d) Optical microscope image of the wing of a *Morpho didius* butterfly, displaying many localized glints rather than a uniformly specular reflection. e) Cross-sectional SEM image of the deposited multilayer thin film. The bright layers are the SiO_2 layers, and the dark layers are TiO_2 layers. Note the Cr-covered monolayer of silica microspheres at the bottom of the multilayer structure. The red rectangle indicates the region shown in more detail in (f). f) A close-up view of the multilayer, showing a vertical off-set of 44 nm between two neighboring columns. Note that such vertical offset and curvature of the layers are maintained throughout the deposition process. g) Top-view image of the multilayer thin film. Each 'tile' corresponds to a multilayer column with a silica microsphere underneath. h) Optical microscope image of the thin film. The entire film buckles and partially delaminates from the Si substrate during the post-deposition cooling process, creating the raised ridges and bumps (scale bars: a,e) 2 μm; b,f) 500 nm; c,g) 2 μm; d,h) 200 μm).

In short, while the film does not reproduce the exact shape of *Morpho* butterfly wings, it reproduces both the ordered periodicity

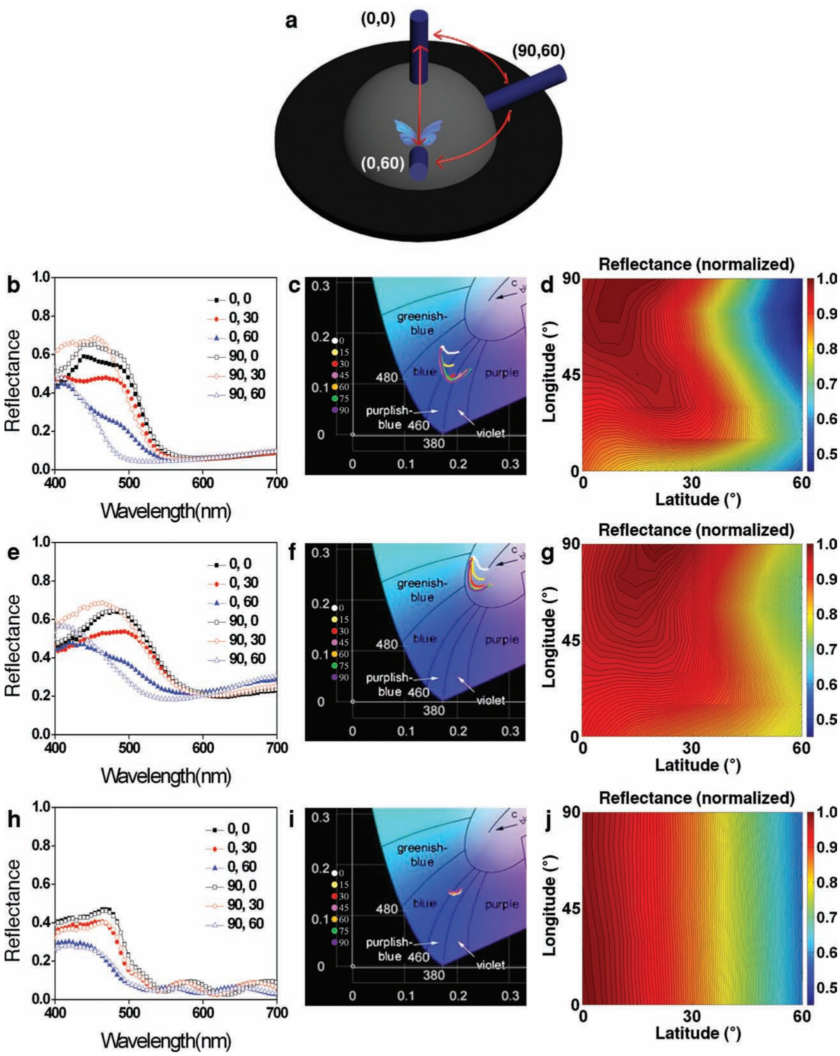

Figure 2. Analysis of optical performance. a) A schematic description of the reflectance measurement system and the nomenclature used in the paper regarding the detection angles. 0 degrees longitude is defined to be along the length of the butterfly, and 90 degrees longitude is defined to be across the wing of the butterfly, perpendicular to its body. b) Selected reflectance spectra of *Morpho rhetenor* butterfly, and c) the corresponding changes in its apparent color. Different colors indicate scans at different longitudes. d) The angle-dependence of overall brightness, determined by integrating the reflectance in the visible range (400–700 nm). The values are normalized to the maximum obtained value. e–g) The corresponding data for *Morpho didius*. h–j) Corresponding data for the thin film. The color is extremely stable, appearing dark blue at all viewing angles. Note that both the color and integrated reflectance are completely independent of longitude: there are 7 lines superimposed upon each other in (i).

necessary for color generation and the structural disorder, from the nanoscale within a single multilayered element to the macroscopic across the entire wing, that have been reported to be necessary for angle-independent iridescence. Indeed, it is this disorder, not the exact shape of the reflecting elements, that is critical for reproducing the angle-independent iridescence (see SI, Figure S2). In fact, such disorder has been reported to play an important role in other biological, or bioinspired photonic nanostructures as well.[33,34] More importantly, they all arise spontaneously during the single, simple deposition step without any complicated lithography or other sample-preparation steps.

The absolute reflectance spectrum of fabricated thin film was compared to that of *Morpho didius* and *Morpho rhetenor* butterflies by measuring their reflectivity with a DMS 505 of Autronic using a uniformly diffuse, hemispherical white light source. **Figure 2**a shows the schematic of the measurement setup. Figure 2b, c, and d show the reflectance spectra, the CIE map showing the change of color with viewing angle, and the normalized brightness obtained by integrating the reflectance in the visible range, respectively, of a *Morpho rhetenor* butterfly. We find that in case of *Morpho rhetenor*, the shape of the reflectance spectra actually changes significantly as the viewing angle is changed from normal to oblique. Consequently, the color, even though it remains bluish, shows substantial movement across the CIE map. The overall brightness, too, varies nonmonotonically with the viewing angle, and is reduced by nearly 60% at oblique viewing angles. *Morpho didius,* too, shows significant changes in color and brightness with changing viewing angle, as shown in Figure 2e–g. Its overall brightness is more stable than that of *Morpho rhetenor* due to a nearly uniform background reflection across the entire visible wavelength range. Unfortunately, for the same reason, its color purity is low, and can look nearly whitish at certain angles.

Corresponding results for the thin film are shown in Figure 2h–j. When viewed normally, the film displays a saturated blue comparable to that of *Morpho rhetenor* with a peak reflectance of 55%. More importantly, the change in both its color and brightness are much smaller than that of the *Morpho* butterflies across all viewing angles: its color remains deep blue at all viewing angles, and its overall brightness changes by about 40% only. Furthermore, neither its color nor its brightness changes as the film is rotated about its normal axis, consistent with its corresponding structural isotropy seen in Figure 1g. This contrasts with *Morpho* butterflies that display different colors and brightnesses depending on viewing directions (i.e, the longitudinal viewing angle, either from behind or from the side), and suggests that such longitudinal anisotropy may not be necessary to obtain high reflectance, as has been suggested before.[21]

It is worth noting that, despite the complex overall structure, the entire film including the base layer of silica microspheres is less than 2 μm thick and is only loosely attached to the substrate, with empty voids underneath the raised ridges (see SI, Figure S3). These voids are easily impregnated with liquid PDMS during the final spin-coating step. As a result, the film becomes encased in a transparent, solidified PDMS thin film that can simply be

Figure 3. Images of fabricated films. a) Comparison of the fabricated reflector (PDMS-encased thin film) with *Morpho rhetenor* (above) and *Morpho didius* (below). The size of the reflector is 6 inches in diameter. b) Various colors ranging from deep blue through green to coppery red realized by controlling the layer thicknesses. c) Image of the deep blue reflector shown in Figure 3b wrapped around a rod with a diameter of 1 cm. Note that the color appears the same throughout, even though the reflector is bent, and thus presents a viewing angle that varies from 0 to 90°.

pulled off the Si substrate. As shown in **Figure 3** and accompanying video (see SI), the result is a thin, flexible reflector that can be applied to the surface of a nonplanar object or even be folded repeatedly in half, yet retains the bright color and angle-independent iridescence of the encased multilayer thin film. Multiple colors ranging from *Morpho*-blue to coppery red can be realized, and samples have been made as large as 6 inches in diameter, limited only by the size of our deposition system.

In conclusion, we have fabricated a *Morpho*-mimetic thin film by depositing a dielectric multilayer on top of a silica microsphere base layer with a random size distribution. Such a combination induces a spontaneous emergence of both order and disorder across many length scales without any lithography or complicated fabrication process. This enables us to fabricate, at a large scale, thin films that not only reproduce the bright, brilliant glossy colors comparable to *Morpho rhetenor* butterflies, but actually outperform both *Morpho rhetenor* and *Morpho didius* butterflies in maintaining their color and brightness over a wide range of viewing angles in ambient conditions. Furthermore, by impregnating the structure with a polymer and lifting off, a flexible thin-film color reflector that can be bent, folded, and applied to nonplanar surfaces without losing either its color or brightness is created.

Experimental Section

Silica Base Layer Fabrication: A mixture of silica microspheres with diameters ranging from ≈200 to 400 nm were synthesized by a seeded-growth method,[35] which was a modification of the conventional Stöber–Fink–Bohn method.[36] After growth, a monolayer of the microspheres was spin-coated on a 6-inch Si wafer by spin-casting a 10 wt% ethanolic silica suspension at 3000 rpm.

Multilayer Deposition: All layers were deposited in a single, multitarget sputter deposition system with a base pressure of $<10^{-7}$ Torr. A 300 nm thin layer of Cr was first sputtered onto the monolayer of silica microspheres using direct current magnetron sputtering. Subsequently, alternating layers of TiO_2 and SiO_2 were deposited using radio frequency magnetron sputtering using TiO_2 and SiO_2 targets, and Ar gas. The deposition pressure was 0.3 mT.

Optical Measurements: Reflectance measurements were performed using a DMS 505 made by Autronic. The equipment provides a hemisphere of diffuse, white light, and is a standard method of evaluating flat-panel displays as it closely resembles lighting condition of living space. A point-sensor detects how much light is reflected in visible ranges from specimen, and absolute reflectance is obtained by comparing the result with $BaSO_4$. The latitude of measurement angles ranges from 0° to 60° (a physical angle limitation of the detector), and the longitude of measurement angles ranges from 0° (along the length of the butterfly) to 90° (across the wings of the butterfly, perpendicular to its body). An automatic analytical system gives a reflection spectrum curve and chromaticity coordinates on a 1931 CIE chromaticity diagram per detection point.

Supporting Information

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

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