Bio-inspired micro-grating arrays: mimicking the reverse color diffraction elements evolved by the butterfly Pierella luna

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Recently, diffraction elements that reverse the color sequence normally observed in planar diffraction gratings have been found in the wing scales of the butterfly Pierella luna. Here, we describe the creation of an artificial photonic material mimicking this reverse color-order diffraction effect. The bio-inspired system consists of ordered arrays of vertically oriented micro-diffraction gratings. We present a detailed analysis and modeling of the coupling of diffraction resulting from individual structural components and demonstrate its strong dependence on the orientation of the individual miniature gratings. This photonic material could provide a basis for novel developments in bio-sensing, anti-counterfeiting and efficient light management in photovoltaic systems and light-emitting diodes.

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Three-dimensional photonic crystals (1-5), materials with two-dimensional micro- or nano-sized periodic morphologies (6-8) and one-dimensional multilayer configurations (9) have been identified as the primary cause of structural coloration in a wide variety of non-related biological organisms. In contrast, surface-confined diffraction elements for the separation of incident light into specific colors are less abundant in nature and have only been discovered in a handful of organisms (10), including a fossil poly-chaete (7), the sea mouse Aphrodita sp. (6) and some flowering plants (11). Recently, diffraction elements that reverse the color sequence normally observed in planar diffraction gratings have been found in the scales of the butterfly Pierella luna (12).

Inspired by this biological light manipulation strategy, we devised an artificial material morphology mimicking the butterfly's diffraction effect by creating periodic arrays of vertically oriented individual micro-diffraction gratings. In addition to the butterfly-inspired reverse color order diffraction arising from each individual micro-grating, the periodicity between the individual gratings causes diffraction on a different length scale, leading to complex intensity distributions in experimentally measured angularly resolved reflection spectra. An in-depth analysis of the observed diffraction phenomenon complemented by optical modeling revealed a strong dependence of the optical signature on the orientation of the gratings. Such an effect can only be seen because of the hierarchical nature of the superposed, orthogonal grating features. To further elucidate the role of the different structural components for the emerging reflection spectra, the initially vertically oriented individual micro-gratings were subjected to a tilt, resulting in a predictable change of the surface's optical signature.

The dorsal side of the fore and hind wings of P. luna males are dull brown in diffuse ambient illumination (Fig. 1A, left). When exposed to directional illumination at grazing incidence, a coin-sized spot on each forewing displays an angle-dependent color variation across the whole visible spectrum (Fig. 1A, right). The color changes from red to blue with increasing observation angle unlike the variation from blue to red normally observed in conventional diffraction gratings (13). This reverse color diffraction effect results from the local morphology of individual scales within the colored spot on the fore wings (12). The top parts of the scales are curved upwards, orienting lines of periodically arranged cross-ribs perpendicular to the wing surface and the wing surface normal. (Fig. 1C,D). Light incident at an angle onto the curled parts of the scales is diffracted by the cross-rib structure acting as a diffraction grating, with a periodicity of ~400nm. The alignment of the grating perpendicular to the surface results in the reverse color sequence that can be observed in angularly resolved reflection spectra and in the diffraction pattern (Fig. 1E,F).

The identification of this unusual diffraction effect on the wings of P. luna (12) provided inspiration for the development of a bio-inspired photonic system that incorporates vertically oriented micro-diffraction gratings with sub-micrometer periodicity analogous to the key features observed in the natural structure. In addition, the artificial system displays a periodic arrangement of the individual vertical gratings in large arrays with two-dimensional micro-scale periodicity. This structural feature, which is not found in the natural organism, enriches the optical signature of the artificial system via coupling of the diffractive modes of the two present hierarchical morphologies. In the following, we discuss the optical properties of the artificial system and demonstrate that the modification of either one of the grating morphologies changes the diffraction signature in predictable ways.

Significance

In the course of evolution, many organisms have developed unique light manipulation strategies that rely on intriguing combinations of a broad range of optical effects generated by materials with sophisticated multi-scale hierarchical structural arrangements. By exploiting the optical principles underlying natural structural color, we can generate new photonic materials. Researchers have only just begun to match nature's morphological and compositional complexity in man-made materials using nanofabrication. We present a bio-inspired photonic material that mimics the reverse color order diffraction found in the butterfly Pierella Luna. Exploiting and improving the butterfly's strategy, we create new photonic materials that increase our basic understanding of the optical interplay of hierarchical structures and provide a platform for the development of novel photonic devices.
The artificial system consists of an array of individual 10 μm long, 2 μm wide and 18 μm high plates arranged in rows with an inter-plate spacing of 10 μm and a separation of 5 μm between individual rows of plates (Fig. 2A). These parameters result in an overall periodicity of 12 μm in the direction perpendicular to the plates and 15 μm in the direction collinear with the plane of the plates and the sample surface. A periodic wave pattern—termed "scallops"—of ~500nm pitch runs along the sides of each individual plate (Fig. 2B).

The bio-inspired diffraction elements are fabricated in a double-molding procedure. Starting from a silicon master, a periodic array of scalloped micro-plates is first cast into polydimethylsiloxane to form a negative mold (14), which is then replicated with a UV-curable epoxy to produce a positive replica of the master silicon structure with the original scallops on the individual plates well preserved. The silicon master is formed using the Bosch process (15), in which multiple etching and passivation steps give rise to the periodic undulations on the micro-plate surface. The pitch and height of these grating structures can be controlled by adjusting the etching parameters (16, 17). Here, they are chosen to be comparable to the spacings and dimensions of the diffraction-inducing micro-ribs on the P. luna scales (Fig. 2B), and hence are expected to cause a similar diffraction effect.

It is important to notice that in the biological system, the periodicity of the diffraction grating-supporting scales is of the order of 80 ± 10 μm along their length and 60 ± 10 μm perpendicular to the scale axis (Fig. 1B). Due to these large distances between diffraction elements and a non-negligible amount of irregularity in the location of individual scales, no coherence is observed for light diffracted from adjacent scales. The overall color splitting only results from the diffraction caused by the cross-rib gratings on the individual scales, which is confirmed by variable angle spectroscopy and by diffraction microscopy measurements (Fig. 1D). Unlike in the biological system, the individual micro-diffraction gratings in the artificial system are intentionally arranged in a highly periodic manner, which is expected to result in a richer diffraction signature and provide additional possibilities of tailoring the interaction of light beyond the diffraction induced by the scallops on the plates.

Variable observation-angle spectroscopy performed on the artificial system serves to spectrally and angularly resolve parts of the complex diffraction pattern (Fig. 2C). For each measurement, the plane of light incidence is chosen to be perpendicular to the surface of the individual micro-plates. The light incidence angles θ1 and θ2 is fixed and the observation angle θD is varied in the plane of light incidence to capture light reflected in an angular range of ±75° around the sample surface normal. Two main features are observed in these measurements:

(1) Straight lines of higher intensity resulting from diffraction caused by the inter-plate periodicity represent the individual diffraction orders; the experimentally observed locations of these diffraction orders (shown in Fig. 2C,H) can be directly calculated using the grating equation (13). An example of such a calculation can be seen in Fig. 1. Due to the large inter-plate pitch of 12 μm the angular separation between adjacent diffraction orders and the free spectral range of each individual order are small. For light incident at an angle θ1 = 45°, eight positive propagating diffraction orders (left of the 0th order at sin(θD) = -0.71 in Fig. 2C) and 53 negative propagating orders are captured with the highest intensity in the direct reflection (0th order) and in the adjacent orders.

(2) There is an arc-shaped distribution of intensity maxima across different diffraction orders (emphasized by dashed red lines in Fig. 2C).

This anomalous redistribution of light in the diffraction orders is caused by the scallops on each individual plate. To properly describe the diffraction resulting from the micro-diffraction gratings oriented normally to the substrate, the grating equation (13) has to be reformulated taking into account their vertical orientation for diffraction in the plane of the scallops:

\[ I = \frac{I_0}{\pi} \left( \cos \theta_1 + \cos \theta_2 \right), \]

where \( I \) is the diffraction periodicity, \( m \) is the diffraction order, \( \theta_1 \) is the light incidence angle and \( \theta_2 \) is the diffraction angle. This equation describes the arc shape-like pattern observed in the experiment under the assumption that the plates are vertical (Fig. 2C red shaded region).

Imaging of the diffraction patterns by diffraction microscopy provides a direct visualization of the effects observed in the variable-angle spectroscopy measurements. The angle range that can be visualized in these measurements is determined by the numerical aperture of the microscope objective. For a given light incidence angle \( \theta_1 \) the diffraction caused by the periodic ensemble...
Fig. 2. Geometry and optical properties of the artificial photonic structure mimicking P. luna with vertically oriented (top row) and tilted (bottom row) diffraction gratings. A, SEM of the array of scalloped microplates. Scale bar 5 μm. B, SEM of an individual plate with regular scallops. Scale bar 2 μm. C, Variable angle spectroscopic data for 45° light incidence showing the arc-shaped diffraction pattern caused by the diffraction from the scallops coupled with the diffraction due to the plates. The measurement geometry is shown in the top right inset. The red overlay displays where the first diffraction order of the scallops based on the grating equation (eq. 2) is expected for tilt angles of -3° to 5°. The color bar under the graph shows the human-eye perceived color for the spectra observed at the corresponding angles calculated by the CIE 1931 standards (18). D, Diffraction pattern caused by the periodic ensemble of micro-plates for 45° light incidence. A choice of propagation angles is visualized by the white dashed lines. The diffraction orders within the blue frame correspond to the diffraction observed in the angular range marked in blue in (C). E, Diffraction pattern resulting from the scallops on individual plates. The diffraction orders within the yellow frame correspond to the diffraction observed in the angular range marked in yellow in (C). F-K, Same as (A-E), for tilted gratings. Red overlay in (H) marks the range where higher intensities are predicted by the grating equation for tilt angles between 19° and 27°.

Fig. 3. Modeling of the expected diffraction patterns originating from the ordered array of gratings with 45° illumination. A, Calculated diffraction pattern for upright plates with scallops. B, Calculated diffraction pattern for upright plates without scallops. C, Calculated diffraction pattern for 23° tilted plates with scallops. D, Calculated diffraction pattern for 23° tilted plates without scallops.

Fig. 4. Diffraction discretization. A, 1 micron wide unit cell for diffraction grating simulated via FDTD. B, Reflected spectra calculated from FDTD simulation of (A) showing bright spots in each diffracted order with discrete jumps in the diffracted wavelength.

on the sample through the microscope objective, allows for the capturing of the diffraction component induced by the scallops on the individual plates (Fig. 2E, with the signal in the yellow box corresponding to the yellow shaded spectral range in Fig. 2C). This feature is easily distinguished from the diffraction of the plate ensemble by the wider color spread.

Overall, the measurements provide clear evidence of coupling between the first order mode of the scalp diffraction and the
inter-plate periodicity based diffraction modes. The diffraction
coupling can be controlled by adjusting the pitch of the scallops
on individual plates and the inter-plate geometry in the manufac-
turing procedure. Likewise, a change in inclination of the micro-
diffraction gratings with respect to the substrate is expected to be
reflected in a variation of the diffraction patterns. This change
can indeed be observed by imposing a controlled tilt of approximately 20° on
the micro-plates by shearing the sample (Fig. 2FG).

The bending leaves the locations of the diffraction modes
resulting from the inter-plate periodicity largely unaffected. Only
minor wavelength-dependent intensity variations in each diffrac-
tion mode are apparent (Fig. 2H,I). At large angles γ2, measured
from the sample surface normal, a region of higher reflection
intensity appears, which is related to the inclination of the in-
dividual plates, i.e. the blaze of the grating array. By contrast,
the diffraction caused by the scallops on the individual plates is
strongly influenced by the variation in tilt angle shifting the
observed arc-shaped pattern in wavelength and angular position
across the different diffraction orders in the variable angle spec-
dtroscopic data (Fig. 2H, red shaded region), the tilt angle of the
diffraction gratings which have a tilt angle, β, relative to the surface normal, the diffraction grating

equation can be reformulated as:

\[
\sin(\theta) \approx \frac{\lambda}{d} \cos(\theta_2 - \beta) + \cos(\theta_2 - \beta)
\]

By calculating a fit for the arc-shaped intensity distribution
across the different diffraction orders in the variable angle spec-
dtroscopic data (Fig. 2H, red shaded region), the tilt angle of the
plates relative to the surface normal is found to be \( \beta \approx 23^\circ \), in
agreement with the SEM image analysis.

These findings are further supported by Finite Difference
Time Domain simulations (19). By comparing the plates with and
without scalloping, the arc-shaped intensity distribution across
diffraction orders is clearly identified as the diffraction resulting
from the scallops (Fig. 3). Simulations of 23° tilted plates with
45° incident illumination show that this arc-shaped diffraction
pattern gets skewed and spectrally shifted as predicted by Eq. 2
and observed in the experiments; the influence of the blaze of
the regular array of individual gratings, separate from the effect
of the scallops, can also be seen by closely examining Fig. 3 and
noting that the two tilted plate simulations have regions of high
intensity reflection at \( \sin(\theta) = 0 \) where the upright plates do not.
Furthermore, the simulations serve to predict and optimize the
influence of variations in inter-plate geometry, scallop gratings
pitch and shape and plate tilt angle prior to the manufacturing
of the system.

While the angular positions of the diffraction modes resulting
from the inter-plate periodicity only vary with the angle of light
incidence \( \theta_2 \); for a given \( \theta_2 \) the diffraction pattern caused by
the regular scallops on individual plates is strongly affected by
a change in tilt of the plates relative to the sample normal. Con-
sequently, a means of reversibly varying the plate tilt angle can
provide the possibility to dynamically tune the diffraction pattern
independent of light incidence. Possible means of achieving such
reversible actuation include embedding the plates in a stimuli-
responsive hydrogel (20-23), using a soft material negative of the
structure and applying shear force to bend the micro-gratings,
modifying the tips of the plates with ferromagnetic particles to
allow for dynamic reconfiguration of the plate geometry using
magnetic fields (24), or implementing tuning mechanisms shown
for simple planar diffraction gratings that rely on electric fields or
mechanical deformation (25-28).

Biological strategies for light manipulation have already been
successfully implemented in nanophotonic devices for applica-
tions in chemically selective vapor sensing, pH determination,
infrared imaging, SERS-based chemical analysis, and localized
heating from infrared absorption (29-34). The rich and tunable
optical signature of our hierarchical bio-inspired diffraction-
based photonic material platform could provide a basis for novel
developments in bio-sensing (35-37), efficient light management
in photovoltaic systems (38-40), enhanced light extraction and
radiation profile shaping in light emitting diodes (41-43) and
optically variable devices in consumer product design and anti-
counterfeiting (44-46).

Our results demonstrate the versatility of a bio-inspired ap-
proach towards the creation of novel photonic systems. The
unique diffraction-inducing nano- and micro-scale architecture
previously discovered in the scales of the male butterfly P. luna
served as inspiration for artificial micro-diffraction grating arrays.
While our photonic system mimics the reverse diffraction color
sequence found upon interaction of light with the butterfly’s scales, it also provides additional complexity in the diffraction
patterns due to a periodic arrangement of the diffraction ele-
ments not found in the natural structure. Such arrays provide
a platform for hierarchical photonic systems displaying unique
diffraction coupling. A detailed optical analysis and modeling of
the diffraction patterns allowed us to observe, understand and
decouple diffraction effects induced by the plate ensemble and
by the regular scalloping of individual plates. A variation of the
light incidence angle results in the expected shifting of the plate
ensemble diffraction modes but does not affect the diffraction
resulting from individual plates. On the other hand, a variation
in plate inclination leaves the inter-plate geometry diffraction
modes untouched but has a strong influence on the scallop-
induced diffraction.

The intensity distribution of the diffraction induced by the
scallop is modulated by the diffraction induced by the plate
ensemble. Where the scallop diffraction arc coincides with a
plate ensemble diffraction order a peak in intensity is observed.
A decrease in the plate ensemble period would result in fewer
propagating plate ensemble diffraction orders with a larger free
angular range in between. This would lead to a discretization of
the scallop diffraction pattern (seen in the FDTD simulation in
Fig. 4) inducing a discrete and easily perceivable color variation
with potential applications in the development of novel optically
variable devices in security printing and consumer product la-
beling. Currently, efforts are underway to fabricate the diffrac-
tion structures in different material combinations that provide
a higher refractive index contrast, thereby strengthening the
diffractive signal.

Materials and Methods

Manufacture of artificial diffraction structures

When Bosch etching (15) is used in conjunction with photolithography,
the multiple etching and passivation steps give rise to a periodicity in
the sidewalls of the structures due to the repeated underetching. While,
typically, the goal of this etching method is to create vertical sidewalls, these
undulations in the sidewall can form a diffraction grating similar to that on
the Pierella luna scales if the periodicities are chosen to fall within the range of
optical wavelengths.

Once structures with the correct geometry are created in silicon, they
can be replicated in other materials with better optical properties by using
soft lithographic methods (16). By using soft, transparent materials instead
of silicon, the structures can be bent much more easily and the optical
properties can be changed by applying metal coatings or doping the material
with pigments or other materials with interesting optical properties. The
replication is achieved by using a polydimethylsiloxane (PDMS) mold of the
silicon master and curing an epoxy via UV light before removal from the
mold.

Structural and optical analysis

Once scalloped plate structures are made, optical characterization is
performed for comparison of the structures observed on Pierella luna and
the fabricated systems. Several different types of characterization were em-
ployed, including variable-angle spectroscopy, diffraction microscopy, and
scanning electron microscopy.

For the variable angle spectroscopy setup, an Ocean Optics DH-2000
UV-VIS-NIR light source was used to illuminate a small spot (~1 mm) of the
sample at a given incidence angle \( \theta \). For each angle of illumination,
light was collected at half degree increments for \(-75°\) to \(+75°\) relative to the
sample normal and spectrally analyzed using an Ocean Optics Maya Pro
2000 spectrometer.

For the diffraction microscopy images, a Bertrand lens was used to focus
on the back focal plane of the objective of an upright BXFM Olympus optical
microscope. The sample was illuminated either from an external source

Footnote Author
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