Structural coloration and photonic pseudogap in natural random close-packing photonic structures

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Abstract: Scales on the elytra of longhorn beetle Anoplophora graafi display diverse non-iridescent colors ranging from blue, green, yellow, and red to purple. By structural characterizations, optical measurements, and theoretical calculations, we found that the scale colors stem from an amorphous photonic structure possessing only short-range order: random close-packing of chitin nanoparticles. Our results showed that direction-independent photonic pseudogaps found in the photon density of states of the random close-packing photonic structure are the ultimate physical origin for non-iridescent coloration of scales. The color steering strategy of scales is ingenious, simply by varying the size of chitin nanoparticles. Revealed natural random close-packing photonic structures and the color steering strategy of scales could render valuable inspiration for the artificial fabrication and design of photonic structures and devices as well.

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References and links

1. Introduction

Random packing of hard spheres is an elusive problem that has fascinated scientists for long [1,2]. This problem has found important practical applications in a wide range of fields, from granular media, liquids, and amorphous solids to living cells. When identical hard spheres are randomly thrown into a container and shaken, it results in the most compact way of packing, i.e., random close-packing (RCP). RCP model has been successfully used to describe the atomic structures of amorphous solids such as metallic glasses [3,4]. These amorphous solids possess only short-range order of atomic positions, giving rise to extraordinary mechanical, and unusual thermal stability, electronic transport, and magnetic properties [5,6].

In recent years, there have been considerable efforts towards the organizations of colloidal nanoparticles into ordered lattices [7]. These crystalline assemblies can be used as templates or serve directly as photonic crystals [8,9], periodic photonic structures that can offer unprecedented opportunities in the control of the flow of light [10]. On the other hand, the photonic analog of amorphous solids, amorphous photonic structures that have only short-range order, exhibits many unique and unusual optical properties that do not exist in photonic crystals [11–14], manifesting a new kind of optical media: photonic glasses [12]. Self-assembly of colloidal particles usually leads to crystalline structures possessing both short- and long-range order. The fabrications of amorphous photonic structures based on colloidal nanoparticles are still very challenging [7,11,12,15], especially for operating wavelengths in the visible and near infrared ranges.

Interestingly, photonic structures with submicron featured sizes have been widely exploited in the biological world for color production, dubbed structural coloration [16–18].
Intriguing examples include photonic-crystal structures [19–21] and amorphous photonic structures [22–26] which can produce iridescent and non-iridescent structural coloration, respectively. Nanoscale photonic structures and mechanisms of coloration revealed in the biological world have been a great source of inspiration for our design and fabrication of photonic devices for future technological applications. Here, we report on our discovery of a RCP photonic structure in non-iridescent scales on the elytra of longhorn beetle *Anoplophora graafi* (Coleoptera), the ultimate physical mechanism of non-iridescent structural coloration, and the subtle steering strategy of scale colors.

2. Materials and methods

2.1. Samples

Beetle *A. graafi* belongs to a family of Cerambycidae (longhorn beetles), found in the Borneo rainforest of Indonesia and Malaysia. Specimens under study were bought from the Shanghai Natural Museum, Shanghai, China. Beetles were observed and recorded using a digital camera (Canon EOS 5D). The optical microscopic images of scales were observed and recorded using a digital microscope (Keyence VHX-600) under 500 × magnification. The microstructures of scales were characterized by scanning electron microscopy (SEM) (Philips XL30 FEG).

2.2. Measurements of reflection spectra

Reflection spectra of single scales were measured by micro-optical spectroscopy which consists of a tungsten lamp light source, a microscope (Leica DM6000 M) with objective 50 × and NA 0.55, and an optical spectrometer (SpectraPro 500i). The field diaphragm of the microscope can be adjusted so as to enable the detection of a single scale. Diffuse reflectance standard (Ocean Optics) was used as reference. For micro-optical spectroscopic measurements, scales were scraped off and placed on a glass slide separately. Owing to the high absorption of the glass components of the microscope in ultraviolet, we cannot detect reflection spectra in ultraviolet by our micro-optical spectroscopy.

For macro-optical spectroscopy, a Xenon lamp was used as the light source which can cover the wavelength range from 250 to 800 nm. Samples were illuminated by the collimated light beam from the light source after passing a beam splitter (Edmund Optics) at the 45° angle. An aperture was used to adjust the size of the light spot. Diffuse reflectance standard (Ocean Optics) was used as reference.

2.3. Generation of RCP photonic structures

RCP is defined statistically and can obtain a maximum volume fraction for hard spheres when they are packed randomly [1,2]. To study theoretically the optical response of RCP photonic structures we used a popular rate-dependent densification algorithm [27] to generate RCP structures of equal hard spheres starting from a random distribution of points. Four thousand randomly distributed points were generated in a cubic unit cell with periodic boundary conditions applied. Each point represents the center of an inner and an outer sphere. The inner diameter defines the true density while the outer one specifies the nominal density. Within the framework of this algorithm, the inner diameter is set to the minimum center-to-center distance between any two spheres in each iteration. To eliminate the worst overlap, in each step both spheres move an equal distance along the line joining their centers until this distance is equal to the outer diameter. This can slowly shrink the outer diameter, leading to reduced overlaps. When the inner and outer diameters approach each other, the true and nominal densities coincide with each other eventually such that RCP photonic structures can be attained.
2.4 Numerical simulations

A finite-difference time-domain (FDTD) method [28] was used to simulate the optical properties of model RCP photonic structures generated. Within the framework of the method it is possible to calculate the reflection spectrum of a slab of a RCP photonic structure.

For the calculations of the photon density of states (PDOS) of a RCP photonic structure, a FDTD spectral method [29] was used. The computation procedure is as follows. We first initialized the electric and magnetic fields and then recorded the time evolution of the fields by the FDTD method under perfectly matched layer absorbing boundary conditions [30]. Spectral intensities can be calculated by Fourier transforming the time dependences of the fields at random sampling points. The PDOS was finally obtained by the sum of the spectral intensities over the sampling points [14,29].

2.5 Color conversion and chromaticity values

For color characterization, measured or predicted reflection spectra can be converted into colormaps. Suppose a body under study is illuminated by a CIE (Commission Internationale de l’Eclairage) daylight simulator illuminant, D65 [31]. This illuminant, characterized by a wavelength distribution \( D(\lambda) \), matches closely that of the sky daylight. For a given reflection spectrum \( R(\lambda) \), we can compute the CIE tristimulus values as [32]

\[
X = \frac{1}{k} \int D(\lambda)R(\lambda)\bar{x}(\lambda)d\lambda,
\]

\[
Y = \frac{1}{k} \int D(\lambda)R(\lambda)\bar{y}(\lambda)d\lambda,
\]

\[
Z = \frac{1}{k} \int D(\lambda)R(\lambda)\bar{z}(\lambda)d\lambda,
\]

where \( \bar{x}(\lambda) \), \( \bar{y}(\lambda) \), and \( \bar{z}(\lambda) \) are the CIE 1931 color matching functions [33], and

\[
k = \int D(\lambda)R(\lambda)\bar{y}(\lambda)d\lambda
\]

is a normalization factor which ensures that an object with \( R(\lambda) = 1 \) yields the component \( Y = 1 \). For numerical calculations, all integrals were replaced by discrete sums. The sums in the visible range (380–750 nm) were calculated at an interval of 10 nm.

In the CIE \( XYZ \) color space, the \( Y \) parameter was deliberately designed as a measure of the brightness of a color. The chromaticity of a color can thus be represented by the two derived parameters \( x \) and \( y \)

\[
x = \frac{X}{X + Y + Z},
\]

\[
y = \frac{Y}{X + Y + Z},
\]

\[
z = \frac{Z}{X + Y + Z} = 1 - x - y.
\]

The derived color space specified by \( x \), \( y \), and \( Y \) is known as the CIE \( xyY \) color space.

The CIE \( xyY \) color space is widely used in practice for color specification. The brightness of a color is given by the value of \( Y \), while the values of \( x \) and \( y \) render the color chromaticity from which we can specify the hue and saturation.
3. Results and discussions

3.1 Optical observation and reflection measurement

Beetle and its scales were observed and recorded using a digital camera and a digital optical microscope, shown in Fig. 1. With the naked eye, this beetle has a dull metallic blue or green color on its elytra depending on inter-species, marked with brilliant greenish white lateral stripes [Fig. 1(a)]. Under the optical microscope, these stripes are composed of differently colored scales imbricated on the elytra and pronotum [Fig. 1(b)]. Scales are seed-like, about 50 µm long and 20 µm wide. Each scale has a distinct non-iridescent color. Interestingly, scale color can cover almost the whole visible range. Indeed, blue, green, yellow, red, and purple scales can be found. The perceived greenish white is thus a mixed color composed of diverse colors from differently colored scales in a pointillistic way.

![Image of beetle and scale](image.png)

Fig. 1. Optical images and reflection spectra. (a) Optical image of beetle A. graafi. (b) Optical microscopic image of a greenish white stripe under 500 × magnification. (c) Normalized reflectance spectra of differently colored single scales measured by micro-optical spectroscopy under normal incidence.

To characterize the optical properties of scales, reflection spectra of single scales were measured by micro-optical spectroscopy [Fig. 1(c)]. The measured spectrum of each scale is basically characterized by two reflection peaks, one in the visible and the other in ultraviolet, consistent with our perception. The latter is, however, outside the measured range due to the limitation of our micro-optical spectroscopy but can be detected by macro-optical spectroscopy (see Fig. 3).

3.2 Structural characterization and analysis

Microstructures of scales were characterized by SEM, shown in Fig. 2. SEM cross-section images revealed that scales have an outer chitin cortex with a thickness varying from about 1 to 3 µm [Fig. 2(a)]. The optical cross-section image of a scale shows that the cortex is transparent and the inner part displays coloration [Fig. 2(b)]. From SEM images the interior of scales is an array of chitin nanoparticles with uneven surfaces [Fig. 2(c)] In each scale the size of the chitin nanoparticles is nearly identical. However, it is different in differently colored scales. The size of chitin nanoparticles increases in scales with color changing from blue, green, yellow, and red to purple. In blue scales the nanoparticle size is the smallest, about 200 nm, while it is the largest in purple scales, about 270 nm. To determine whether scale colors are caused by the array of chitin nanoparticles or not, sliced scale slabs were immersed in liquids such as water and alcohol. The slabs became transparent after the liquid infiltration, indicating that scale colors are indeed produced by the array of chitin nanoparticles in the scale interior rather than by pigments.
By inspecting the arrangement of chitin nanoparticles, we can assert that chitin nanoparticles are organized in a way of RCP. To verify this, we used the popular rate-dependent densification algorithm [27] to generate a model RCP structure of equal spheres [Fig. 2(d)] and compare with the photonic structure in scales. Obviously, the photonic structure in the scale interior is closely similar to the generated RCP one. We also calculated the two-dimensional radial distribution function (RDF) of both structures, also showing close similarity [Figs. 2(e) and 2(f)]. These findings render convincing evidence that the array of chitin nanoparticles is no more than a RCP photonic structure. It is obvious from the RDF that the RCP photonic structure in the scale interior has only short-range order, analogous to amorphous solids [3].

Fig. 2. (a) SEM cross-section image of a green scale. (b) Optical cross-section micrograph of the green scale. (c) Close-up SEM cross-section image of the interior of the green scale. (d) Cross-section of a generated RCP structure of equal spheres with surfaces roughened arbitrarily. (e) and (f) Histogram of two-dimensional RDF with (e) for the RCP photonic structure in the green scale and (f) for the generated one.

3.3 Photon density of states and structural coloration

The reflection spectrum of a slab of a generated model RCP photonic structure was calculated by the FDTD method [28], shown in Fig. 3. The slab of the model RCP photonic structure has a thickness of 3.58 µm and extends infinitely along two in-plane directions by imposing periodic boundary conditions. In the calculations, the nanospheres take a refractive index of 1.56, a typical value for chitin, and their diameter is assumed to be 240 nm, a typical value for the chitin nanoparticles in green scales. Two reflection peaks exist in the calculated spectrum:
one at green wavelength and the other one at ultraviolet. The measured reflection spectrum of green scales (with chitin nanoparticles about 240 nm) by macro-optical spectroscopy is also given for comparison. The overall agreement between theory and experiment is satisfactory. For the ultraviolet peak, there exists a bit discrepancy in the peak position and intensity which can be understood since in scales chitin nanoparticles are nonspherical, unequal in size, and absorbing at ultraviolet.

Fig. 3. Calculated (solid line) and measured (dashed line) reflection spectra. Measured reflection spectrum for green scales was obtained by macro-optical spectroscopy.

For periodic photonic structures (photonic crystals) their optical properties can be well described by photonic band structures [10]. In amorphous photonic structures, however, photonic band structures are ill-defined due to the lack of long-range order. To get insight into the coloration mechanism of RCP photonic structures, we calculated the PDOS of model RCP photonic structures by the FDTD spectral method [29] as a function of reduced frequency $d/\lambda$, where $d$ is the diameter of nanoparticles and $\lambda$ is the wavelength in vacuum, shown in Fig. 4.

Fig. 4. Calculated PDOS of a model RCP photonic structure (inset) as a function of reduced frequency $d/\lambda$. The PDOS of a homogeneous medium with a refractive index of 1.38 (dashed line) is given for comparison. Photonic pseudogaps are indicated by arrows.

The PDOS of a system describes the number of photonic states available at each frequency and is a fundamental quantity that determines many optical properties and quantum behaviors of the system. Model RCP photonic structures for theoretical calculations were generated by the popular rate-dependent densification algorithm [27]. A cubic supercell of $(14.9d)^3$ that contains 4000 nanospheres and perfectly matched layer absorbing boundary conditions [30] in three dimensions were used. In our calculations, the nanoparticles were assumed to be spherical with a refractive index of 1.56. For reference, the PDOS of a homogeneous medium...
with a refractive index of 1.38, the volume-weighted average value of the model RCP photonic structure, was also calculated. It is known that the PDOS of homogeneous media scales quadratically with frequency. For the RCP photonic structure, significant deviations occur due to light scattering. The quadratic scaling with frequency holds only at low frequencies (long wavelength limit) as expected. Two prominent dips (photonic pseudogaps) appear in the PDOS of the model RCP photonic structure, one at the reduced frequency $0.45d/\lambda$ and the other at $0.73d/\lambda$. The photonic pseudogap at $0.73d/\lambda$ is due to the Mie resonance of the nanospheres [34], while the other at $0.45d/\lambda$ stems from short-range order. This can be confirmed by reducing the nanoparticle diameter. Unlike photonic bandgaps in photonic crystals within which the PDOS is zero [10], photonic pseudogaps have nonzero PDOS.

Compared with the PDOS, the calculated reflection peaks and photonic pseudogaps show one-to-one correspondence. The green reflection peak stems from the photonic pseudogap at high wavelength, while the ultraviolet peak originates from the pseudogap at low wavelength. This demonstrates unambiguously that photonic pseudogaps are the ultimate physical origin for the structural coloration of RCP photonic structures. Non-iridescence can be understood by the fact that light is scattered evenly in all directions since there is no direction discrimination in RCP photonic structures.

Structural coloration by amorphous photonic structures is currently understood conceptually by coherent scattering [22–26] and the positions of reflection peaks were quantitatively predicted based on the Fourier analysis of the cross-section images obtained by SEM or transmission electron microscopy. As is known, the Bragg condition is only valid for very weak scattering, e.g., in the case that the refractive index contrast between scatters and background is small or scatters are very small compared with their inter-distance. In RCP photonic structures, however, nanoparticles are randomly close-packed and the refractive index difference between nanoparticles and ambient background is far from small. As a result, the Fourier analysis combined with the Bragg condition cannot give a correct prediction of the positions of reflection peaks. This is not surprising since the Fourier analysis only provides structural information. On the other side, reflection by a surface of a RCP photonic structure depends not only on its geometrical configuration but also on the detailed structural and refractive index parameters of nanoparticles. To predict reflection peaks, one has to solve the Maxwell’s equations numerically.

It should be pointed out that photonic pseudogaps were also found in ordered photonic structures like opal [35], a structure composed of submicron silica spheres close-packed in a three-dimensional face-centered cubic lattice. But photonic pseudogaps in ordered structures are fundamentally different from the ones in amorphous counterparts. In amorphous photonic structures, photonic pseudogaps are due to short-range order while in ordered structures they are due to long-range order. As a result, photonic pseudogaps in ordered structures are direction dependent [10], leading to iridescent coloration. On the contrary, photonic pseudogaps in amorphous photonic structures do not depend on direction, causing non-iridescent coloration.

### 3.4 Color steering of scales

Note that photonic pseudogaps scale linearly with the chitin nanoparticle size. As a result, different chitin nanoparticle sizes will give different scale colors. This can be seen from the calculated reflection spectra of model RCP photonic structures with different nanoparticle sizes. To see the color variations with the nanoparticle size, both the calculated and measured reflection spectra were converted into the CIE chromaticity $x$ and $y$ values, plotted on the CIE 1931 chromaticity diagram, shown in Fig. 5. The outer curved boundary of the tongue-shaped area in the chromaticity diagram is the spectral locus which corresponds to monochromatic light. The straight edge of the lower part represents the line of purples which have no counterparts in monochromatic light. Mixed or less saturated colors appear in the interior with white at the center. Clearly, the predicted colors agree well with real ones in scales. Importantly, the resulting non-iridescent structural colors can cover almost the whole visible
spectrum. In other words, the beetle can steer its scale color simply by varying the chitin nanoparticle size.

Fig. 5. CIE chromaticity values for the model RCP photonic structures with different nanoparticle size (solid line), converted from the corresponding calculated reflection spectra. Dots are the converted data for single scales from the measured spectra in Fig. 1(c). Labels are in units of nanometers representing the nanoparticle size.

4. Conclusions

Scales on the elytra of longhorn beetle *A. graafi* were studied by structural characterizations, optical measurements, and numerical simulations. Scales have diversified non-iridescent coloration ranging from blue, green, yellow, and red to purple, leading to a greenish white color via color mixing in a pointillistic way. We found that chitin nanoparticles in the scale interior are arranged in RCP. Theoretical calculations revealed that such RCP photonic structures possess photonic pseudogaps in the PDOS, giving rise to non-iridescent structural coloration. Scales can alter their coloration simply via the change in the chitin nanoparticle size, producing diverse colors. Interestingly, these RCP photonic structures may have potential applications in coating, painting, and display owing to the advantageous features of their structural coloration, namely, high brightness and non-iridescence. On the other hand, natural RCP photonic structures revealed can be used as templates to fabricate artificial counterparts or serve as candidates to study many intriguing optical phenomena. Revealed photonic pseudogaps may help us get deeper insight into the optical transport properties of disordered optical media.

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