STRUCTURAL COLOURS IN THE FOCUS OF NANOENGINEERING AND THE ARTS: A SURVEY ON STATE-OF-THE ART DEVELOPMENTS

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1 INTRODUCTION

Be it photonic crystals with functional elements some few nanometers in size in peacock feathers, or butterfly wings with nanostructured hydrophobic surfaces and shiny metallic colours generated by the interaction of light with nanoscale Christmas tree-like structures - functional nanostructures that give rise to colours are omnipresent in biology. Colour production in nature shows structural colouration and/or pigmentation. Structural colours result from the interaction of light with structures having the same order of size as the light wavelength [1 – 9].

Researchers and developers already utilize structural colours in science and technology, e.g. by mimicking structures found in the wings of tropical butterflies, yielding e.g., applications in the security printing industry via photolithographic methods, helping to make bank notes and credit cards harder to forge [1, 10, 11].

The objective of this paper is to describe the physical basics of structural colours, to introduce examples from biology and man-made structural colours and to give an outlook on possible future applications in science and art. The described research on structural colours is highly interdisciplinary, bridging nanotechnology, biology and the arts via material science.

2 PHYSICAL BASICS, BIOLOGICAL EXAMPLES AND TECHNICAL IMPLEMENTATIONS OF STRUCTURAL COLOURATIONS

Physical Basics of Structural Colours

Structural colours arise via thin film interference, multilayer interference, diffraction, scattering and photonic crystals [1].

Thin film interference occurs when an incident light wave is partly reflected by the upper and lower boundaries of a thin film (Figure 1). Light that strikes a thin film surface can be either transmitted or reflected from upper or lower boundary, respectively. The thickness of the film layer (*d*), the refractive index of the film (*n*) and the angle of incidence of the original wave on the film (θ_1) determine the colour seen [1]. There are two conditions that should be satisfied for constructive interference. The thin film should be thin enough to crest the reflected waves and the two reflected

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waves should be in one phase [12]. A light wave can be reflected from both boundaries of a thin film layer and dependent on the phase of two reflected light waves, either destructive or constructive interference occurs.

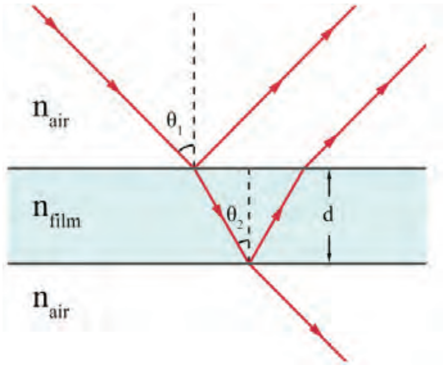

Figure 1. Thin film interference [13].

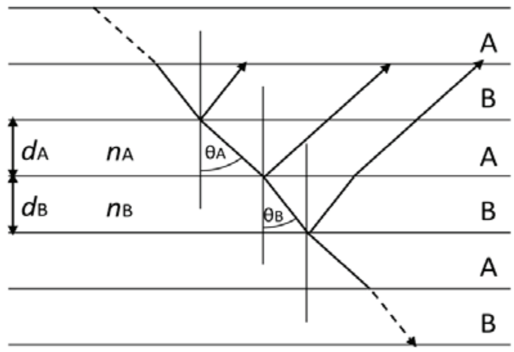

Figure 2 (right). Multilayer interference $n_B > n_A$. A change in viewing angle corresponds to a change in the perceived colour, due to changes in the phases of the interfering waves.

The same phenomenon occurs in a series of thin films, a so-called *multilayer* (Figure 2). With $n_B > n_A$ between each A-B interface a 180° change in phase takes place, while at the B-A interface there would be no phase change.

The *diffraction grating* in Figure 3 shows the correlation of the spacing of the grating (d) with the angles of the diffracted and incident beams (α, β). The colouration in a particular direction (viewing angle) is generated by interfering components from each slit of the grating. The 0th order reflection corresponds to direct transmission and is denoted as m=0. Other maxima occur at angles with $m = \pm1, \pm2, \pm3$ and so on. [2, 4]

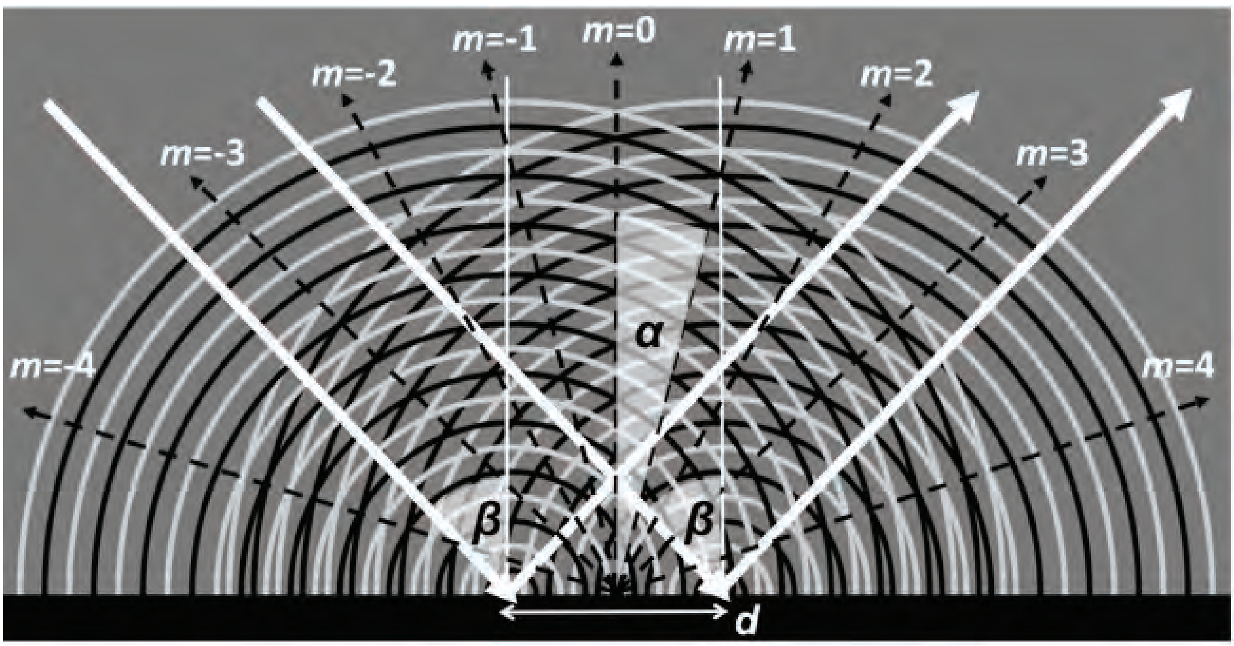

Figure 3. Colour production in a diffraction grating, represented by the black bar on the bottom.

The term *scattering* in general means the interference of light with different wavelengths reflected from scattering objects either in a constructive or destructive way (Figure 4). In coherent scattering there is a definite phase relationship between incoming and scattered waves, whereas in incoherent scattering this is not the case [5, 6].

The two main types of scattering are termed *Rayleigh scattering* and *Tyndall scattering*. In Rayleigh scattering, the scatter particles are much smaller than the wavelength of the incident light, whereas in Tyndall scattering, the scatter particles are macroscopic. The scattering of sunlight off the molecules of the atmosphere causes the blue colour of the sky. Since Rayleigh scattering is more effective at short wavelengths (the blue end of the visible spectrum), the light scattered down to the earth at a large angle with respect to the direction of the sun's light is predominantly in the blue end of the spectrum.

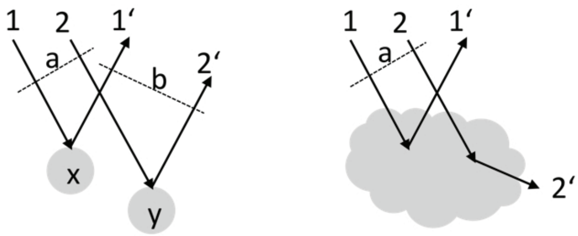

Figure 4. Coherent (left) and incoherent scattering (right).

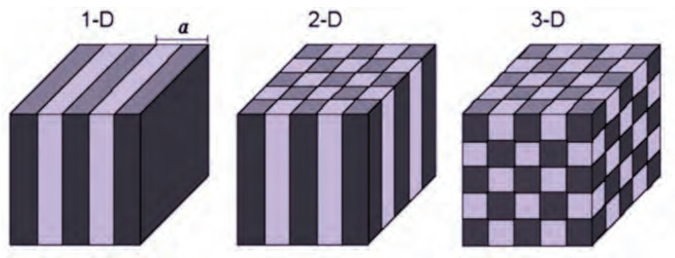

Figure 5. Schematics of one-, two- and three-dimensional photonic crystals (1-D, 2-D, 3-D). The colours represent materials with different refractive indices. The spatial period of the material is called the lattice constant, a.

Photonic crystals exhibit a nanoscale periodicity in their refractive index (Figure 5). There are one-, two- and three-dimensional photonic crystals. Depending on their wavelength, photons either can be transmitted through the crystal or not (allowed and forbidden energy bands) [14, 15]. For effects in the visible range, the periodicity of the photonic crystal has to be of the between about 200 nm (blue) and 350 nm (red).

Examples from Biology

In peacock feathers a Fabry-Perot type of interferometer causes interference between the multiple reflections of light between two reflecting surfaces. Light is reflected on the front and backside of the structures, whereby colour in a specific wavelength range is enhanced. Melanin structures with a photonic crystal-like shape are embedded in larger spike-like structure of keratin including the melanin cylinders, in the green region of the feather, about 10 rows of cylinders, and in the yellow region about 6 rows. The distances between the single melanin cylinders are in the blue area 140 nm and in the green one 150 nm. [7]

The structural colour in Morpho butterflies (Figure 6) originates mainly from light interference within a shelf structure on the butterfly scale through quasi-multilayer interference. The colours are generated by Christmas tree-like structures, whose characteristic dimensions are a couple of hundreds of nanometres (Figure 6). Transmission electron microscopy of wing-scale cross-sections of *M. rhetenor* (Figure 6a) and *M. didius* (Figure 6b) reveal discretely configured multilayers in the two species: The high occupancy and the high layer number of *M. rhetenor* creates an intense reflectivity that contrasts with the more diffusely coloured appearance of *M. didius*, in which an overlying second layer of scales effects strong diffraction. [1]

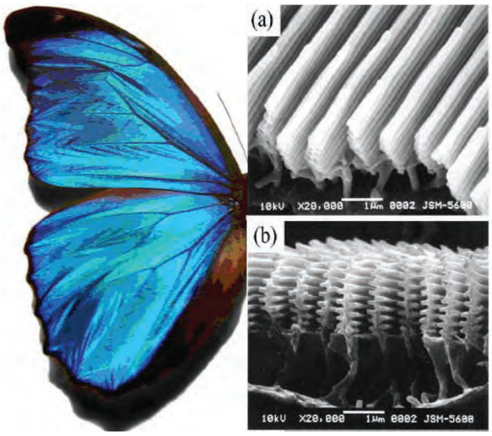

Figure 6. Left: Morpho menelaus. Image reproduced with permission under the terms of the GNU Free Documentation License [16]. Scanning electron microscopic images of the cross-sections of ground scales of M. rhetenor (Fig. 6a) and M. didius (Fig. 6b). Images reproduced with kind permission from The Royal Society [17].

Figure 7. Parides sesostris [18]. Image reproduced with kind permission from Kim Davis.

In the butterfly *Parides sesostris* (Figure 7) photonic crystals are responsible for the green colour. Transmission electron microscopy reveals neighbouring differently oriented domains of identical 3D structure that are distinguished by contrasting 2D patterns [9].

The beetle *Dynastes hercules* appears khaki-green in a dry atmosphere and turns black under high humidity levels. The visible dry-state greenish colouration originates from a widely open porous layer located 3 μm below the cuticle surface (the cuticle is a multilayered, extracellular, external body covering in insects). The structure of this layer is three-dimensional, with a network of filamentary strings, arranged in layers parallel to the cuticle surface and stiffening an array of strong cylindrical pillars oriented normal to the surface. Diffraction plays a role in the broadband colouration of the cuticle in the dry state. The backscattering caused as this layer disappears when water infiltrates the structure and weakens the refractive index differences. [19]

Man-made Structural Colours

There are heaps of man-made structural colours. The ill termed "effect pigments" for example mainly consist of flakes mimicking the marvelous colours introduced above. Their main properties are high refraction index, colourlessness and transparence generating pure interference colours with the optimum thickness in the range of the wavelengths of visible light. Such flakes are made of different basic materials such as alkaline-Plumbum-carbonate, platelets of Titanium oxide, metal oxide mica pigments, Aluminum oxide flakes, borosilicate flakes, Silicon dioxide flakes, Iron oxide flake covered with alternating layers of high and low refractive index materials from oxides of Iron, Titanium, Silicon, Chromium, Copper, and also the combinations in-between supplying their specialized colours. Their composition offers a wide choice of opportunities either generating just a certain colour or a colour change in a coating application called "flip-flop effect" with up to three colours depending on the viewing angle [10].

Multilayer structural colours with a Fabry-Perot interferometer-like structure produced via physical vapor deposition are used for security of banknotes and identification papers. Such structures have a diameter of 1 – 100 μm and a thickness of 0.2 – 2 μm [10].

Effect structural colours consist of *liquid crystal polymers* whereas the polymerised structural colour platelets are based on polysiloxanes. Their thickness of 4 µm restricts their usability due to a lack of stability [10].

The above-mentioned structural colours produce colours by interfering light of thin layers. On the other hand there are structural effect colours based on the diffraction of periodical structured surfaces such as *holographic structural colours* with a thickness of 10 µm and a diameter of 10 – 300 µm and *diffractive structural colours* with a thickness less than one µm, a periodical structure of 1 µm and a depth of some nanometres, synthesized in vacuum; the latter ones are for security prints [10].

Functional effect structural colours are metal oxide mica pigments. Their coating contents additional features such as corrosion limitation, magnetism, electrical conductivity or dielectric properties, reflecting infrared and more. Used in printing industries especially for packaging, textiles, wallpapers, furniture deco-foils, papers and others the interference colours have already conquered the market. [10]

Structural colours can also be produced through photonic crystals and magnetism. The commercially available material is a photonic crystal, termed M-Ink. Its colour is magnetically tuneable and lithographically fixable in a three-phase material system consisting of super-paramagnetic colloidal nano-crystal clusters (CNCs), salvation liquid and photo-curable resin. The super paramagnetic CNCs, each consisting of many single-domain magnetite nano-crystals, are capped with silica shells according to Mr. Sunghoon Kwon, Seoul National University, who demonstrated rapid production of high-resolution patterns of multiple structural colours. Under an external magnetic field, the CNCs are assembled to form chain-like periodic structures.

As the photocuring is instantaneous it is possible to freeze the self-assembled photonic nanostructure fast enough to prevent distortion to retain the structural colour [20]. Another already patented technology concerns an instrument that can fabricate surface structures showing interference colours in a determined wavelength. The embossed and rolled surfaces are in the range of nanometers as in the case of the well-known one-ounce silver dollar in Australia. The mechanical deformation especially of metal surfaces happens in the range of nanometers. The technical implementation is about colouration without pigments called colour embossing. The used technique enables a higher safety standard concerning forgery; the abrasion resistance of this coin is high. [21]

There are also techniques fabricating 3-dimensional photonic laser crystals through laser holographic lithography that enables to produce a large defect-free area [22]. The structure of the Morpho butterfly scales has already served as a template for a fabricated shelf structure produced by the focused-ion-beam chemical-vapor-deposition method that could be used to cover an area. In the textile world a fiber was invented, also micking the scale structure of Morpho sp. This fiber is made of polyester and has a flattened shape (thickness 15 – 17 µm) within 61 layers of Nylon 6 and polyester (thickness 70 – 90 nm). By weaving a dress it demonstrates the possibility of aligning the direction of the multilayer that increases the reflectivity, indicating that it differs from the template referring to the colour impact and luster. [3]

3 CONCLUSION

Lustrous colours have a long history: even the old Romains put their glasses rested under high humidity beneath the earth obtaining a shimmering patina. Also Tiffany (USA) produced glass with interference phenomena in the beginning of the 20th century. Kate Nichols (USA), a contemporary artist, compiles her structural colours in a laboratory producing nanosilver. The ordering in the system determines the colour. [23, 24]

First steps are already taken to develop new technologies in a biomimetic direction copying strategies of colouration in the field of nanostructures by producing pigments without pigmentation or designing machines which can emboss a nanostructure on several materials to evocate structural colours. In the future structural colours could be inserted with changeable properties dependent on a given condition of their surroundings, like humidity, but also alkali or acid levels in the air could be an index for their altered visual appearance. Structural colours could displace toxic chemicals currently used for colouration. Their durability can be tuned depending on the material used for the structure. [10, 20-22, 25]

Art offers a wide experimental field to transfer structural colours from biology to human applications, in finding suitable materials for the applicable nanostructures. Imagine something like a pen with a nanostructure, colouring a substrate without pigments! The next possible generation of colours are the structured ones connected with their ecosystem – not only beautiful but also functional!

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