Bioinspired Microstructured Materials for Optical and Thermal Regulation

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Precise optical and thermal regulatory systems are found in nature, specifically in the microstructures on organisms' surfaces. In fact, the interaction between light and matter through these microstructures is of great significance to the evolution and survival of organisms. Furthermore, the optical regulation by these biological microstructures is engineered owing to natural selection. Herein, the role that microstructures play in enhancing optical performance or creating new optical properties in nature is summarized, with a focus on the regulation mechanisms of the solar and infrared spectra emanating from the microstructures and their role in the field of thermal radiation. The causes of the unique optical phenomena are discussed, focusing on prevailing characteristics such as high absorption, high transmission, adjustable reflection, adjustable absorption, and dynamic infrared radiative design. On this basis, the comprehensive control performance of light and heat integrated by this bioinspired microstructure is introduced in detail and a solution strategy for the development of low-energy, environmentally friendly, intelligent thermal control instruments is discussed. In order to develop such an instrument, a microstructural design foundation is provided.

1. Introduction

Light and heat are the basic factors necessary for the survival of humanity. In addition, throughout human history, the development of optical and thermal regulatory technology has been evidenced. In modern society, the manipulation of light and heat needs to be subtle and powerful to advance science and reduce energy consumption.[1–4] Unfortunately, materials, such as metals, polymers, and oxides, have their inherent limits on the demands of optical and thermal regulation.[5]

Over millions of years, through natural selection, nature has provided a valuable “solution manual” to render unique optical properties through the efficient manipulation of light and heat through absorption, reflection, scattering, transmission, and emission.[3] Furthermore, the beauty of optical engineering in nature is epitomized by the effective use of a limited set of rather ordinary materials that often exhibit outstanding optical processes. Nature has enabled complex microstructures on multiple scales and dimensions to realize optimized optical performance in response to environment changes and stimulations.[6–7] Structural colorations are a widespread phenomenon in nature, consisting of various biological functions, such as conspicuousness (e.g., increased reflection, warning, or attraction to conspecifics), camouflage, signaling, and thermoregulation.[8–10] Most of this vivid color comes from the interaction between light and microstructures without the need for pigment,[8] in which the organism can realize the color of the surface by solely regulating the period and type of its microstructure.[10] For example, the compound eye of an insect, with hundreds of non-close-packed nanopillars covering the hexagonally close-packed micro-ommatidia on spherical macro-bases, is a typical example of an antireflection photonic structure (Figure 1A).[5,11,12] The non-close-packed nanopillars structures show excellent antireflection performance and high ability to absorb light, so the compound eye of an insect shows black. The butterflies of Pieridae family consists of a 10 μm grid of pterin pigments and 500 nm spherical particles of cuticle (Figure 1B).[5,11–15] The compound structure shows a strong scattering of visible light (300–700 nm) and its surface reflectance is greater than 80%, so the butterflies of Pieridae family exhibit bright white coloration. The nanoscale ordered helicoidal features composed of biological stratum corneum is on the exoskeleton of Jewel beetles (Figure 1C)[5,16–18] The Jewel beetles also exhibit a brilliant iridescence owing to the ordered helicoidal features, which exhibit its selective reflection of circularly polarized light. The heads of Saharan silver ants are covered with densely arrayed triangular hairs that can enhance the reflectivity in the visible to near-infrared (Vis–NIR) range and enlarge the emissivity in the mid-infrared...
(MWIR) band for their survival in extremely hot surroundings (Figure 1D).[20]

In addition, chameleons have a thick layer of D-iridophores with disorganised guanine crystals that can reflect infrared light for thermal protection.[6,20] Cephalopod skin can be altered autonomously and repeatedly for the purpose of concealment or signaling, through the use of chromatophore pigment cells and reflective cells called iridocytes.[5,9] Further, some mammal animals, such as the polar bear, Tibetan antelope, and yak, use their thick fat fur covered by hollow and crimped hairs to effectively absorb and reflect infrared radiation to maintain their bodies warm.[21-25]

All of these elaborated photonic structures and the underlying physical mechanisms have provided much inspiration for the construction of new photonic materials,[20] producing a great variety of bioinspired microstructures for light and heat regulation.

Herein, we summarize the various optical phenomena of living organisms and their underlying physical mechanisms. On this basis, the effects of the types of microstructures and material properties on optical performance are presented, and their role in guiding the design and preparation of optical devices and photothermal systems are discussed in detail. This review is mainly focused on three sections. Each section introduces a bio-optical phenomenon in nature and its role in living organisms and presents its important influence on optical devices and optical engineering. The first section introduces the optical phenomena and principles of low-reflection surfaces in living organisms, including the increase in absorption and enhancement of transmission. In this discussion, the enhancement effects of these structures on optical devices and systems are summarized. The second section introduces the highly reflective surfaces of organisms and their principles, including high wide-band reflection and adjustable narrow-band reflection. Through bioinspired design, the movement of the spectral peak and color change under the action of an external field are realized, and the biological mimicry of the material and toxic substances of the sensor object are revealed. The third section introduces the regulation of infrared light by the organism and its mechanism, including the optical performances of dynamic infrared radiation regulation and multi-wavelength regulation, to regulate the body temperature of the organism and improve its viability. With dynamic infrared radiation regulation materials and their unique structures, infrared adaptive camouflage can be achieved. In addition, thermoregulatory materials have been presented by adjusting the optical performance at solar radiation wavelengths (0.2–2.5 μm) and the infrared radiation band (2.5–25 μm). Although this review provides a comprehensive introduction and summary of light and heat regulation by organisms in nature, it is not possible to cover all aspects of this topic in detail, considering the breadth of the topic and the numerous studies that have addressed. We hope that this review will provide researchers in this field with a comprehensive introduction, inspire researchers to investigate, and solve related practical engineering and scientific problems.

2. Bioinspired Antireflective Microstructures (ARS)

Solar radiation is the major energy source of the earth surface and organisms. How to effectively exploit it is vital to most living creatures, especially to small ones. It is beneficial not only for photosynthesis, which is main energy source for all organisms, but also for keeping body warm, perceiving surroundings and communication. Under these circumstances, different microstructures were evolved to suppress unwanted reflection in different creatures for different purposes. The moth eye and the butterfly wing (BW) are two of the most widely researched models for biological ARS, and some bioinspired materials have been developed based on these two models. With smaller feature sizes in sub-wavelength range and an ordered pattern, moth eye structures exert little interference on the light penetrating the surface so that they are preferred in the
application such as imaging and optoelectronic devices. On the contrary, more complicated hierarchical microstructures on the scales of BW are suitable for the application in broad band light absorption, photothermal, and photocatalysis. New biological ARS in other organisms are keeping to our vision in recent years. Herein, we introduce architectures and mechanisms of these biological ARS.

2.1. ARS Inspired by Moth Eyes

Fresnel reflection is caused by a sudden change in the refractive index, which reduces the light energy utilization rate of the optical device or system and severely limits its image analysis ability. Although traditional coating technology can reduce the surface reflection, problems arise, such as the lack of materials and thermal stress cracking, which cannot meet the needs of high-end equipment. In nature, the compound eye structure of moths (Figure 2A,B) uses cone-shaped arrays at below 300 nm
to reduce reflections by the compound eyes. The cone-shaped arrays of the compound eyes slow the change in the refractive index from the air to the compound eye, serving as an ARS.\cite{12,26}

2.1.1. Antireflection Mechanism of Moth Eye

The strong reflective light on the material surface comes from the Fresnel reflection due to discontinuities refractive indices at interface between two materials. The ARS mainly reduces the abrupt change in the refractive index at the interface between two materials. At present, the main theories considered in the investigation of this mechanism are the theory of equivalent medium, and theory of vector diffraction.\cite{27} Frequently, the finite-difference time-domain (FDTD) or finite element analysis (Comsol) or rigorous coupled-wave analysis was used to solve Maxwell’s equation in vector diffraction theory.\cite{28,29} Of these theories, the theory of equivalent medium is the most widely used and accepted. In the theory of equivalent medium, the ARS on the substrate is equivalent to a uniform dielectric film. The equivalent refractive index of the film is shown in Equation (1).

$$n_{\text{eff}} = \sqrt{\frac{(1-f) + fn_s^2}{(1-(1-f)n_s^2) + n_f^2}}$$

where $n_s$ is the refractive index of the substrate, $n_{\text{eff}}$ is the equivalent refractive index of the ARS, and $f$ is the fill factor of the ARS, which represents the ARS volume percentage. Figure 2C shows that the refractive index with the ARS structure exhibits a slower change than the refractive index with polished Si (remove sudden change of refractive index at the two phase’s interface); thus, the ARS demonstrates lower reflectance.\cite{30,31}

2.1.2. Enhance Light Transmission with ARS

There is a sudden change in the refractive index at the interface between quartz and air. And the quartz surface exhibited a reflectance of 10% and transmission of 90% (Figure 3A-a,b). The additive loss of reflection is especially detrimental to high-power laser systems. For example, optics can cause laser components to fail, reducing the amount of laser energy. In order to improve the transmittance of the quartz, researchers have developed many methods to prepare an ARS.\cite{32-41} A typical fabrication method combines reactive ion etching (RIE) and self-assembly to prepare the ARS on the surface of a quartz substrate. Through this method, the transmittance of the quartz with double-sided ARS was increased from 90% to 99% at wavelengths from 400 to 1000 nm (Figure 3A-b). Furthermore, the transmittance can be maintained at a large angle (Figure 3A-c). In addition, the quartz with an ARS can be seen in the optical photograph, which shows improved optical transmission and high-definition field-of-view (Figure 3A-d).\cite{34}

In order to reduce the cost of the etching mask, Yang et al. used an inexpensive single-layer polystyrene (PS) nanosphere as an etching mask to prepare an ARS on the quartz surface. The ARS achieved a transmittance greater than 99% in the wavelength range of 400–900 nm, achieving high visible-light transmission. By adjusting the size of the microspheres and etching process, the optimal antireflection wavelength band can be adjusted by the period of the ARS, yielding a surface with ARS that exhibits a good antifog effect.\cite{35,36} The above research can produce quartz with excellent transmission in the visible-light range; however, some high-end instruments require excellent transmission performance at deep UV wavelengths, such as deep ultraviolet lasers, deep ultraviolet lithography machines, and ultraviolet light detectors. The deep ultraviolet wavelength range is 200–350 nm, which requires the period of the ARS to be less than 120 nm. At present, it is difficult to obtain a periodic structure of less than 120 nm by colloidal assembly, photolithography, or annealed metal film.\cite{39} Spatz et al. used the process shown in Figure 3B to prepare an ARS with a period of 110 nm. The ARS increased the transmittance from 88% to 95% and demonstrated an increase in the average transmittance of ≈3% from 200 to 300 nm (Figure 3B-b).\cite{40}

Although the study demonstrates the preparation of an ARS with excellent performance, etched mask preparation is complex, which limits its range of application. To overcome these problems, Ye et al. used SF$_6$/He/CHF$_3$ as the etching gas. Figure 3C shows the mechanism for self-mask formation, in which this mixed gas was used to form a passivation layer of FC$_x$ compounds under plasma. The FC$_x$ compound was formed as small particles during the etching process, serving as a mask for RIE. Finally, the ARS was created by a one-step process on silica surfaces by self-masking RIE, solving the complicated process of mask preparation. Figure 3D-a showed a spectrum and SEM cross section of the ARS fabricated by this self-masking technology. The ARS showed a high transmittance of >99% from 510 to 1360 nm for the double-sided ARS samples (Figure 3D-b). In Figure 3D-b, the ARS exhibits a size of ≈280 nm, corresponding to a wavelength band of 510–1360 nm transmitted by the spectrum. When the average size of the ARS is reduced, the ARS structure can be extended to the ultraviolet band, and its transmission can reach 96% (200–350 nm), which meets the needs of ultraviolet lasers.\cite{41} To further reduce costs and simplify the process, Wathelm et al. spin-coated a mixture of poly(methyl methacrylate) (PMMA) and PS on a glass substrate, and then selectively dissolved PS to fabricate a PMMA ARS. The antireflection performance of ARS can be improved from 88% to 98% in the range of 400–800 nm.\cite{42} In order to further improve the transmittance band of ARS, researchers have developed micro–nano composite ARS which further reduced the reflectance on surface and increased the applicable angle.\cite{43,44} From the above studies, it can be seen that the reduced reflected light of the ARS served to increase the optical transmission for transparent substrates, which is of great significance for improving the energy utilisation of the optical system and improving the image quality.

2.1.3. Enhance Light Absorption with ARS

Previous studies have demonstrated that an ARS increases the optical transmission for transparent substrates, such as quartz, PMMA, and glass. The ARS has also been
demonstrated to increase absorption for light-absorbing substrates, such as Si, metal, GaAs, and Ge. The ARS has also been shown to improve light-energy utilization for Si-based photodetectors and optical components. Cui et al. used monolayer SiO$_2$ nanospheres as an etch mask for an ARS on the surface of polysilicon (Figure 4A).\cite{45} The spectrum proved that the absorption rate of the ARS was higher than that of the nanopillars and thin film. The absorption rate from the wavelength of 400 to 800 nm was 98%, and the angle of absorption over 95% was 0–50°. In order to further broaden the spectral region of ARS, Shi et al. fabricated 3D biomimetic moth-eye coating with ternary materials (conducting polymer nanoparticles, TiO$_2$ nanorods, and Si micropyramids), which reduced the reflectivity to <4% at wavelengths ranging from 200 to 2300 nm and exhibited remarkable superhydrophilicity.\cite{46,47} Meanwhile, Shi et al. fabricated bioinspired TiO$_2$ micropyramids with conducting polymer nanoparticles by soft imprinting and self-assembly, which exhibited excellent reflection with a broader spectral region from 200 to 2000 nm and was applied to the photocatalytic degradation of organism dye.\cite{48,49} In order to reduce costs, Lu et al. fabricated pyramid structures on P-type silicon by photolithography and wet etching. A layer of ZnO nanorods was prepared on the surface of the pyramid by hydrothermal synthesis. The composite ARS exhibited an absorption rate that varied from 60% to 95% and improved its photocatalytic performance.\cite{50} Li et al. fabricated an ARS with a high aspect ratio on the silicon surface by a self-masking technique during the etching. From 200 nm to 25 μm, the reflectivity of the ARS was less than 2%. This method effectively overcomes the problem of tedious preparation of the etching mask.\cite{51} In addition, Bodena et al. calculated that the antireflection performance was related to the period and aspect ratio of the ARS. The aspect ratio mainly affects the reflectivity, and the period mainly affects the best antireflection band. Lu et al. verified the correctness of the calculation method through experiments.\cite{52}
The ARS was fabricated not only on surface of silicon or silicon hybrid materials, but also on other materials such as Ti,[53] GaSb,[55] and poly(3,4-ethylenedioxythiophene) (PEDOT).[56] Zhou et al. had fabricated an ARS on surface of Ti using laser etching, which can reduce the reflectance from 60% to 5%.[53] The ARS of other metal materials was fabricated using laser etching and can improve the detection sensitivity of surface-assisted laser desorption/ionization (SALDI) mass spectrometry (MS).[54] Jiang et al. had fabricated an ARS on GaSb using RIE, which can reduce the reflectivity from 50% to 2%.[55] Sun et al. fabricated the bioinspired moth-eye patterned PEDOT:PSS polymer films by self-assembly, which are expected to be potentially useful in optoelectronic applications.[56]

2.1.4. Application of ARS

The ARS can reduce the loss of incident light on the surface due to reflection and effectively improve the utilization of light. It is widely used in optical and optoelectronic devices, such as solar cells,[45] light sensors,[57] and displays.[58]

A high optical absorption is a prerequisite for improving the photoelectric efficiency of solar cells. Therefore, researchers are devoted to preparing structures with high absorption to improve the light absorption of solar cells. Cui et al. used an ARS to increase the polysilicon absorption rate from 50% to 95% and confirmed that the antireflection structure can enhance the optical absorption of polysilicon (Figure 4B). On this basis, they designed and fabricated an ARS on a quartz surface and used physical vapor deposition to construct a silicon solar cell with an ARS. By conducting a reflectivity investigation, absorption test, and FDTD simulation of silicon solar cells, it was demonstrated that the antireflection structure can improve the photoelectric conversion efficiency of solar cells. The efficiency of the solar cell with antireflection structure was 10.6%, higher than that without the structure, and the solar cell demonstrated excellent self-cleaning performance.[45]

The solar sensor is an important element in the positioning process of the planetary probe, and it has been used in multiple planetary exploration missions, such as NASA’s Mars Exploration Program. At present, the development of the solar sensor is advancing toward miniaturization; however, a significant drawback is that the sensitivity of the satellite detector is too low to meet the needs of planetary detector positioning, owing to the high reflection from the backplane. Manohara et al. placed a microporous camera on a silicon surface where an ARS was prepared. The surface reflectivity of the silicon with antireflection structure was less than 1%, which effectively reduced the reflectivity influence on the solar sensor, improving the sensor’s sensitivity.[57]

Lu et al. also fabricated an ARS composed of PMMA with fluorescent molecules using nanoimprint technology, achieving an ARS surface reflectance of less than 1%. The ARS was found to increase the absorption strength of dye molecules by suppressing the surface reflection. The ARS PMMA films exhibited an absorption intensity 1.5 times that of flat PMMA films. Meanwhile, the ARS PMMA film demonstrated a higher critical angle (73.1°) than that of the flat PMMA film (43.6°), increasing the fluorescence overflow. The solid angle of the escape cone is calculated from the critical angle of luminescent thin films through Equation (2)

$$\Omega = \int_0^\theta \sin \theta \, d\theta = 2\pi (1 - \cos \theta)$$  (2)

where $\Omega$ is the solid angle of the escape cone and $\theta$ is the critical angle. The total enhancement fluorescence intensity of an ARS is the product of the absorption enhancement and the light cone angle enhancement. It has been demonstrated through calculation and experiment that the fluorescence intensity of the ARS was 18 times the fluorescence intensity of the flat film. This method has excellent universality and does not that absorption or emission wavelengths of the fluorescence are analyzed. It is independent only on the optimized antireflection band.[58]

The nanostructure modulates the distribution of laser energy; thus, the nanostructure can be used to increase the laser damage threshold of quartz. Hobbs et al. fabricated an ARS on the quartz surface by RIE, and the interaction between the ARS and the 1064 nm laser was examined. The ARS can distribute most of the laser energy in the air, slowing the damage of the laser to the material. Compared with the quartz surface without ARS, the laser damage threshold of the quartz surface with ARS was significantly increased from 38.3 to 60 J cm$^{-2}$. Compared with the thin-film antireflection layer, the damage threshold of the ARS was increased from 22 to 60 J cm$^{-2}$, a threefold increase. The ARS focuses the most of the laser energy in the gaps of the structure, thereby increasing its damage threshold compared to a flat surface.[59,60] The ARS demonstrated strong prospects for application.[61]
Solar photothermal technology is an effective way to utilize solar energy, which has gradually attracted the attention of researchers. However, current research into solar thermal conversion is mainly concerned with two issues: increasing absorption and reducing radiation. The ARS can improve the light absorption performance of materials, warranting wide application in the field of photothermal conversion. For example, Wang et al. grew a layer of nanorod black TiO$_2$ on a C surface using a hydrothermal method. This nanorod structure can achieve an absorption rate 60% to 95% higher than that of unstructured film. An infrared camera revealed the temperature of the C cloth with ARS reaching as high as 54 °C, whereas the temperature of the unstructured C cloth was 27 °C. The C cloth with ARS can be used for desalination of seawater, demonstrating a freshwater acquisition of 1.5 kg h$^{-1}$.[62]

Electrochromic materials exhibit tunable optical property under the action of an electric field, reducing the energy consumption of office buildings and residential buildings, which is of great significance for energy conservation. However, the tuning range of transmittance in electrochromic materials is a technical problem in this field. The ARS can enhance optical absorption and transmission, as well as the range of transmittance change. Corn et al. prepared a layer of PEDOT film on ITO by electro-polymerization and used RIE to etch the PEDOT film with a monolayer nanosphere as a mask to fabricate an ARS for the PEDOT film. The reflectance of the flat PEDOT film was 5%, while the reflectance of the PEDOT film with ARS was less than 1.5%. Also, the reflectance of the PEDOT with ARS was lower than that of the flat PEDOT film under different applied voltages.[64] This is of great significance for regulating the change in the transmittance. In order to reduce the cost of preparation, Zhao et al. fabricated TiO$_2$ nanoray arrays with an ARS on the surface and hydrothermally synthesized Prussian blue (PB) on the ARS of the TiO$_2$. Compared to flat PB films, the PB with ARS exhibited a reduced reflectance from 8% to 1% and an increased transmittance from 70% to 78%.[63,64]

SALDI-MS is a suitable technique for detecting small molecules, exhibiting advantages of high sensitivity and rapid detection. However, the main drawback of SALDI-MS is that the absorption rate of the auxiliary substrate is low, and the laser energy of the laser cannot be effectively used. Lu et al. used RIE to fabricate a composite ARS of silicon and Au. The absorption of the ARS was greater than 99.65% at 355 nm, which was applied for SALDI-MS detection. The ARS exhibited high energy efficiency, through which the sensitivity of SALDI-MS was greatly improved. For example, 100 amol μL$^{-1}$ of R6G and 100 nmol μL$^{-1}$ of glutathione can be analyzed. The limits of detection and quantitation are $1.35 \times 10^{-14}$ and $1.35 \times 10^{-7}$ mol L$^{-1}$ on the ARS, respectively.[65]

The ARS can effectively improve the utilization of light energy by suppressing reflection at interface. Although the ARS is limited by the fabrication cost and technology, it is promising for light regulation devices. It is currently used in solar cells, white light sensors, fluorescence sensors, SALDI-MS, electrochromism, seawater evaporation, and laser loss thresholds. There is no doubt that ARS can play an important role in the future due to its novel optical regulation ability.

2.2. ARS Inspired by Butterfly Wings (BWs)

Owing to a delicate hierarchical microstructure, BWs exhibit various excellent multifunction properties, such as super-hydrophobic,[66] iridescent color,[67] and antifogging,[68] and its antireflection function has received particular interest recently. Vukusic et al. found that the reflectance of the black regions on the butterfly Papilio ulysses would increase upon immersion in a broma fluid to match the refractive index, which indicated that the complex nanostructures contribute to the extremely low reflectance of those regions.[69] The biological function of “ultra-blackness,” which means a broadband reflection much lower than theoretical reflection determined by chemical component, is hypothesized to beneficial to courtship display because the adjacent colors may appear more brilliant for sensory bias.[70,71] Additionally, the high absorptance of BWs is helpful in absorbing heat from the sun to facilitate autonomous flight.[72] Different from moth eyes, opaque BWs can employ scattering structures with sizes much larger than the light wavelength. The typical ARS of black BWs are summarized below.

2.2.1. Antireflection Mechanism of BWs

The micromorphology of the black zone on BWs is different from the other colored regions, achieving a high absorptance.[73] Numerous black BWs with ARS were reported.[69,73–93] Although the detailed morphologies are different from each other in these reports, three types of typical structures can be extracted. The first type is a shelf-like structure, as shown in Figure 5 (in yellow circles), also named as an inverse V-type structure[75,80] or ridges[74,75] shown in Figure 5 (in blue circles) or referred to as a honeycomb-like structure[80] or ribs in some other studies. The second type is a nanohole array,[74,75] shown in Figure 5 (in blue circles) or referred to as a honeycomb-like structure[80] or ribs in some other studies. The last one is a bottom layer, shown in Figure 5 (in white circles).

The shelf-like structure featured on a small vertex angle can reflect a small part of the incident light that is not absorbed into the nanohole arrays, resulting in an increase in the overall absorption through multi-absorption. Zhao et al. prepared a α-C film with an inverse V-type structure and found that the reflection of a structured sample is only 1/13 that of an unstructured one.[77] The nanohole arrays can function as a low effective refractive index layer when the dimensions of the holes are smaller than the wavelength and as a backscattering area when the dimensions of the holes are larger than the wavelength; both cases demonstrate a highly absorbing area. The absorption efficiency of nanohole arrays is proved to be higher than that of thin films with the same material.[84] Major absorptance occurs in the nanohole arrays rather than in the ridges.[85] Different from the ordered pattern of the moth eye structure, most of the quasi-honeycomb-like structures on BWs are disordered to avoid reflection with an incident or azimuth angular dependence.[74] The bottom layer is flat and non-structured and can reflect back the light escaping from the two top structures, in which the light will be absorbed again.[80]
2.2.2. Artificial Microstructured Materials Inspired by Butterfly Wings (AMMIBWs)

The hierarchical ARS of BWs is very delicate. It is still very difficult to fabricate such complicated microstructures with current technology; thus, the easier way is to borrow the architecture from BWs.

Han et al. replicated the ARS of BWs with transparent materials, such as silica and poly(dimethylsiloxane) (PDMS).\cite{82,91} The transparent replicas exhibited an antireflection property to some extent.\cite{82} However, the reflection of the replicas were still much higher than those of the original black BWs or silica with a moth-eye structure.\cite{94} The reason may be that the transparent materials cannot absorb the light penetrating through the first antireflection surface. Therefore, the light will arrive at subsequent multiple interfaces without attenuation and be reflected and accumulated at each surface. Apparently, the hierarchical ARS of the black BWs is better suited for absorption applications; for this purpose, it should be synthesized from highly absorptive materials.

Different absorptive materials were used to fabricate AMMIBWs.\cite{76,77} Carbon was naturally first considered by scientists. By calcining BWs in an inert atmosphere, an α-C AMMIBW film was prepared with much lower reflectance than that of a flat α-C film.\cite{77} The absorption intensity of noble metal nanoparticles is very high, especially in the infrared region because of surface plasmon resonance, which makes it a popular candidate as an absorptive agent in AMMIBWs. Gold nanostars were assembled on BWs, in which the near-infrared light absorption of the BWs was enhanced greatly, leading to a water evaporation efficiency as high as 83.3%.\cite{95} Au-CuS combination nanoparticle was reported to show better absorptive property than Au nanoparticle on a BW template.\cite{96} Ag nanoparticles were also deposited on carbonized BWs, resulting in a dramatically improved absorption in the infrared range. Simulation results indicated that a subtle HMS helps to achieve coherent coupling between adjacent resonant systems.\cite{96} This coupling effect is a key factor for surface-enhanced Raman spectroscopy (SERS) as well. The SERS signal magnitude increased when Ag nanoparticles were deposited on different BWs.\cite{95} It is very interesting that the greatest enhancement of the SERS signal was observed at excitation wavelengths most closely matching the color of the BWs. Most noble metal nanoparticles were randomly deposited on BW templates. Meanwhile, Palmer et al. studied SERS on quasi-periodically arranged gold nanostrips on BWs. The plasmonic coupling effects were detected, reaching a peak for an Au thickness of 90 nm.\cite{98}

The hierarchical ARS of BWs can improve the absorption of light as well as increase the specific surface area, which is very important to catalysis as well. In the case involving the noble metal nanoparticles, enhancing the electric-field amplitude of localized surface plasmon resonance (LSPR) by hierarchical ARS of BWs can facilitate photocatalysis even further. Several examples are given below.

The Bi₃WO₆ was employed as a structural material, an absorptive agent as well as a potential photocatalyst to fabricate AMMIBW powder by using BWs as a sacrifice template. And, using the microstructure inherited from BWs, the absorption intensity was improved by more than a factor of two.\cite{86} A C-doped BiVO₄ photocatalyst with HMS borrowed from BWs was synthesized by the sol–gel method. The photocatalytic activity in both the photocatalytic degradation and O₂ evolution from water splitting was greatly improved. It is believed that both the HMS and C-doping contributed to the improvement synergistically.\cite{79} Later, the same group assembled gold nanorods on a BiVO₄ AMMIBW, increasing the absorptance in the wavelength range of 700–1300 nm by up to 25%.\cite{83} Simulation results showed that the electric field amplitude near gold nanorods was amplified by more than 3.5-fold as well. Consequently, the photocatalytic degradation performance of the BiVO₄ AMMIBW was 2.85 times that of the non-structured one. As a high efficiency photocatalyst, TiO₂ has been employed...
2.3. Miscellaneous Bioinspired Antireflection Microstructures

A recent antireflection microstructure was proposed by Yang et al. They fabricated artificial brochosome coatings by employing a double-layer colloidal crystal as templates as well as through electrodeposition technology. The fabrication process is shown in Figure 7B. The artificial brochosome coatings exhibited excellent omnidirectional antireflection in the Vis–NIR range. It is very interesting that the appearance of the brochosome coatings to a ladybird beetle, which is a predator of a leafhopper, may look very much like green leaves.

Finally, the compatibility of this method was demonstrated by constructing the hierarchical architectures with various materials, including metals, metal oxides, and conductive polymers. Subsequent studies showed that the brochosome-like structure has many photonic-related potential applications. Pan et al. synthesized a brochosome-like photoelectrochemical anode with TiO$_2$/WO$_3$/BiVO$_4$, achieving outstanding performance, as high as six times that of a planar WO$_3$/BiVO$_4$ film electrode. Ding et al. fabricated Ag brochosomes; their broadband and omnidirectional high absorbance in conjunction with their hierarchical surface architectures make them a remarkable SERS substrate. Si et al. prepared a hierarchical porous polymeric carbon nitride microsphere by utilizing the solubility difference between cyanamide and dicyanamide and the in situ transformation of PCN precursor from cyanamide to dicyanamide along the wall surfaces of the hierarchical porous SiO$_2$ microspheres. The brochosome-like structure improved the hydrogen evolution activity of polymeric carbon nitride by a factor of 31.7. Guo et al. manufactured similar hierarchical porous carbon spheres with poly(vinylidene chloride-co-vinyl chloride) as a precursor. The hemispherical reflectance of the coatings cast from brochosome-like carbon spheres were as low as 0.14% in the range of 300–2000 nm.

Another novel antireflection structure was found on the black scales of the West African Gaboon viper (Bitis rhinoceros). As shown in Figure 8A, the leaf-like microstructures on the black scales consist of crowded crests with an average height of 30 ± 4 nm. Branched nanoridges with an average height of 600 ± 10 nm and thickness of 60 ± 10 nm covered the entire crests. The reflectance of these black scales was four times lower than the reflectance of other scales over a broad wavelength range. The independence of the view-angle with respect to the low reflectance of the black scales were believed to be the synergistic result of the microstructures and dark pigments. This leaf-like HMS was mimicked by Li et al. with sequential thermal actuations on Ti$_3$C$_2$Tx MXene. Broadband light absorption (up to 93.2%), improved light-to-heat performance (equilibrium temperature of 65.4 °C under one-sun illumination) and high steam generation performance (1.33 kg m$^{-2}$ h$^{-1}$) were demonstrated as the resulting prominent properties of the microstructures. The bioinspired MXene was also processed into wearable heaters dual-powered by sunlight and electricity to display its scalability resulting from its mechanically deformed structures.

Similar micro/nano hybrid structures were fabricated on the metallic surface by an ultraviolet laser direct writing approach. Typically, micropillars with a diameter and height in dozens of microns were induced by laser pulse to increase the multireflection and cotton-like nanostructure of their hierarchical surface architectures—soccer-ball-like microscale granules with nanoscale indentations (Figure 7A). They fabricated artificial brochosome coatings by employing a double-layer colloidal crystal as templates as well as through electrodeposition technology. The fabrication process is shown in Figure 7B. The artificial brochosome coatings exhibited excellent omnidirectional antireflection in the Vis–NIR range. It is very interesting that the appearance of the brochosome coatings to a ladybird beetle, which is a predator of a leafhopper, may look very much like green leaves.

Finally, the compatibility of this method was demonstrated by constructing the hierarchical architectures with various materials, including metals, metal oxides, and conductive polymers. Subsequent studies showed that the brochosome-like structure has many photonic-related potential applications. Pan et al. synthesized a brochosome-like photoelectrochemical anode with TiO$_2$/WO$_3$/BiVO$_4$, achieving outstanding performance, as high as six times that of a planar WO$_3$/BiVO$_4$ film electrode. Ding et al. fabricated Ag brochosomes; their broadband and omnidirectional high absorbance in conjunction with their hierarchical surface architectures make them a remarkable SERS substrate. Si et al. prepared a hierarchical porous polymeric carbon nitride microsphere by utilizing the solubility difference between cyanamide and dicyanamide and the in situ transformation of PCN precursor from cyanamide to dicyanamide along the wall surfaces of the hierarchical porous SiO$_2$ microspheres. The brochosome-like structure improved the hydrogen evolution activity of polymeric carbon nitride by a factor of 31.7. Guo et al. manufactured similar hierarchical porous carbon spheres with poly(vinylidene chloride-co-vinyl chloride) as a precursor. The hemispherical reflectance of the coatings cast from brochosome-like carbon spheres were as low as 0.14% in the range of 300–2000 nm.

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or nanoparticles covered on the micropillars to decrease the equivalent refractive index. Ultralow reflectance can be achieved on different metals. For instance, a reflectance as low as 0.29% was demonstrated on the surface of Ti,\cite{53} which is commonly used for space cameras. Laser direct writing could achieve a printing speed as fast as 10 million elements per second\cite{104} and is a well-developed technology to fabricate diverse microstructures with different functions. It is a promising preparation technology with alluring prospects for bioinspired microstructures.

Antireflection microstructures also were found on birds. McCoy et al. revealed the relation between super black plumages from five species of birds of paradise (Aves: Paradisaeidae) and their microstructures.\cite{71} It can be seen from Figure 8B that highly modified barbules with microscale spikes along the margins were discovered on super black feathers. The resulting array of deep, curved cavities between the smallest branches of the feather vane trapped incident light and absorb it in multiple scattering and reflection. The lowest reflectance (0.05–0.31%) was achieved when viewed from the distal direction. In further investigation, McCoy et al. examined super black plumages in 32 bird species from 15 families and five orders that were significantly darker than the normal black plumages for their microstructural variation.\cite{70} These super black feathers were classified into five types and were believed to have evolved independently multiple times. All of them shared some common features, such as a minimal horizontal exposed tip-top area and micrometer-scale deep cavities. This phenomenon is a typical convergent evolution. We believe that artificial super black plumages will be fabricated in the near future.

McCoy et al. also reported the super black phenomenon related to microstructures on the peacock spiders.\cite{96} One type of microstructure is an array of cuticular bumps, which was found in two species and may function like a reduced version of the moth-eye structure. The other type of microstructure is micro-brush-like scales on top cuticular bumps, which is illustrated in Figure 8C-b,c; this type of microstructure was only found in Maratus karrie and may function like an enhanced version of the moth-eye structure.

3. Bioinspired Reflective Microstructures

Although solar light is necessary for all creatures on the earth, it can be harmful, considering the dangers of overheating and exposure to predators. High reflectance over the entire Vis–NIR
band for thermal regulation or in a tunable band for camouflage would be needed in those circumstances. The architectures for these two properties are quite different. The research on these two biological microstructures are introduced below.

3.1. Bioinspired Highly Reflective Microstructures in Broadband

High reflection through the entire Vis–NIR band can be easily obtained with metal materials in our daily life. However, the only type of material available for other organisms is dielectric material. It is also common to achieve a high level of whiteness by the diffuse reflection of transparent dielectric powders or fibers in broadband. Nevertheless, organisms need to accomplish high reflection with as small depth and weight as possible. Therefore, different high-efficient scatterers and geometric organisations have evolved. Herein, we introduce them according to the dimensions of the scatterers or reflectors.

3.1.1. 3D Scatterers

Brilliant whiteness was observed on the scales of Cyphochilus spp., a type of white beetle living in equatorial regions, by Vukusic et al. for the first time. A high whiteness value of 60 was observed in a thickness of only 5 μm. A thickness hundreds of times greater than normal was expected for an equivalent-quality whiteness. The remarkable broadband scattering efficiency was attributed to the 3D network of interconnected cuticular filaments with diameters of ~250 nm (Figure 9A,B). Detailed optical properties of the scales were measured. Similar 3D network and high-broadband reflections were also revealed in other white beetles—Lepidota stigma and Calothyrsa margaritifera. The 3D morphology of Cyphochilus scale was investigated by X-ray nanotomography and was used in simulation studies. The simulation results of Wils et al. showed that the natural morphology was the optimal design for broadband reflection. However, Burg et al. argued that a slightly lower filling fraction might be more optimal. Vukusic et al. assumed the network morphology to be optimized by finding a balance between increasing the scattering center numbers and avoiding optical crowding. From another point of, Burresi et al. and Jacucci et al. explained the superiority of the network morphology by shorter transport mean free path, which refers to the average distance that light travels before losing the information of its original direction. The transport mean free path is commonly tens of microns in white materials with similar refractive indices but only about 1.40–1.47 μm in Cyphochilus scales.

The acquisition of high whiteness in a small thickness is also necessary in the paper and coating industries. Some efforts have been made to fabricate bioinspired 3D polymer networks with high broadband reflectance. Julia Syurik prepared porous PMMA films by foaming with CO₂ saturation and optimized their pore diameter and fraction for high broadband reflectance (Figure 9I). Reflectance of 57% and 90% was achieved in 9 and 60 μm thick thin films, respectively. Nevertheless, the transport mean free path of the porous PMMA films was between 3.5 and 4 μm, which is lower than that of normal paper but still much higher than that of Cyphochilus, implying that some key factors of the structure might be neglected. A higher reflectance of 94% was reported in 12 μm thick bioinspired porous cellulose acetate films by Burg et al. through the liquid–liquid phase separation process (Figure 9H), with a lower filling fraction. However, more research needs to be carried out to determine whether this is the missing key factor. Zou et al. fabricated another bioinspired porous PS film by a water-vapor-induced phase separation method (Figure 8C-a).
The film with a thickness of 3.5 μm exhibited a diffuse reflectance of 61%. The corresponding transport mean free path in the visible range was below 1 μm, even shorter than that of the Cyphochilus beetle. The potential application of this film as a water vapor sensor was demonstrated as well.

Although a bioinspired material with even better performance than that of a nature prototype has been constructed under the inspiration of white beetles, there are still improvements that can be implemented. The most obvious one is to prepare a network with higher refractive index materials. A higher refractive index can result in a higher scattering efficiency for the nanonetwork. However, all the structural parameters need to be optimized again.

### 3.1.2. 2D Reflectors

One-quarter wavelength thin film stacks have been used as reflectors in a narrow band by humans for a long time. To extend the band of reflection, two fish species in the family Trichiuridae developed a strategy of a thin film stacks with random thickness. The disordered stacks worked as camouflage by generating a silvery glitter at the water surface when viewed from beneath. A similar phenomenon was found in squid (S. lineolate), Japanese Koi fish (Cyprinus carpio), and lookdown (Selene vomer). Typically, the two types of films in the stacks are guanine crystals sheets and cytoplasm. The difference in the refractive index between these two substances is so small that it is difficult to believe that they can produce such a wide reflection band over the entire visible range. According to Zhao et al., stacks of guanine platelets in the lookdown generated a narrow reflection with color when viewed through a microscope. The colors varied owing to the random yaw angles of the stacks and were mixed together to form a silvery macroscopical appearance.

### 3.1.3. 1D Scatterers

Fibers and their products have been widely used to reflect light through scattering in daily life, such as in papers and fabrics. In fact, the first fibers in both examples originated from organisms. Thus, it would not be a surprise that many plants and animals use fiber to shield the sunshine. Ye et al. reported the shadow function of the hollow hairs on the poplar leaf. It is very interesting that the hairs are on the lower surfaces of leaves and will turn toward the outside only when the plant is short of water. At that time, the hairy layer will protect the plant.
from sunburn and dehydration. A hollow PS fiber was fabricated in the light of poplar leaf hair, which demonstrated the abilities of light block and superhydrophobic, without surprise. Similar hair was found in the lower surfaces of Boehmeria nivea, which revealed a similar function and similar bioinspired fiber was produced by Yu et al.\cite{121} However, the reflective efficiency and superiority of the hair structure, compared with the fibers already used, is left to further research.

The most famous high-reflection fiber from natural creatures is the hair of the silver ant (Cataglyphis bombycina). It was first revealed by Shi et al.,\cite{19} showing that triangular hair could highly reflect sunlight because of total internal reflection. Willot et al. calculated the range of incident angle in which total internal reflection would occur with an optical ray-tracing model.\cite{122} However, a quantitative comparison to normal round fiber for scattering efficiency is still needed to demonstrate the superiority of the triangular fiber. In addition, the triangular fiber with a much larger diameter has been developed commercially. Therefore, the superiority of smaller diameter or the optimal diameter needs to be investigated before the development of new fabricating technology.

To increase the number of scattering centers, comet moth (Argema mittrei) evolved a silk fiber with plenty axial long voids.\cite{124} The microstructure and properties were imitated with regenerated silk fibroin as well as poly(vinylidene difluoride). Xie et al. discovered similar but shorter axial voids in the hairs of white beetles Goliathus goliatus (Figure 9B,E).\cite{114} The voids could enhance the reflectance in whole visible band, according to simulation results.

3.1.5. Prospects

Broadband reflective materials containing scatterers with lower dimensions are common in our life. Zero dimensional scatterers, that is, transparent ceramic particles, are most widely used in white paints for its lower price and higher scattering efficiency, which originate from their higher refractive index. 1D scatterers, that is, fibers, are mainly utilized in white textiles and papers for its flexibility. However, most fibers are constructed with organics, which refractive index are usually around 1.5. Sometimes zero dimensional scatterers such as TiO$_2$ nanoparticles are employed in fibers for a higher scattering efficiency and a higher whiteness as consequence. 2D reflectors, that is, multilayer thin films, are usually prepared by vacuum process, leading to a high cost and show themselves only in where very high reflectance is needed such like in lasers. Normally high reflectance can be achieved in only a narrow band, but a broad band can be realized too by varying the thickness in different layer;\cite{127} just like what Trichiuridae fishes do. 3D scatterers are rare and still in the research stage.\cite{128} Bioinspired high reflective microstructure is a shortcut to achieve high reflection. And the fabrication of bioinspired microstructure with higher refractive index materials can generate a better performance.

3.2. Bioinspired Dynamic Photoregulatory Microstructured Materials

In nature, BWs and peacock feathers display vibrant colors, which are caused by the reflection of a specific wavelength of light by their structures. Through SEM and AFM, it was observed that these biological surfaces are composed of specifically ordered microstructures, namely, photonic crystals. The photonic bandgap (PBG) is an important feature of photonic crystal and is related to many factors. According to the Bragg diffraction equation

$$m\lambda=2nd\sin\theta$$

where $m$ is the diffraction order, $\lambda$ is the diffraction peak wavelength, $n$ is the effective refractive index of the material, $d$ is the lattice period or lattice spacing, and $\theta$ is the angle of the incident light with respect to the lattice plane. According to Equation (3), the incident angle, effective refractive index, and lattice spacing are the main factors affecting the PBG. This position of the PBG can be changed by adjusting the three parameters, and the position of the reflection peak of the photonic crystal can be changed as well. Therefore, the above parameters can be changed by external stimuli to realize the control of the reflection peak position of the photonic crystal.

3.2.1. Adjusting the Equivalent Refractive Index

Tian et al. penetrated the acrylamide solution into the P(ST-MMA-AA) photonic crystal template and then photopolymerized it to prepare a photonic crystal responsive to humidity.\cite{129} The responsive photonic crystal achieved reversible color changes from transparent to purple, blue, cyan, green, and red
under different humidity conditions, covering almost the entire visible range. In order to improve the stability of photonic crystals, Song et al. fabricated inverse opal silica photonic crystals and then filled the photonic crystals with the response molecule tetraphenylethene polymer (TPEP). When tetrahydrofuran and acetone vapor interact with TPEP, the effective refractive index of the photonic crystal changes, which causes the color of the photonic crystal to change. The result demonstrated that the reflection peak of a photonic crystal can be adjusted by organic molecules, such as tetrahydrofuran and acetone.

In order to realize the large-area preparation and patterning of photonic crystals, Gu et al. used an inkjet printing method to prepare mesoporous silica photonic crystals, as shown in Figure 10. The leaves appeared green (photonic crystal color), as monodispersed mesoporous silica and ordinary silica microspheres were printed into a leaf shape. When the photonic crystal pattern was exposed to ethanol, the trunk remained green because the ethanol could not enter the solid silica nanospheres, and the overall effective refractive index remained mostly unchanged. However, ethanol can enter the mesoporous silica photonic crystal, causing a redshift in the leaves owing to the large change in the overall effective refractive index.

3.2.2. Control Reflectance Peak Using Dielectric Constant by LSPR

It is widely known that plasmonic nanostructures can be utilized for color generation, owing to the strong interaction with light. This property has wide application in many fields, such as sensing, imaging, and displays. Noble metals such as Au, Ag, and Cu are materials commonly used to generate plasmonic nanostructures. The surface plasmonic is caused by free-electron oscillations at a metal–dielectric interface. In ancient times, these noble materials were used in objects such as the Lycurgus cap and church windows. The LSPR properties can be tuned by altering the size, morphology, composition, and dielectric function of the surrounding medium of these noble metal nanostructures.

The significantly enlarged scattering or absorption at resonance wavelengths cause the plasmonic structure to exhibit distinct colors. Such structures can be orders of magnitude thinner than pigment. Compared with the photonic crystal as we mentioned above, plasmonic nanostructures have greater potential in producing images with high resolution.

The use of such dielectric nanostructures for color generation has attracted more interest. However, most of the previous studies have focused on static colors in nanolithography providing complex plasmonic building blocks that generate a rich range of colors. The dynamic response to external stimuli in a reversible manner envisions excellent opportunities in creating novel optical bioinspired microstructured materials and devices. It is highly desirable to reverse tune the colors presented by plasmonic pixels over a wide range. The active plasmonic color can be obtained through several approaches. In one case, individual plasmonic elements with pre-determined colors tune the subpixel color to turn on/off. An alternative to realization of the dynamic plasmonic color display is to take advantage of plasmonic coupling between adjacent noble metal nanoparticles by controlling their assembly and disassembly. By various stimuli such as stress, electric field, pH, and temperature, the LSPR properties could be regulated. In one approach, combined with conductive polymers and phase-change
materials, changes in the state of the materials can be presented as a typical on/off switch.\textsuperscript{117,118} Another way is to take advantage of the electro-redox chemistry to modify the morphology, chemical composition, and fundamental coupling mechanism of plasmonic nanoparticles in a reversible manner.\textsuperscript{136,139,140}

Chameleons developed camouflage by the introduction of variety of colors that can assist in avoiding detection from natural predators. The key to this bioinspired technology is to realize electrically driven actuation of broad reflection bands. Kobayashi and co-workers carried out an electrochromic device fabricated with Ag nanoparticles, which exhibited reversible color changes between the transparent and vivid colored states fabricated with Ag nanoparticles, which exhibited reversible color changes between the transparent and vivid colored states in response to an electric voltage (Figure 11A).\textsuperscript{141,142} Depending on the direction of the electric field, the oxidation and reduction of the Ag atoms processes have been conveniently controlled, corresponding to the bleaching and coloring process, respectively. Ag is continuously deposited on the flat and the rough particle—modified ITO electrodes. By varying the potential, the size of the Ag nanoparticles could be maneuvered, which allows the dynamic modulation of the optical signals within seconds. They cell turns to a mirror state and a black state from the transparent state, respectively. Wang et al. prepared with a mechanical chameleon based on the combination of bimetallic nanodot arrays and electrochemical bias to allow for plasmonic modulation.\textsuperscript{143} As illustrated in Figure 11B, a biomimetic mechanical “chameleon” as well as a $64 \times 32$ “plasmonic cell”-matrix was designed, effective in the full-visible region of 430–650 nm. These fabrications were operated by altering the Au/Ag core-shell structures through an electro depositing/stripping process. This approach permits real-time light manipulation readily matchable to the color setting in a given environment. This capability was used to fabricate a biomimetic mechanical chameleon with dynamic color rendering covering the entire visible region.

However, for bio-camouflage, not only is multiclor desired, but also with stable cycle performance. In a conventional electrochemical process, anodized aluminum oxide (AAO) and SiO$_2$ templates\textsuperscript{144} were used to avoid formation of large agglomerates after repetitive deposition/dissolution cycles. However, these templates worked well in isolating the nanoparticles from each other and therefore contributed to the improved reversibility, which involved complex procedures. Our previous work presented a new strategy to prepare electrochromic film through the electro-responsive dissolution and deposition of Ag on hollow shells of Au/Ag alloy as stable anchoring sites, and eliminated the random self-nucleation during the Ag deposition to achieve optimal reversibility in color switching in the range from near-infrared to a shorter wavelength.\textsuperscript{145}

3.2.3. Control Reflection Peak by Photonic Lattice Changing

According to the Bragg diffraction equation, the reflectance peak can be shifted by changing the lattice distance. Consequently, the expansion and contraction of the photonic crystals may influence the coloration in an environment with a fluctuating temperature owing to the inherent dependence of the reflection wavelength on the interparticle separation. Ge et al. prepared a flexible photonic crystal film by mixing ethylene glycol (EG), poly(ethylene glycol) diacrylate (PEGDA), and SiO$_2$.\textsuperscript{146} When an external force was applied to the photonic crystal film, the PC film became deformed, and the lattice distance $d$ of the silica colloidal crystal changed accordingly, causing the color to change significantly (Figure 12A). Further selective polymerization of the elastic photonic crystal film can yield optical crystal regions with different mechanical properties. Therefore, when an external force is applied, the change in the lattice spacing $d$ of the photonic crystal pattern region is much larger than that of the background region, causing an asymmetrical color change and the appearance of a pattern. After the external force is removed, the crystal
structure is restored to the original state; thus, the force controls the color change. In controlling the reflection peak and color of the photonic crystal by force, although excellent optical performance can be obtained, it cannot be controlled precisely. Ozin et al. fabricated composite photonic crystal with polyferrocenylsilane and SiO$_2$ on the ITO.$^{[147]}$ This composite photonic crystal and LiClO$_4$/PC then formed a photonic crystal color changing device (Figure 12B). In this device, when the voltage is not applied, the reflection peak of the photonic crystal is 500 nm, corresponding to a green color. When the voltage is applied, the polyferrocenylsilane expands, resulting in a larger SiO$_2$ pitch and a redshift in the reflection peak position. With a continuous change in the applied voltage from $−2$ to 2 V, the color changes from green to red (from 500 to 800 nm). The precise control of the reflection peak and color of the photonic crystal by the applied electric field is realized. Hayward et al. constructed a photonic crystal using poly(n-isopropyl acrylamide)(PNIPAM) as a response that was sensitive to temperature changes by alternate spin coating.$^{[148]}$ The photonic crystals exhibited a thermally sensitive swelling effect in the water environment. When the temperature changes from 20 to 50 °C, the swelling of the PNIPAM changes the lattice spacing of the photonic crystals, shifting the reflection peak position by more than 300 nm and resulting in macroscopically visible color changes on the photonic crystal surface. Photonic crystals exhibit slow discoloration and necessitate expensive polymer preparation, which cannot meet the needs of the application. In order to improve the response time, Li et al. filled the link of SiO$_2$ photonic crystal with poly(vinyl alcohol) (PVA) to obtain a composite photonic crystal of PVA and SiO$_2$.$^{[149]}$ When water vapor is present, the rapid swelling of PVA causes the photonic crystal lattice spacing to increase, shifting the reflection peak from 650 to 700 nm, with a response speed of less than 1 s.

3.2.4. Control Reflectance Peak by Magnetic Nanoparticles

Recently, magnetic fields have been widely used to regulate the optical performance of magnetic photonic crystals by controlling its space and orientation.$^{[150–152]}$ This can be applied to liquid crystals$^{[153,154]}$ adaptive camouflage$^{[155,156]}$ and sensors.$^{[157]}$ By taking advantage of the novel sol–gel process, Fe$_3$O$_4$@SiO$_2$ nanocrystal clusters can be fixed to stable photonic labyrinths.$^{[20]}$ The lithographically patterned nonmagnetic substrate was successfully introduced to modulate the local magnetic field distribution to obtain a more organized labyrinth structure. In addition, by varying the size of the Fe$_3$O$_4$@SiO$_2$ nanocrystal clusters, photonic labyrinths with different reflected colors can be readily obtained along with self-assembly (Figure 13A). A drop of Fe$_3$O$_4$@SiO$_2$ aqueous was sandwiched between two cover glasses, and the suspensions of superparamagnetic soft spheres were transformed into a single-crystalline-like hexagonal structure, demonstrating the further separation of diffraction spots.$^{[151]}$ As the magnetic field gradually increased to 1460 G, a higher diffraction intensity of 80% was easily observed. During this process, the diffraction wavelengths of the 3D photonic structures also experienced a blue shift (Figure 13B). Yin et al. prepared the FeOOH ellipsoids coated by silica and transformed to 3D ordered structures by self-assembly with anisotropy in both morphology and magnetic properties.$^{[152]}$ Furthermore, their photonic properties can be widely tuned by varying the external magnetic field. When the magnetic fields were either parallel or perpendicular to the incident light, the intensity of reflectance both reached a maximum, resulting in an overall U-shaped profile of the reflectance peaks (Figure 13C). In addition, a liquid crystal was constructed using ferrimagnetic inorganic nanorods (FeOOH nanorods), and their optical properties can be instantly controlled by manipulating the nanorod orientation in an external magnetic field of just 1 mT (Figure 13D). Yin et al. created patterns of different polarizations in a thin composite film and controlled the transmittance of light in particular areas by combining magnetic alignment and lithography processes. In addition, different bright responses are achieved within the same film.$^{[153]}$ Furthermore, with the incident light perpendicular to the $x$–$z$ axis or along the $γ$-axis, it is found that the elliptical shape magnetic AuNRs (gold nanorods) could be selectively excited on transverse or longitudinal modes by changing the direction of the external magnetic field, displaying two typically observed bands in the extinction spectrum.$^{[154]}$ When the angle between the direction of the incident light and the magnetic field was changed from 90° to 0°, the
resonance band at 700 nm became significantly suppressed, and a slight change was observed at 520 nm. In contrast, when AuNRs were aligned along the y-axis, the electron oscillation only occurred along the short axes, leading to the excitation of the transverse plasmon. Thus, the modulation of the optical properties of magnetic AuNRs can be attributed to the mechanism of plasmonic excitation on the transverse or longitudinal axis in the varying magnetic fields. The excitation of plasmonic modes of AuNRs can be controlled under the incidence of both ordinary and polarized light.

Moreover, Kim et al. reported a novel trilayered microdisk composed of one middle magnetic layer containing BaFe₁₂O₁₉ sandwiched between two distinctive photonic layers. The thickness of each layer of the photonic microdisks was 30 μm, exhibiting red, blue, and no color, depending on the magnetic field orientation, as shown in Figure 13E. The unique structure can provide a permanent magnetic moment for the photonic crystals and significantly broaden the use of photonic crystals in the mode of active color pigments. Furthermore, a new type of photonic crystal PDMS fiber was synthesized, exhibiting a tunable structural color upon exposure to an external magnetic field (Figure 13F). It displayed brown in the absence of an external magnetic field; however, upon application of the external magnetic field, it turned yellow-green, similar to leaves. The magnetic field responsive fiber was composed of the core-shell structure. The core comprised embedded ethylene glycol droplets, which contain Fe₃O₄@C nanoparticles positioned in PDMS fiber in a microtubule. The shell consisted of pure PDMS coated on the surface of the fiber to prevent the evaporation of ethylene glycol molecules, smoothing the surface. Furthermore, it is confirmed that the PDMS fiber also has excellent mechanical properties through a series of experiments, such as stretching and twisting.

In addition, a novel Fe₃O₄@SiO₂/PEG acrylate photonic crystal humidity sensor was fabricated by combining magnetic assembly and photopolymerization, which exhibited different colors according to the change in humidity. Fe₃O₄ particles coated with a silica layer were first dispersed in a mixture of PEGDA and poly(ethylene glycol) dimethacrylate solution with photo-initiator 2,2-dimethylpropionic acid. Finally, a precuring mixture was sandwiched between a regular cover glass and a fluorinated glass slide for photopolymerization. The effects on sensitivity and response speed of the cross-linking (CL) level...
and film thickness were explored, indicating that Fe₃O₄@SiO₂/PEG acrylate film with a CL of ~50% and a thickness of ~60 μm exhibits the best performance (Figure 13G).

4. Bioinspired Infrared Radiative Microstructured Materials

Thermal radiation enables the operation of many ubiquitous modern technologies, including electronic circuits, aircraft and spacecraft components, clinical warming devices, power generation platforms, building environment control systems, infrared detection, and radiative cooling. The thermal radiative energy from a hot object is characterized by the Stefan–Boltzmann law, \( P = \varepsilon \sigma T^4 \), where \( \varepsilon \) is the emissivity of the object, \( \sigma \) is the Stefan–Boltzmann constant, and \( T \) is the temperature of the surface. In addition, the emissivity is a material-dependent parameter that varies with the wavelength and temperature. When the temperature of an object is fixed, the wavelength specific thermal emissivity is equal to the optical absorption of the surface, for example, \( \varepsilon(T,\lambda) = \alpha(T,\lambda) \). At ambient temperatures, the thermal radiative energy primarily comes from infrared wavelengths. One can engineer the infrared radiation emitted by coating the surface with photonic crystals and optical structures. To date, a large number of infrared radiative materials have been introduced in modern society. Recent reports have focused on the dynamic and effective regulation of the infrared radiation of materials, specifically with regard to thermal regulation and anti-infrared detection. In such configurations, the infrared radiation of the material is dynamically modulated with an external input or significantly enhanced by strong light and matter interaction, e.g., photonic crystals, surface phonon resonance, and surface plasma resonance.

Nature has optimized materials and structures for infrared radiation over the course of millions of years through natural selection. The result is highly complex and sophisticated engineering models at various multi-scales that have inspired humanity throughout history. Bioinspiration involves identifying nature’s design principles and developing sustainable solutions for infrared radiation in modern society. Learning from nature and applying the engineering principles of nature is a promising approach, not only for generating sustainable solutions for dynamic infrared radiation regulation but also for achieving revolutionary advances in the design and fabrication of multi-wavelength optical regulation materials and systems.

4.1. Optical Engineering in Nature

Through the use of limited materials, optimally designed micro- and nanostructures, and tightly regulated processes, nature demonstrates exquisite control of light–matter interactions at various length scales. In fact, control of light–matter interactions is an important element in the so-called evolutionary arms race and has led to highly engineered optical materials and systems. Here, a brief review is introduced to focus on optical regulation models, manifested in species such as Cephalopoda, the silver ant, beetle, and yak.

4.1.1. Dynamic Regulating Optical Performance

The dynamic color-changing skin of animals (e.g., Cephalopoda, chameleons, and hummingbirds) represents an abundant source of inspiration for infrared regulation systems. For instance, the patterning and coloration of cephalopod skin can be altered autonomously and repeatedly for the purpose of concealment or signaling (Figure 14A). Such remarkable feats stem from chromatophore pigment cells (as part of larger chromatophore organs) and reflective cells called iridocytes. The two types of cells operate in tandem but perform distinct optical functions. The adaptive chromatophore pigment cells contain pigment granule—packed internal sacculi, which expand and contract through the mechanical action of radial muscle cells. The adaptive iridocytes contain alternating arrangements of membrane-enclosed nanostructured protein layers and extracellular space, for which the geometries and refractive index differences are altered via a biochemical signaling cascade. Accordingly, the unique structure and function of cephalopod skin has motivated the engineering of various unconventional color- and appearance-changing technologies, including biomimetic soft active surfaces, optoelectronic displays, sm smart radiation devices, and adaptive infrared camouflage. In this regard, natural squid skin and its constituent components exhibit nearly all of the capabilities required for dynamic infrared regulation, making them promising models for novel thermoregulatory platforms. Mammal animals living in extremely cold environments have an incredible ability to keep their bodies warm. The polar bear, Tibetan antelope, and yak use their thick fat fur covered by hollow and crimped hair to effectively absorb and reflect infrared radiation from their bodies, making themselves invisible, even under an infrared camera. In contrast to the polar bear, the yak lives in a cold plateau area at an elevation of more than 4000 m and has thick covered long hair with a large amount of microcrimps (Figure 14B). The black fur and hair not only absorbs visible and infrared radiation from the sun that warms the body but also prevents the thermal radiation generated from inside the body from leaving the body. The feature of a single yak hair shows various natural spiral microcrimps. In addition, the stretched yak hair has shown the ability to recover its original spiral microcrimps, like a spring, when the constraint is released. The fine and coarse parts of the hair both display solid cross sections without porous medulla, indicating the high significance of hair microcrimps in its comprehensive warmth retention.

4.1.2. Multi-Wavelength Regulation Optical Performance

Some insects living in the desert can survive in extremely high temperatures owing to their evolution of a novel body surface. The silver ants of the Sahara desert may reach maximal foraging activities when temperatures of the desert surface reach as high as 60 to 70 °C. In order to survive under these conditions, they need not only reduce the absorption of solar radiation but also be able to efficiently dissipate excess heat generated by its own infrared radiation. Wehner et al. showed that the silvery appearance of the ants is created by a dense...
absorbed and dissipated heat energy. However, the influence of cuticular structures on infrared radiation is still largely unclear. Pavlović et al. reported the micro- and nanostructured setae covering the elytra of the longicorn beetle Rosalia alpina, which help the insect to survive in hot, summer environments (Figure 14C). The hind wings and abdomen are protected by subcylindrical blue-grey elytra (hardened forewings), with several dominating black patches. The long antennae and legs have the same blue-grey coloration, with striking black tufts of hair-like structures on the central segments of the antennae. The specific, velvety appearance is created by a large number of very fine setae—transparent hair-like structures on the blue-gray zone of elytra. A) Reproduced with permission. Copyright 2017, American Chemical Society. B) Reproduced with permission. Copyright 2018, Elsevier B.V. C) Reproduced with permission. Copyright 2019, Elsevier B.V.

Figure 14. A) a) Blue-green iridescence and white scattering leucophore stripes in cuttlefish (Sepia apama). b) Camouflaged S. apama with pink iridescent arms and white markings caused by leucophores. c) Iridescent spots in the squid Loligo pealeii. d) Blue-ringed octopus, Hapalochlaena lunulata, well camouflaged in a laboratory tank. e) Bright blue iridescence is typically seen when a blue-ringed octopus flashes its rings. f) Electron microscopy image of the blue rings, showing closely packed iridophore plates (scale bar 1 μm). g) Brown, red, and yellow chromatophores of the squid L. pealeii (scale bar 1 μm). h) Combination of chromatophores and iridophores to illustrate the range of colors (scale bar 1 mm). i) Electron microscopy image showing iridophore plates (ir.) and spherical leucophores (leuc.) of cuttlefish (Sepia officinalis) skin (scale bar 1 μm). B) Yak living in cold plateau area with thick and warm fur and hair layers, a) photograph of a yak living in the Tibet plateau at more than 4000 m above sea level, b) raw yak hairs with guard and down hairs. C) a) Optical reflection microscopy image of a boundary between gray (on the left) and black (on the right) areas of R. alpina elytra. In the black area, the scales are just a dark shadow on the rugged cuticular surface, Inset is a Rosalia alpina characterized by six prominent black patches and a blue-gray body. b) Elytra are shown within the red rectangle. Grating-like structure and a herringbone shaped sub-wavelength grating with a lattice period of 1 μm, observable on the R. alpina scale at higher magnification. Inset is an individual scale of R. alpina, recorded on a SEM. c) Tent-like-organized scales concentrated in the black patch of elytra; d) rugged elytral surface with polygonal depressions and dark scales; e) hairs covering the blue-gray zone of elytra. A) Reproduced with permission. Copyright 2017, American Chemical Society. B) Reproduced with permission. Copyright 2019, Elsevier B.V. C) Reproduced with permission. 

array of triangular hairs with two thermoregulatory effects: one is the enhancement of reflectivity of the ant body surface in the visible and near-infrared range of the spectrum, where solar radiation peaks; the other is the increase in the emissivity of the ant in the MWIR. In particular, the latter effect enables the ant to efficiently dissipate heat back to the surroundings via blackbody radiation under full daylight conditions. This biological solution for a thermoregulatory problem may lead to the development of bioinspired coatings for the radiative cooling of objects. Different from silver ants, some insects regulate their body temperature through the cuticle, whose colour, structure, and material properties determine the amount of absorbed and dissipated heat energy. However, the influence of cuticular structures on infrared radiation is still largely unclear. It seems that the scale-like setae, covering the black patches of the elytra, efficiently absorb light, owing to the radiation trap effect in the visible part of the spectrum. Meanwhile, the setae of the entire elytra significantly contribute to the radiative heat exchange in the infrared part of the spectrum. From the biological point of view, insect elytra facilitate camouflage, enable rapid heating to the optimum body temperature, and prevent overheating by emitting excess thermal energy.

4.2. Dynamic Infrared Radiation Regulatory Microstructured Materials

Infrared regulation materials are the main inspiration from the active color-changing squid skin, which can dynamic modulate its radiation energy in infrared wavelength by an external stimulus. Because the object emits infrared radiation, the regulation infrared radiation can be used to infrared camouflage and thermoregulation. As mentioned above, the Stefan–Boltzmann law reveals that the emitting infrared energy is relative to ε and T at ambient temperatures. Thus, the dynamic regulation of the ε of materials at infrared wavelengths facilitates infrared camouflage and thermoregulation.

Infrared camouflage is a vitally important technique for the purpose of cloaking in thermal imaging, which has attracted
an increasing amount of attention for many commercial and military applications.[194–196] However, the infrared detection mainly relies on thermal cameras, which can only detect and visualize thermal radiance pattern from targets throughout atmospheric transparent windows (3–5 and 8–14 μm). Usually, the thermal cameras do not directly reflect the real temperature of an object; thus, infrared camouflage can be realized by modulating the temperature or thermal emissivity. As most high-temperature targets need to be hidden from surroundings at low temperature, the engineering of emissivity is an alternative and practical way for thermal camouflage. However, the blending of the thermal image of an object naturally into the dynamic surrounding environment remains a great challenge. Recent reports have focused on a series of materials that can change their infrared radiation property under a voltage or particular temperature.[189,197–206]

Among these dynamic infrared regulatory materials, VO₂ is well known for its novel metal–insulator transition, which can change from transparent to opaque at infrared wavelengths.[197] It has also been intensively investigated as an adaptive infrared radiation regulation material. Xiao et al. prepared a fast adaptive thermal camouflage device based on VO₂ film.[198] The device seems to achieve rapid switchable thermal camouflage with low power consumption and excellent reliability. Chanda et al. reported an adaptive infrared camouflage system by a VO₂ cavity-coupled tunable plasmonic system, which can be engineered to operate at any technologically relevant wavelength (Figure 15A).[199] This system demonstrates the active thermal camouflage of multispectral infrared information that was encoded on a designer surface composed of sub 20 μm pixels. Zhou et al. developed a VO₂-based metamaterial emitter, which converts broadband thermal-switching light to MWIR atmospheric windows.[200] At room temperature, the emitter radiates energy in both the 3–5 and 8–14 μm atmospheric windows. At high temperature, the radiation peaks move outside the atmospheric windows and result in a strong radiation at 5–8 μm. Although the VO₂-based infrared camouflage devices can dynamically regulate infrared radiation, they are temperature-dependent, which is not suitable to practical application. Furthermore, it is also limited by the
r egregiously fabricates condition of VO₂ films, which suppresses the infrared regulation capability.

Furthermore, the optical property of another type of materials can be controlled by an applied voltage, which is more flexible in regulating infrared radiation. Noda et al. experimentally demonstrated dynamic control emissivity based on the dynamic control of inter-subband absorption in n-type quantum wells, achieving a speed four orders of magnitude faster than that of conventional temperature-modulation methods. The emissivity changes from 0.74 to 0.24 at the resonant wavelength while a much lower emissivity is maintained at all other wavelengths. Kocabas et al. fabricated an active thermal surfaces capable of efficient real-time electrical control of thermal emission over the full infrared spectrum without changing the temperature of the surface. The device is light (30 g m⁻²), thin (<50 μm), and ultra-flexible. Furthermore, it can reconfigure its thermal appearance and blend itself with the varying thermal background in a few seconds. Li et al. constructed a serial of visible-to-infrared broadband flexible devices for infrared radiation regulation (Figure 15B). High infrared emission changes of 0.5 and 0.42 for the device are observed at the wavelength range of 8–14 and 2.5–25 μm, respectively. Promising cycling stability and flexibility of the device are also observed. Furthermore, the results demonstrate that the device exhibits different heat transfer rates, facilitating thermal management of the indoor object.

Beyond the infrared radiation regulation materials, Gorodetsky et al. developed a universal platform inspired by the highly evolved bio-optical components of squid skin while leveraging the technical foundation established for dielectric elastomer actuators (Figure 15C). Before actuation, relatively small but size-variable active areas are featured, analogous to cephalopod chromatophores, with the surfaces covered by a dense but geometrically reconfigurable arrangement of reflective microstructures, analogous to squid iridocytes. After actuation, the devices expand their active areas to modulate the amount of absorbed incident infrared light, again analogous to cephalopod chromatophores, as well as alter the geometry of their active microstructured surfaces to modulate the relative intensity of the reflected incident infrared light, again analogous to squid iridocytes. The devices also feature low working temperature, tunable spectral range, weak angular dependence, fast response, stability to repeated cycling, amenability to patterning and multiplexing, autonomous operation, robust mechanical properties, and straightforward manufacturability. In addition, the systems have been intrinsically designed for ready manufacturability and straightforward integration and may enable new autonomous portable or wearable thermoregulatory technologies.

4.3. Thermoregulatory Microstructured Materials

Thermal radiation is a universal method of heat transfer method. According to the Stefan–Boltzmann law, the thermal radiative energy depends not only on the emittance but also the temperature; thus, thermoregulation can be achieved by controlling the emittance of materials. Considering thermodynamic equilibrium, the temperature can be regulated by controlling the absorbed and emitted energy. In general, objects absorb solar energy and emit infrared radiation below 100 °C. In addition, the solar energy is consistent, depending on the distance from the sun. Therefore, the temperature can be obtained by

\[ P(T) = P_{\text{rad}}(T) - P_{\text{atm}} - P_{\text{sun}} - P_{\text{other}} \]  (4)

where \( P(T) \) is the final obtained power; \( P_{\text{rad}}(T) \) is the emitting power in infrared wavelengths; \( P_{\text{atm}} \) is the atmosphere radiative power, \( P_{\text{sun}} \) is the solar radiative power, and \( P_{\text{other}} \) is the sum of conduction and convection power. As \( P_{\text{atm}} \) and \( P_{\text{other}} \) are not dependent on the radiation wavelength and are often constant at ambient temperature, the temperature of an object is mainly reliant on \( P_{\text{rad}}(T) \) and \( P_{\text{rad}}(T) \), which is given by

\[ P_{\text{rad}}(T) = A \int dQ \cos \theta \int_\lambda \lambda_{\text{BB}}(T, \lambda) \epsilon(\lambda, \theta) \]  (5)

\[ P_{\text{sun}}(T) = A \int dQ \cos \theta \int_\lambda \lambda_{\text{sun}}(\lambda) a(\lambda, \theta) \]  (6)

where \( A \) is the area of the object, \( dQ \) is the angular integral over a hemisphere, \( \lambda_{\text{BB}}(T, \lambda) \) is the blackbody radiation curve, \( \epsilon(\lambda, \theta) \) is the infrared emissivity, \( \lambda_{\text{sun}}(\lambda) \) is the solar radiation curve, and \( a(\lambda, \theta) \) is the solar absorptance.

Thus, \( P(T) \) mainly depends on \( \epsilon(\lambda, \theta) \) and \( a(\lambda, \theta) \). As \( \epsilon(\lambda, \theta) = \lambda, \theta \) at infrared wavelengths in thermodynamic equilibrium, thermoregulatory materials can be obtained by engineering the optical performance at solar radiation (0.2–2.5 μm) and infrared radiation wavelengths. \( P(T) < 0 \) indicates a heating effect, whereas \( P(T) > 0 \) refers to a cooling effect.

4.3.1. Radiative Cooling Materials

Among thermoregulatory materials, the “space blanket,” which was introduced by NASA in the 1960s to mitigate temperature fluctuations in space, represents arguably one of the most famous and impactful technologies. It consists of a plastic sheet coated with a thin continuous layer of metal, which is highly effective at reflecting solar radiation to avoid overheating while maintaining infrared radiation to keep warm in space. Meanwhile, recent reports have mainly focused on the radiative cooling of the earth. Cooling is a widespread necessity faced by humans today. The Earth’s atmosphere has a transparency window for infrared radiation between 8–13 μm, which coincides with the peak thermal radiation wavelengths at ambient temperatures. By exploiting this window, cooling can be achieved on the Earth’s surface by radiating extra heat away into cold outer space. This radiative cooling mechanism is promising for efforts to improve energy efficiency because it provides a purely passive cooling strategy for terrestrial structures without the need for energy inputs. Gentle and Smith designed a special material compose of SiC and SiO₂ nanoparticles embedded in a polyethylene foil with an aluminum plate in the back side to radiate infrared energy to space. By utilizing crystalline SiC nanoparticles with a surface phonon resonance of 10.5 to 13 μm and resonant SiO₂ nanoparticles with absorption from 8 to 10 μm, mixing SiC and
SiO₂ nanoparticles yields high performance cooling at low cost with an actual stagnation temperature of 17 °C below ambient temperature in Sydney at ≈3 mm of water vapor pressure. However, the designed radiative cooling device has been limited at night owing to the lack of available solar radiative energy to absorb. In general, daytime radiative cooling needs to reflect sunlight (0.3–2.5 μm) and radiate infrared radiation to the cold space through the atmosphere transparent window (8–13 μm). When the radiation energy in the transparent window is larger than the absorption energy from sunlight, the cooling effect can be achieved. Unfortunately, the energy density mismatch between solar irradiance and infrared radiation from an ambient-temperature surface requires materials with ultrahigh ε and suppressed α.

Inspired by the hierarchical feature structure of ant hairs, Song et al. prepared a flexible photonic architecture on PDMS.[210] The gradual taper at the tip acts as a gradient refractive index layer in the MIR spectral range, yielding an average normal incidence emittance of 0.98 at the 8–13 μm atmospheric window. For the first time, a metal–dielectric photonic structure (Figure 16A) capable of radiative cooling in daytime outdoor conditions was designed by Fan et al.[208] Taking advantage of the phonon-polariton resonances of 2D periodic array quartz and SiC photonic crystal and utilizing a solar reflector made of chirped 1D photonic crystals below, the device behaves as a broadband mirror for sunlight while simultaneously generating strong emission in the mid-IR within the atmospheric window, achieving a net cooling power in excess of 100 W m⁻² at ambient temperature. In particular, the cooling persists in the presence of significant convective/conductive heat exchange and nonideal atmospheric conditions. Furthermore, Fan et al. experimentally demonstrated radiative cooling to nearly 5 °C below the ambient air temperature under direct sunlight (Figure 16B).[211] By integrating a photonic solar reflector and thermal emitter, 97% of incident sunlight was reflected and strong and selective infrared radiation was emitted in the atmospheric window. When exposed to direct sunlight exceeding 850 W m⁻² on a rooftop, the photonic radiative cooler cooled to 4.9 °C below ambient air temperature, generating a cooling power of 40.1 W m⁻² at ambient air temperature. Cui et al. processed a material by nanoporous polyethylene (nanoPE) to develop a textile that promotes effective radiative
cooling (Figure 16C). This nanoPE material is transparent to MWIR human body radiation but opaque to almost all visible light, owing to the Mie scattering of the pore size distribution (50–1000 nm). Furthermore, a processed nanoPE cloth was developed to simulate skin temperature, exhibiting temperatures 2.0 °C lower than cotton cloth. Yang et al. embedded resonant polar dielectric microspheres randomly in a polymeric matrix, resulting in a metamaterial that is fully transparent to the solar spectrum while having an infrared emissivity greater than 0.93 across the atmospheric window. When backed with a silver coating, the metamaterial shows a noontime radiative cooling power of 93 W m⁻² under direct sunshine. More critically, it demonstrated high-throughput, economical roll-to-roll manufacturing of the metamaterial, which is vital for promoting radiative cooling as a viable energy technology.

Yu et al. presented a more simple, inexpensive, and scalable phase inversion-based method for fabricating hierarchically porous poly(vinylidene fluoride-co-hexafluoropropene) [P(VdF-HFP)] HP coatings with excellent passive daytime radiative cooling capability. The substrate-independent hemispherical solar reflectance reach as high as 0.96 ± 0.03 along with long-wave infrared emittances (0.97 ± 0.02), allowing for sub-ambient temperature drops of approximately 6 °C. Furthermore, the technique offers a paint-like simplicity, applicable to any surface.

4.3.2. Dynamic Thermoregulatory Microstructured Materials

Radiative cooling materials have attracted a great amount of attention owing to their unique properties. Furthermore, the
associated simple large-scale fabrication process and multi-functionality have advanced the practical application of these materials. However, a thermostat is required for most applications because humans can only work in a small temperature range. Therefore, dynamic thermoregulatory materials have been widely investigated. As mentioned above, the temperature at thermodynamic equilibrium is mainly dependent on $\varepsilon$ and $\alpha$. The dynamic thermoregulatory materials should ideally change their optical performance in response to a stimulus.

As is well known, thermoregulatory materials were first introduced to maintain the temperature of spacecraft and satellites, which require internal temperature control to minimize thermal fluctuations. As an infrared radiation regulatory material, VO$_2$ has been studied to be used as a smart optical solar reflector over the past 10 years. However, the reflectors with VO$_2$ deposited directly on a polished aluminum substrate can only tune an emittance of 0.1–0.3. Therefore, Musken et al. fabricated a VO$_2$ thermochromic metamaterial-based smart optical solar reflector (Figure 17A). Combining the benefits from the thermochromic and plasmonic properties of metallic VO$_2$, the smart optical solar reflector exhibits a tunable infrared emittance of 0.48 with an acceptable solar absorptance below 0.6. Ito et al. presented VO$_2$ metasurfaces that promoted the radiative heat flux in the metallic state. The metasurfaces exhibited similar but broader resonance compared with conventional metal–insulator–metal metamaterials based on localized gap-plasmons when VO$_2$ was in the metallic state. The broad resonance facilitates the maximization of the radiative thermal exchange, exhibiting a high thermal radiation contrast between the phases. Wilton et al. had designed an adaptive radiative “thermostat” by VO$_2$ photonic nanostructures for thermal regulation at room temperature. The solar spectrum weighted average absorptivity of the system at normal incidence is $\approx$15% for the dielectric phase and 6% for the metallic phase, which is sufficient to empower a radiative thermostat with the desired properties to perform passive temperature regulation. For VO$_2$ thin films in the purely metallic phase, a good quality mid-IR Fabry–Perot cavity was constructed with the fundamental mode resonating at $\lambda \approx 10 \mu m$, which leads to near unity emissivity at this wavelength. Further, the temperature can be kept below or maintained at ambient temperature during the day and night.

Unlike traditional thermoregulatory materials, Yu and Yang et al. investigated the broadband electrochromic properties of Li$_4$Ti$_5$O$_12$ (LTO) and its suitability for infrared camouflage and thermoregulation (Figure 17B). Large tunabilities of 0.74, 0.68, and 0.30 are observed for the solar reflectance, MWIR emittance, and long-infrared emittance, respectively. Under different daytime and night-time skies, LTO shows both solar heating and radiative cooling capabilities. The large tunable temperature range (18 °C) and sub-ambient (by 4 °C) temperatures attained by LTO under sunlight make it attractive for energy-efficient thermoregulation in space and terrestrial settings. Furthermore, LTO exhibits steady electrochromic performance under different electrochemical cycling tests. The range of $\varepsilon$ attained by LTO on Al allows LTO-based electrodes to camouflage themselves by reflecting the temperature and thermal features of their environment, making them appealing for thermal camouflaging applications.

Inspired by the squid skin, Gorodetsky et al. further developed a composite material with tunable thermoregulatory properties (Figure 17C). This material includes an on/off switching ratio of $\approx$25 for the transmittance, regulates a heat flux of 36 W m$^{-2}$ with an estimated mechanical power input of 3 W m$^{-2}$, and features a dynamic environmental set point temperature window of 8 °C. Owing to the functionality and associated figures of merit, this material may substantially reduce building energy consumption upon widespread deployment and adoption.

By replicating the unique properties of desert ants and chameleons, Marti et al. presented a stretchable selective emitter based on corrugated nickel that can modulate the emissivity to provide dynamic thermal control on human bodies (Figure 17D). By evaporating nickel on a pre-strained polymer, a corrugation with a period of 700 nm increases the nickel absorptance from 0.3 to 0.7 at 0.2–2.5 $\mu$m, owing to multiple scattering. Furthermore, the infrared radiation emittance increases with a decrease in the absorptance at 0.2–2.5 $\mu$m. The reversible optical change accompanies ambient surface temperature variations in 305–315 K. The wearable system and the corrugated nickel on a human body at 309 K allows a heat flux of 62 W m$^{-2}$ out of the skin when stretched and 79 W m$^{-2}$ into the skin when released. Gu et al. reported a controllable approach to hair microcrimps, using its shape memory function stimulated by water to investigate the contribution of hair crimpness to thermal insulation in yaks. The temporary hair microcrimps were achieved by switching on and off the hydrogen bonds between macromolecules through penetrating into and removing aqueous molecules. The controllable thermal insulation was realized by managing the hair microcrimps; thus, the multiple reflectance of infrared light was managed by hair hierarchical microcrimps from root to head. Infrared images showed that the temporarily fixed shapes of unconstrained hairs, fabricated using its water-induced shape memory function, produce different thermal insulations. By coating triacetate-cellulose bimorph fibers with a thin layer of carbon nanotubes, Wang et al. effectively modulated the infrared radiation by more than 35% as the relative humidity of the underlying skin changed. Both experiments and modeling suggest that this dynamic infrared gating effect mainly arises from distance-dependent electromagnetic coupling between neighboring coated fibers in the textile yarns. This effect opens a pathway for developing wearable localized thermal management systems that are autonomous and self-powered, as well as expanding the human capability to adapt to demanding environments.

5. Summary and Outlook

Over billions of years of evolution, nature has developed numerous ingenious microstructures for efficiently manipulating light and thermal radiation, two vital sources necessary for survival for not only natural creatures but also human beings. These microstructures give us invaluable examples to learn from. Over the past few decades, a great amount of effort has been devoted to revealing the delicate architectures of these biological prototypes, illuminating the mechanisms for superb optical and thermal properties, developing fabrication methods...
from bioinspired materials, and demonstrating potential applications.

The various microstructures of living organisms in these studies are divided into three main classes, according to their featured optical properties—bioinspired antireflective microstructures, reflective microstructures, and infrared radiative microstructures. Herein, each type of microstructure is further categorized into several subsections based on their biological prototypes or potential applications. The optical phenomena of microstructures and the physical mechanism underlying them are summarized from different reports. The characteristics and unsolved problems of some studies are discussed in each section. We believe that the currently discovered biological optical microstructures are only the tip of the iceberg. Thanks to the increasing interest in this field, an increasing amount of attention from different disciplines is being devoted to searching for new amazing biological optical prototypes for mimicry. Multidisciplinary collaboration is necessary not only for the search but also the explanation and bionic preparation of these microstructures. A thorough understanding of the regulation mechanism of microstructures on extraordinary optical performance is still needed for some already known prototype. Explanations such as “synthetic effect” may need to be converted into an executable design strategy before effective bionic fabrication research can be conducted. And the excellent performance of the bionic devices is comprehensively affected by the materials and microstructure, which is deeply dependent on the processing technology. Although the technology is currently applied to the engineering field, there are some obstacles in the preparation process. Even for some well-explained bioinspired microstructures, such as the moth-eye-like structure, fabrication with a large area, low cost, and excellent durability remains an obstacle for application, let alone more complicated structures such as BWs. Practical application requires low-cost mass production rather than just making direct replicas of nature. Again, multidisciplinary collaboration is urgently needed for this problem. Learning not only the microstructures but also the biological manufacturing process from nature may be another attractive approach, especially in terms of cost, from a long-term view. Looking into the future, the main research work must focus on the understanding of “micron and nanomanufacturing methods of organisms in nature,” synthetic bionic optical materials are created based on analyzing these preparation methods. In addition, the main indicators of many biological light and heat regulation are dynamic response and redistribution of optical reflectance. The ability to mimic this versatile materials strategy will bring huge benefits in terms of cost, size, and deployability of next-generation devices.

Finally, the application of these versatile bioinspired microstructures may explode when new attention is applied from more industries. Despite all the existing difficulties, we still believe that a rapid increase can be expected in the field of bioinspired optical and thermal microstructured materials, bringing significant advancement in optical and thermal regulation.

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Conflict of Interest

The authors declare no conflict of interest.

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