Smart Materials for Dynamic Thermal Radiation Regulation

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Thermal radiation in the mid-infrared region profoundly affects human lives in various fields, including thermal management, imaging, sensing, camouflage, and thermography. Due to their fixed emissivities, radiance features of conventional materials are usually proportional to the quadruplicate of surface temperature, which set the limit, that one type of material can only present a single thermal function. Therefore, it is necessary and urgent to design materials for dynamic thermal radiation regulations to fulfill the demands of the age of intelligent machines. Recently, the ability of some smart materials to dynamically regulate thermal radiation has been evaluated. These materials are found to be competent enough for various commands, thereby, providing better alternatives and tremendously promoting the commercial potentials. In this review, the dynamic regulatory mechanisms and recent progress in the evaluation of these smart materials are summarized, including thermochromic materials, electrochromic materials, mechanically and humidity responsive materials, with the potential applications, insufficient problems, and possible strategies highlighted.

1. Introduction

Thermal radiation is a ubiquitous natural aspect. Due to random energy level transitions in matters, all objects whose temperatures exceed absolute zero can emit or absorb thermal radiation. Regulating thermal radiation from objects has become an attractive method for applications in thermal management,[1–4] infrared imaging,[5] camouflage,[6,7] thermography,[8] and nighttime thermoelctric generator device.[9] As widely known for one of three main heat exchange ways, thermal radiation has a considerable potential in regulating temperature.[10] According to the Stefan–Boltzmann law, the surface of conventional materials at temperature $T$ emits thermal radiation with radiated power ($P$) proportional to surface emissivity and $T^4$, as shown in Equation (1):

$$ P = \varepsilon \sigma T^4 \tag{1} $$

where $P$ represents thermal radiation power density at temperature $T$, $\varepsilon$ represents the surface emissivity of materials, while $\sigma$ is the Stefan–Boltzmann constant.

Therefore, controlling temperature and surface emissivity are two modes for regulating thermal radiation energy.[11] However, since it requires plenty of additional power to achieve cooling and heating, temperature control is not a cost-effective and flexible way. In contrast, controlling surface emissivity is a facile and inexpensive way because covering the object with a material with desired emissivity can efficiently regulate thermal radiation in a wide range of applications. According to Planck’s law, emissivity is a non-dimensional parameter for quantifying thermal radiation, which can be calculated as Equation (2):

$$ \varepsilon(T) = \frac{\int_{\lambda_1}^{\lambda_2} l(\lambda, T) R(\lambda, T) \sigma T^4 d\lambda}{\int_{\lambda_1}^{\lambda_2} \sigma T^4 d\lambda} \tag{2} $$

where $\lambda_1$ and $\lambda_2$ represent the wavelength range, $\epsilon(T)$ represents the emissivity measured at temperature $T$ ranging from $\lambda_1$ to $\lambda_2$, $R(\lambda, T)$ and $P_{\lambda}(\lambda, T)$ represent the object reflectance and thermal radiation power density of the blackbody measured at temperature $T$ and wavelength $\lambda$. Normally, thermal radiation mainly occurs between 2.5 and 25 $\mu$m, referred to as the mid-infrared (MIR) region. Therefore, in this review, we concentrated on emissivity properties in MIR.

Although the ability to control emissivity is of fundamental importance in thermal radiation regulation, thus far, the contrasting requirements for thermal radiation control in enhancing and suppressing infrared energy have ensured that one type of material can only present a single thermal function. Therefore, it is challenging to achieve dynamic thermal radiation regulation functions.

Within this context, smart materials, whose emissivity can change in response to external stimulations, open the door for dynamic regulation of thermal radiation. These materials have been intensely investigated in practical applications. The widely studied smart materials include thermochromic and electrochromic materials that, under thermal and electronic stimulations, can conserve and dissipate infrared thermal radiation energy in different scenarios. Moreover, graphene, quantum well structures, and reversible metal electrodeposition...
structures have also been found to exhibit thermal regulation abilities under electronic stimulations, which broaden the scope of these smart materials. Recently, some novel materials and structures can also regulate thermal radiance in response to mechanical and humid stimulations, indicating their potential for various applications.

Despite advances in this field within the past few years, to the best of our knowledge, there are rarely comprehensive reviews that have been performed so far. Herein, we will review the recent progress in these smart materials, including thermochromic materials, electrochromic materials, mechanically and humidity responsive materials that can dynamically regulate thermal radiation in MIR. In each category, regulatory mechanisms, and various material structures are listed. Moreover, we highlight potential applications of these materials and discuss the challenges associated with their applications. Based on our findings, analysis and corresponding further research directions are presented in the end. We hope that this review provides readers with a systematic perspective of smart materials for dynamic regulation of thermal radiation, stimulating new ideas, as well as, promoting the progress in thermal regulation fields.

2. Thermochromic Materials

Thermochromic materials can dynamically and reversibly alter their physical properties accompanied by color changes that are a result of external thermal stimuli.[16] This process often involves phase transitions, that leads to clear changes in emissivity. Given that the process can be achieved without any additional energy input, there is a great potential for thermochromic materials in the adaptive dynamic regulation of thermal radiation. We reviewed three kinds of representative thermochromic materials including vanadium dioxide, germanium antimony telluride (GST) alloys, and perovskite manganese oxide. Intrinsic lattice structures, transformation mechanism, thermal radiation properties, potential applications, and perspective for each material are discussed.

2.1. Vanadium Dioxide

Vanadium dioxide (VO₂) is one of the most representative thermochromic materials. Its prominent metal-to-insulator transition occurs at a critical temperature \( T_c \) of 340 K.[13–15] At a temperature lower than \( T_c \), VO₂ is an insulator while, when heated to a temperature above \( T_c \), it becomes metallic and its lattice structure translates from a monoclinic to a rutile structure. The process also involves changes of band structures. When VO₂ becomes metallic, the forbidden gap of 0.7 eV disappears and there is an overlap of \( \pi^* \) and \( d_{xy} \) energy bands, leading to an abrupt change from transparent to opaque in MIR. These properties enhance the use of VO₂ films as variable emissivity devices.[16]

The dynamic emissivity properties of VO₂ based devices, to a large extent, depend on their structures. Briefly, VO₂ deposited on high emissivity layers such as SiO₂ exhibit negative differential emissivity, which can emit more energy at low temperatures but less at high temperatures. However, this phenomenon is reversed when VO₂ is deposited on high reflectance layers like Al, Au, and Ag, which is referred to as positive differential emissivity performance. (Figure 1) Therefore, the choices for constructing the device structures divide the applications of VO₂ into two different scenarios. Table 1 shows the detailed emissivity data although specific data was not measured and announced in some studies.

2.1.1. Positive Differential Thermal Emissivity

Positive differential thermal emissivity properties of VO₂ enable emitting more energy when it is hot, and inhibiting energy dissipation at a low temperature. Thus, positive differential thermal emissivity of VO₂-based devices can maintain objects at a temperature near \( T_c \) to realize smart thermal management.

Even though VO₂ can adaptively change emissivity depending on temperature, the tunable range is generally unsatisfying for practical needs. As aforementioned, the emissivity of VO₂ films directly deposited on high reflection layers, such as Al exhibit typical positive differential with temperature, while the variable emissivity value is 0.1–0.3 depending on crystallinity and thickness.[17] To overcome this limitation, Fabry–Pérot cavity and metamaterials, two widely used methods, can be used to enhance regulation abilities. Here, emissivity tunability (Δε), calculated as the absolute value of the difference of \( ε_{hot} \) and \( ε_{cold} \) which represent emissivity when VO₂ is metallic and insulated, respectively, is proposed to quantify the judgment.

The Fabry–Pérot cavity is a tri-layer structure consisting of two semi-transparent metallic layers and a sandwiched dielectric layer (Figure 2A), that can produce a reflection valley at a certain wavelength, resulting in near-perfect absorption.[18,19] The peak wavelength can be regulated by adjusting the thickness and materials of the middle dielectric layer. Therefore, the reflectivity \( R_{FP} \) can be calculated as

\[
R_{FP} = \frac{2R(1−\cos\delta)}{1+R^2−2R\cos\delta}
\]  

where \( R \) represents the reflectivity of the upper metal layer while, \( \delta \) represents phase differences between each succeeding reflection (Figure 2B). By setting \( \theta_i \) and \( \theta_e \) as incident and emergent angles from air and refraction angle into dielectric layer, respectively, \( \delta \) can be calculated by the formula:

\[
\delta = \left( \frac{2\pi}{\lambda} \right) n \times 2d \cos \theta_i
\]  

where \( n \) represents refractive index of the dielectric layer, and \( d \) is the thickness of the dielectric layer. The peak occurs at a minimum value of \( R_{FP} \), which can be easily used to obtain the resonance wavelength \( \lambda_r \) using the formula:

\[
\lambda_r = 2d\sqrt{n^2 - \sin^2 \theta_i^2}
\]  

It is worth noting that the coefficient in Equation (5) changes from 2 to 4 when the bottom metal layer is replaced by a total
reflective metal layer, which can be attributed to the asymmetry of the structure. Here, the structure blocks waves transmission, so that reflectivity $R$ and emissivity $\varepsilon$ obey Equation (6):

$$\varepsilon = 1 - R$$  \hspace{1cm} (6)

resulting in an absorption peak at the wavelength of reflection valley, and it is still suited for other structures without transmission. To obtain desirable emissivity properties, the thickness of the dielectric layer can be adjusted to move $\lambda_r$.

In a typical Fabry–Pérot cavity, VO$_2$ acts as the upper metal layer to elevate the absorption peak, whereas the peak disappears when VO$_2$ transforms to an insulator, thereby enhancing $\Delta \varepsilon$. Generally, $\lambda_r$ is moved to the center wavelength of the blackbody to obtain a higher $\varepsilon_{\text{hot}}$ so that $\Delta \varepsilon$ can be enhanced. Morsy et al. fabricated a standard VO$_2$/Si/Au tri-layer structure whose $\Delta \varepsilon$ reached 0.22 with a thin layer of VO$_2$.\cite{20} (Figure 3A) Analogously, different dielectric layers such as SiO$_2$,\cite{17} HfO$_2$,\cite{21} CaF$_2$/Si$_3$N$_4$,\cite{22} and poly(methyl methacrylate)\cite{23} were also chosen and fabricated to realize familiar functions, and the $\Delta \varepsilon$ can be enhanced to 0.66 in MIR.

Regarding thermal management, we must consider the energy absorption and dissipation simultaneously because they jointly determine whether object temperatures are up or down.

### Table 1. Detailed data of emissivity tunability in VO$_2$-based structures.

<table>
<thead>
<tr>
<th>Structure design</th>
<th>$\varepsilon_{\text{cold}}$</th>
<th>$\varepsilon_{\text{hot}}$</th>
<th>$\alpha$</th>
<th>Emissivity tunability</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>VO$_2$/Al</td>
<td>0.08</td>
<td>0.34</td>
<td>-</td>
<td>0.26</td>
<td>[17]</td>
</tr>
<tr>
<td>Positive</td>
<td>VO$_2$/Si/Au</td>
<td>0.22</td>
<td>-</td>
<td>0.22</td>
<td>[20]</td>
</tr>
<tr>
<td>Differential</td>
<td>VO$_2$/SiO$_2$/Au</td>
<td>0.35</td>
<td>0.44</td>
<td>0.46</td>
<td>[17]</td>
</tr>
<tr>
<td>Thermal</td>
<td>VO$_2$/HfO$_2$/Ag</td>
<td>0.13</td>
<td>-</td>
<td>0.55</td>
<td>[21]</td>
</tr>
<tr>
<td>Emissivity</td>
<td>VO$_2$/Si$_3$N$_4$/CaF$_2$/Au</td>
<td>0.341</td>
<td>0.81</td>
<td>0.66</td>
<td>[22]</td>
</tr>
<tr>
<td>BP filter/air/VO$_2$/MgF$_2$/W</td>
<td>-0</td>
<td>0.582</td>
<td>(8–13 µm)</td>
<td>[24]</td>
<td></td>
</tr>
<tr>
<td>VO$_2$ metasurface-α-Si-W</td>
<td>0.054</td>
<td>0.68</td>
<td>-</td>
<td>0.63</td>
<td>[27]</td>
</tr>
<tr>
<td>VO$_2$ metasurface-SiO$_2$-Al-Al$_2$O$_3$</td>
<td>0.35</td>
<td>0.801</td>
<td>=0.45</td>
<td>0.63 (7.3 µm)</td>
<td>[28]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>=0.32</td>
<td>0.636</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>=0.98</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>Structure design</td>
<td>$\varepsilon_{\text{cold}}$</td>
<td>$\varepsilon_{\text{hot}}$</td>
<td>$\lambda_r$</td>
<td>Emissivity tunability</td>
<td>Reference</td>
</tr>
<tr>
<td>VO$_2$ nanopowders</td>
<td>0.93</td>
<td>0.59</td>
<td>0.82</td>
<td>0.82</td>
<td>[32]</td>
</tr>
<tr>
<td>Negative</td>
<td>VO$_2$/SiO$_2$</td>
<td>-</td>
<td>-</td>
<td>0.85</td>
<td>[17]</td>
</tr>
<tr>
<td>Differential</td>
<td>VO$_2$/SiO$_2$</td>
<td>-</td>
<td>-</td>
<td>0.84</td>
<td>[29]</td>
</tr>
<tr>
<td>Thermal</td>
<td>VO$_2$/quartz/Silicone</td>
<td>0.63</td>
<td>0.42</td>
<td>0.84</td>
<td>[34]</td>
</tr>
<tr>
<td>Emissivity</td>
<td>VO$_2$/graphene/carbon nanotube</td>
<td>-</td>
<td>-</td>
<td>0.86</td>
<td>[36]</td>
</tr>
<tr>
<td></td>
<td>VO$_2$/carbon hybrid structure</td>
<td>-</td>
<td>-</td>
<td>0.95</td>
<td>[37]</td>
</tr>
</tbody>
</table>

\[\text{Figure 1. Schematic of emissivity properties of VO}_2(\text{M})\text{ film deposited on A) low emissivity layer and B) high emissivity layer. Schematic of emissivity properties of VO}_2(\text{R})\text{ film deposited on C) low emissivity layer and D) high emissivity layer.}\]
Solar absorption ($\alpha$), representing absorbed solar radiation energy in visible and near infrared regions (NIR), is the main source of absorbed energy. For easier regulation of temperature, smaller $\alpha$ is required in thermal management. However, the management of $\alpha$ may lead to a negative influence on $\Delta\varepsilon$. To solve this problem, Fan et al. [24] designed a composited structure for reducing $\alpha$ to nearly zero. A spectrally-selective filter was placed on the top of a VO$_2$ based Fabry–Pérot cavity. The

Figure 2. A) Schematic of the Fabry–Pérot cavity. B) Schematic of light propagation in Fabry–Pérot cavity.

Figure 3. A-a) Schematic of VO$_2$/Si/Au layered structures. b) Calculated radiative heat flux from the VO$_2$ surface as a function of temperature. c) Measured temperature rises relative to ambient (horizontal axis) as a function of the applied heat load (vertical axis) for a complete heating and cooling cycle. d) Dynamic thermal response. B-a–i) Photonic structures for realizing self-adaptive radiative cooling. C) Electromagnetically simulated emissivity of a) the metasurface with $\alpha$-Si and b) the metasurface with Al$_2$O$_3$. The magnetic field in the metasurface with $\alpha$-Si at normal incidence c) at a wavelength of 7.4 $\mu$m in the metallic state and d) at a wavelength of 5.8 $\mu$m in the insulating state. D-a) Cross-sectional and b) top view scanning electron microscopy (SEM) graphs of VO$_2$ meta-reflectors. c) Extracted solar absorptance $\alpha$ as a function of gap size and for the different feature sizes, measured at temperatures of 25 and 80 °C. d) Emittance tunability, $\Delta\varepsilon$, and solar absorptance, $\alpha$, plotted as a function of the VO$_2$ coverage. A) Reproduced with permission (http://creativecommons.org/licenses/by/4.0/). [20] Copyright 2020, The American Association for the Advancement of Science (AAAS). B) Reproduced with permission (http://creativecommons.org/licenses/by/4.0/). [24] Copyright 2018, The Optical Society of America. C) Reproduced with permission. [27] Copyright 2018, American Institute of Physics. D) Reproduced with permission. [28] Copyright 2018, American Chemical Society.
spectrally-selective filter had 11 layers of alternately arranged Ge and MgF₂, which was near transparent in MIR but almost not absorbed in visible to NIR. (Figure 3B) They successfully reduced α without affecting Δε. The average εₜ₉₉ and ε₄₉₉ in 8–13 μm achieved 0.636 and 0.054, respectively.

Recently, metamaterials have been used to promote Δε of VO₂ thermal regulation devices. Metamaterials are composed of designed sub-wavelength metal or dielectric structures that can resonate and couple with incident electromagnetic waves. In addition, they can exhibit some unnatural properties and performance.[25] Metasurface is a special metamaterial with a sub-wavelength thickness, which can effectively avoid the loss of performance caused by the thickness of the metamaterial. Compared to continuous VO₂ films, VO₂ based metasurface can effectively decrease α by degrading of surface coverage. However, Δε is reserved, or even improved by the plasmonic resonance of VO₂(R).

In practical VO₂ device designs, metasurfaces are usually fabricated based on the Fabry–Pérot cavity. At high temperatures, the localized surface plasmonic resonance attributed to VO₂(R) metasurfaces and the Fabry–Pérot absorption exhibit a synergistic effect that further improves εₜ₉₉. However, since the coverage of VO₂ is decreased, ε₄₉₉ is suppressed, leading to elevated Δε. Wang et al.[26] used the VO₂ layer as the metal mirror to fabricate a VO₂ wires/SiO₂/VO₂ metasurface structure, resulting in a huge improvement in cooling power when compared to the VO₂/Si structure at high temperatures. Ito et al.[27] prepared VO₂/α-Si/W and VO₂/Al₂O₃/W metasurface thermal management devices, respectively. The magnetic field on the surface of VO₂(R) patches was relatively strong. It was attributed to the localized surface plasmonic resonance. In addition, the field confined beneath VO₂ patches also proved the existence of Fabry–Pérot resonance. The εₜ₉₉ and Δε of VO₂/α-Si/W reached up to 0.98 and 0.63 at 73 μm, respectively (Figure 3C).

Sun et al. fabricated VO₂/SiO₂/Al metasurface[28] and put forward the concept of surface coverage to explore the relationship between the size of VO₂ metasurface and performance. Δε reached 0.48 with a decreased α of 0.45 being obtained, which elucidated the design of the VO₂ metasurface (Figure 3D).

2.1.2. Negative Differential Thermal Emissivity

Contrary to positive differential thermal emissivity, negative differential thermal emissivity of VO₂ means emitting lower radiation at higher temperatures, which can be basically realized by depositing VO₂ film on high emissivity layers like SiO₂.[17,29] This property can help maintain the consistency of the MIR signals with the surroundings to realize an infrared dynamic concealment.[30] Rather than the whole MIR region, emissivity at 3–5 μm and 8–14 μm is the key point in practical application. This is because electromagnetic waves in other regions are absorbed by the molecular vibration absorptions of atmospheric water, carbon dioxide, ozonosphere, and dust.[31] This chapter emphasizes the emissivity in these two bands referred to as atmosphere windows.

Experimentally, infrared cameras were usually used to evaluate emissivity properties in atmosphere windows using apparent temperatures, which represent the amount of radiance power. Liu et al.[32] prepared VO₂ nanopowders whose emissivity can decrease from 0.93 to 0.59 and from 0.82 to 0.36 at 3–5 μm and 8–14 μm, respectively. Notably, nanopowders are suitable for substrates with large surface areas, which provide options for their future commercial applications. Furthermore, Ji et al.[33] proposed a facile inkjet printing method that can also fabricate uniform VO₂ nanoparticle films whose area reached 560 cm², with a transmittance modulation of 32.4% at 20 μm.

Except for traditional high emissivity substrates like SiO₂, other novel substrates were also used to achieve higher Δε. A silicone elastomer sheet was selected to construct the VO₂/quartz/silicone structure,[34] whose Δε reached 0.5 and 0.21 at 75–13 μm and 3.7–4.8 μm, respectively. At a wide temperature range from 40 to 95 °C, the apparent temperature of VO₂/quartz/Si was lower than that of the structure without VO₂, exhibiting negative differential thermal emissivity properties (Figure 4A). Studies have also determined the outcomes associated with VO₂ deposited on the r-Al₂O₃ substrates.[35] Apart from solid substrates, a flexible free-standing structure of VO₂/graphene/carbon nanotube (VGC) that obtained a large tunability from 0.86 to 0.49 at 75–13 μm was fabricated.[36] The free-standing VGC film can be transferred to any flexible surface for thermal camouflage, and electrical stimulation is also available which can achieve active control. This research shed new light on multiple control of VO₂ based devices (Figure 4B). Moreover, VO₂ can be modified by carbon to construct VO₂/Carbon hybrid structures to realize similar functions with a lower τ, of 45 °C and an excellent Δε of 0.44 at 8–13 μm.[37] The creative hybrid structures provided new insights for promoting the performance of VO₂ based adaptive dynamic thermal regulation devices and may provide new avenues for the doping or modifying process (Figure 4C).

Multiple layer structures such as Fabry–Pérot cavity can also play an important role in designs with negative differential thermal emissivity. The VO₂ layer has different positions and functions between positive and negative differential thermal emissivity devices. A common Fabry–Pérot cavity comprises of VO₂ based dielectric layer and two metal layers so that Fabry–Pérot resonance occurs when VO₂ is an insulator but disappears when VO₂ is metallic, which results in an opposite change when compared to the positive differential thermal emissivity. Based on this structure, Chanda et al.[38] designed a multilayer metasurface of Au/SiO₂/VO₂/SUB/Au disks to realize thermal camouflage. The thickness of the dielectric layer decreases during the phase transition of VO₂ so that the resonance wavelength exhibits a blue-shift, which enhances the regulation ability in former resonance regions. By evaluating the functions of Au array diameters and locations of absorption peak, an encoded image on a designer imprinted surface achieved concealment under the detection of the infrared camera, which provided a successful case for infrared camouflage (Figure 4D). Wang et al.[39] fabricated Au grating/VO₂/Au metamaterials and presented an LC model to describe the mechanism in Fabry–Pérot cavities. This model regarded metals as inductors and a parallel-plate capacitor could be formed in Fabry–Pérot cavities, so that the strongest resonance appeared when the impedance of the LC model was zero. Then, to obtain a better emitted stability in different incident angles and polarizations, they further promoted this structure by replacing Au grating with Al disk.[40]
whose absorbance was close to uniformity within a large incident angle range from \(-60^\circ\) to \(60^\circ\) under transverse magnetic (TM) and transverse electric (TE) polarized wave when VO\(_2\) was an insulator. In complex work environments, the independence property may play a central role and guarantee practicability.

Overall, \(\Delta \varepsilon\) has been evaluated in the promotion of VO\(_2\) optical devices widely. Encouragingly, significant advancements have been proposed by designing various structures whose \(\Delta \varepsilon\) is close to practical applications. And the devices can implement functionality without active input energy, which is critical in some applications, for example, thermal management for spacecrafts. However, several issues, such as the decrease in \(\tau_c\) and improvements in environmental stability, need to be solved. Practically, the demanded transition temperature is usually close to room temperature, while the intrinsic \(\tau_c\) is relatively high. Theoretically, applying voltage or stress can reduce \(\tau_c\), and some methods such as utilizing localized plasmon resonance which absorbs light, to enhance the local temperature are also effective. In addition, the most common and effective way of reducing \(\tau_c\) is doping W, Cr, and some rare earth elements.
literature, $\tau$ is almost ignored when focusing on the improvement of $\Delta \varepsilon$. Generally, doping can change the concentration of carriers and suppress $\Delta \varepsilon$, so that balancing between $\Delta \varepsilon$ and $\tau$ becomes inevitable. As for the environmental stability, VO$_2$ is unstable under exposure to certain atmospheric conditions, especially humid conditions, thereby significantly inhibiting its applications. A common solution is adding suitable protective layers, such as HfO$_2$[42] and Al$_2$O$_3$[43] on the surface of VO$_2$. However, a systematic illustration of the deterioration process of VO$_2$ films in MIR and the effects of protective layers on the thermochromic properties are still unknown. Detailed instructions are needed to help navigate the protection process.

In the future, the establishment of novel approaches may help improve the performance or widen the applications of VO$_2$ in MIR. For example, using a gradient doping process to obtain gradual or permanent radiance properties within a certain temperature range can realize novel thermal management,[44] or utilizing a strong, and positive temperature dependence of emissivity of VO$_2$ combined with proper structural designs[45] can help realize better thermal imaging. Furthermore, various types of metasurface or coupling of multiple resonances may be introduced to explore broadband[46] or dual-band emissivity performance to enhance $\Delta \varepsilon$[47] and obtain great polarization-dependence.

2.2. Germanium Antimony Telluride Alloys and Perovskite Manganese Oxide

2.2.1. Germanium Antimony Telluride Alloys

GST alloys are important thermochromic materials. It has been widely proven to be a fast, robust, and reproducible non-volatile phase transition material.[48] In the original sedimentary state, GST alloys are amorphous (aGST) and transform to a crystalline phase (cGST) under an annealing temperature exceeding 160 °C or a high power pulsed laser irradiation. cGST maintains its stability for several years, unless heated to 640 °C or applying a continuous low-power pulsed laser irradiation. It has an irregular rocksalt structure that is formed when one sublattice is taken by Te, while the other sublattice is randomly occupied by Ge, Sb, and vacancy (Figure 5A-a,b).[49] By adjusting the components, the specific transition temperature $\tau$ and optical properties change accordingly as well as other electrical properties (Figure 5A-c,d).[50] which has attracted great attention as an ideal material for constructing optical devices for dynamic emissivity regulation.

The phase transition between cGST and aGST is a gradual process that, results in an intermediate state comprising amorphous and crystalline phases. By regulating different intermediate phases, a continuous tunable thermal emitter is realized within specific temperature range. Qiu et al. elucidated the influence of thickness and temperature on the emissivity of GST alloys.[51] Emission peak positions were shown to shift further with increasing cGST film thickness, when GST alloys were simply deposited on an Au substrate, thereby showing its potential as a wavelength-selective and broadband thermal emitter. Therefore, a Ge$_2$Sb$_2$Te$_5$/Au double layer structure was fabricated, and a perfect thermal camouflage function from 7.5 to 13 $\mu$m was realized when background temperature was varied between 30 and 50 °C (Figure 5B).[52]

Apart from applications in thermal management, which need a broadband tunability of emissivity, thermal imaging, sensing, and detection, require spectral-selective and narrowband thermal radiance properties. In these cases, GST alloys usually act as the dielectric layer, whose refractive index strongly increases as a result of the change of the chemical bonding from covalent to resonant bonding during the phase transition from an amorphous state to crystallization,[33] thereby achieving obvious spectral shifts for multispectral dynamic modulation. Based on the lower MIR losses, Tittl et al. used Ge$_2$Sb$_2$Te$_5$ as a dielectric layer to fabricate an Al nanoantennas/GST/Al mirror structure for multiband thermal imaging.[54] Multispectral thermal imaging was realized by fabricating a periodic super-pixel arrangement composed of four individual pixels with side lengths of Al antennas ranging from 300 to 450 nm in 50 nm steps, whose surface plasmon resonance wavelengths ranged from 2.5 to 4 $\mu$m. (Figure 5C) The different absorption properties of the four pixels can easily recognize objects with different temperatures. As aforementioned, the phase transition of GST alloys can shift the absorption peak, so that it finally provided the switchable ability between different temperature detection ranges for this structure. In addition, Ge$_2$Sb$_2$Te$_5$ and Ge$_2$Sb$_2$Te$_3$ have been widely studied due to their low switching power and fast-tuning speed. Cao et al.[55] utilized Ge$_2$Sb$_2$Te$_5$ to construct Au arrays/GST/SiO$_2$/Au mirror, which exhibited similar wavelength-selective and switchable features in MIR. Furthermore, Kim et al.[56] used Ag as the nanostructure material because of its superior optical properties in 3–5 $\mu$m when compared to Al and Au. Instead of the square arrays, they fabricated Ag plasmonic hexagonal nanohole arrays (PNAs) to increase overall space utilization and exhibit higher resonance efficiency. Under a nanosecond laser pulse, it is obvious that the transmission peak moves along with the change in the crystallization state of Ge$_2$Sb$_2$Te$_5$, which achieves the fully reversible and continuously tunable narrowband spectral filters (Figure 5D). It is worth noting that most studies on thermal imaging and sensing were mainly concentrated within the wavelength range of 3–5 $\mu$m, however, the wavelength range could be broadened or changed by modulating the size of the surface metal arrays.

In conclusion, the stability of GST alloys is vital for their applications in the dynamic regulation of thermal radiance, whether in amorphous, crystalline, or the intermediate phases. Studies on broadband regulation in MIR seem to stay in the stage that depositing GST alloys on various substrates. Further studies should be performed to develop better methods for enhancing its regulation ability. In narrowband regulation for thermal imaging and sensing, GST alloys often act as the dielectric layer and exert the dynamic regulation ability that is usually triggered by a laser pulse. Moreover, electrical switching can also convert GST from amorphous to crystalline so that it is possible for multiple and active control devices. The doping process with Ni, Al, and Se can effectively alter the phase transition features and optical properties of GST alloys,[37] which could be a potential approach for enlarging the applications of GST alloys in MIR.
2.2.2. Perovskite Manganese Oxide

Perovskite manganese oxides are a series of typical thermochromic materials, that can change from ferromagnetic metals to paramagnetic insulators at increasing temperature. The general chemical formula of perovskite manganese structure is AMnO$_3$, whereby A represents bivalent alkaline earth metals or rare earth metal elements such as La, Ca, Ba, Sr, Pb, Nd, and Pr. Jonker and Van Santen\cite{58,59} found that magnetic features and Curie temperature of LaMnO$_3$ greatly vary when divalent alkaline earth metals such as Sr, Ca, Ba doped, which is attributed to the change in the ratio of Mn$^{3+}$ to Mn$^{4+}$. Zener\cite{60} proposed the “double exchange” (DE) model, and a correlation equation between conductivity and Curie temperature was established, that is, La$_{x}$Sr$_{1-x}$MnO$_3$($0.6 \leq x \leq 0.8$) should be applied when La$_{x}$Sr$_{1-x}$MnO$_3$ has the strongest ferromagnetism. Among the transitions, emissivity changes as well, which makes it a candidate for variable emissivity devices. Tachikawa et al.\cite{61} reported that LaMnO$_3$ exhibited a large $\Delta\varepsilon$ doped with Ca or Sr, which enhanced studies on A-site doped perovskite manganese oxide materials. Shimakawa et al.\cite{62} fabricated (La, Sr) MnO$_3$ films (LSMO) by sol–gel method, whose $\Delta\varepsilon$ of 0.3 in the 220–340 °C temperature range, and the phase transition temperature at about 270 °C was achieved when the La/Sr ratio was 0.9/0.1. To optimize the $\Delta\varepsilon$ of the LSMO film, Ca was introduced to significantly enhance its performance. Li et al.\cite{63,64} synthesized La$_{0.7}$Ca$_{0.3-x}$Sr$_x$MnO$_3$ compositions which exhibited tunable infrared properties and $\Delta\varepsilon$ reached 0.6 finally when heating it to 373 K. Yu et al.\cite{65} prepared La$_{0.67}$Ca$_{0.25}$Sr$_{0.08}$MnO$_3$ whose transition temperature decreased to 9 °C while the emissivity.

Figure 5. A-a) Structural and chemical identifications of rocksalt GST along the[110] direction. b) The classic rocksalt model with Te (green spheres), Ge (red spheres), Sb (blue spheres), and vacancy (grey circles). c,d) Extract $T_c$ and change in relative optical reflectivity $\Delta R/R$ as a function of composition. B-a) Infrared images are recorded by the infrared camera at different background temperatures (30, 40, and 50 °C) and a fixed object temperature (60 °C) after different annealing time. b) The infrared images are recorded by the infrared camera at different observation angles ranging from 0° to 60°. c) Plot of the emitted power of the background, cGST-Au device, and cGST-Au device corresponding to their different temperatures. C-a–d) Device concept of tunable GST-plasmonic nanohole array metasurface for the MWIR waveband. D-a) Color-coded resonance wavelength of an individual perfect absorber superpixel with four distinct mid-infrared absorption bands. b) Representative reflectance spectra for the top right pixel from panel (a) with the GST-326 layer in the amorphous (solid line) and crystalline phase (dashed line). c) Color-coded peak detection temperature after heat-induced phase change of the GST layer from the amorphous to the crystalline phase. A-a–b) Reproduced with permission (http://creativecommons.org/licenses/by/4.0/).\cite{49} Copyright 2016, American Institute of Physics. c,d) Reproduced with permission (http://creativecommons.org/licenses/by/4.0/).\cite{50} Copyright 2017, American Chemical Society. B) Reproduced with permission (http://creativecommons.org/licenses/by/4.0/).\cite{52} Copyright 2018, Springer Nature. C) Reproduced with permission.\cite{54} Copyright 2015, Wiley-VCH. D Reproduced with permission (http://creativecommons.org/licenses/by/4.0/).\cite{56} Copyright 2020, OSA Publishing.
changed from 0.23 to 0.73 when temperature varied between \(-50\) to \(50\) °C. Regardless of \(\alpha\), it satisfies most requirements of thermal control in spacecrafts, and it is believed to be further enhanced for more important roles in the future.

As aforementioned, solar absorption \(\alpha\) is still too high, which even can reach 0.86–0.89. Therefore, multilayer structures were proposed to solve this problem. Li et al.\cite{66} and Shimazak et al.\cite{67} successfully designed multilayer structures assisted by genetic algorithms, the solar absorption ratios of the optimized multilayer films based on \(\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{MnO}_3\) and \(\text{La}_{0.825}\text{Sr}_{0.175}\text{MnO}_3\) decreased from 0.78 and 0.89 to 0.28 and 0.21, respectively. Utilizing the simulations to optimize the structure with better performance will also be an important and necessary approach in the future.\cite{68–70}

In general, wide transformation temperature ranges, slow transformation speeds, and generally high solar absorption inhibit the practical applications of LSMO. To promote its applications in thermal management, solar absorption should be reduced by designing multilayer structures or learning from the metamaterials. Phase transition temperature and its width can be established by further studies on doping modifications.

3. Electrochromic Materials

Electrochromism, a phenomenon by which materials can dynamically and reversibly change their optical properties under external voltage stimuli, has been obtained increasing attention in life. The term not only describes the color change in the visible region, but also includes the change in MIR. Conventional electrochromic (EC) materials can be divided into inorganic EC materials and organic EC materials according to the types of materials. For effective regulation of emissivity, EC materials are often assembled into EC devices (ECDs) that are usually made up of five layers, named the conductor, EC film, electrolyte—ion storage, and EC film—conductor (Figure 6). Besides, some novel materials, such as, graphene and quantum wells have emerged and have been used in the control of emissivity by applying electrical stimulations given the change in Fermi levels and electron concentrations. The reversible metal electrodeposition structures have exhibited great potentials in dynamically regulating thermal radiation so they are included as well. Therefore, this chapter describes EC materials in the order of inorganic, organic, and novel EC materials on the basis of the mechanisms, specific structural designs, applications, analysis, and evaluation.

3.1. Inorganic Electrochromic Materials

Regarding conventional materials, inorganic EC materials, such as \(\text{WO}_3\), \(\text{TiO}_2\), \(\text{V}_2\text{O}_5\), and \(\text{NiO}\) have remained the most important in the past years given their potential in smart windows and screen display, which concentrate on visible regions to NIR. For thermal regulation in MIR, \(\text{WO}_3\) has been studied extensively, hence serves as the representative inorganic material.

\(\text{WO}_3\) is one of the most typical and promising candidates for use in ECDs.\cite{71} Its crystals are generally formed through corner and edge sharing of \(\text{WO}_6\) octahedra which show a \(\text{ReO}_3\) type as the simplest structure.\cite{72} It turns blue when the ions are inserted but turns transparent when upon extraction of ions, the electrochemical reaction can be written as below

\[
\text{WO}_3 + x\text{M}^{+} + xe^{-} = M_x\text{WO}_3
\]  

where \(M\) can be \(\text{H}, \text{Li}, \text{Na},\) or \(K\), while \(e\) denotes electrons.\cite{71} Accompanied by the double injection and extraction of ions and electrons, the emissivity of \(\text{WO}_3\) can also be changed reversibly. Notably, different theories explain the mechanisms underlying the dynamic process of crystalline (c-\(\text{WO}_3\)) and amorphous \(\text{WO}_3\) (a-\(\text{WO}_3\)).

For c-\(\text{WO}_3\), tungsten bronze occurs and electrons are localized as the injection of ions and electrons from the bleaching state to coloration state, so that optical performance in MIR changes following the variety of conductivity according to a familiar Hagen-Rubens formula:\cite{74}

\[
R(\omega) = 1 - \left(\frac{2\omega}{\pi \sigma}\right)^2
\]

where \(R(\omega)\) represents the reflectance corresponding to angular frequency \(\omega\), \(\sigma\) represents the conductivity. On this basis, c-\(\text{WO}_3\) modulates its emissivity dynamically. In simulations, an all-solid-state ECD of \(\text{Au/ NiO/Ta}_2\text{O}_5/c-\text{WO}_3/\text{ITO}\) could modulate the emissivity between 0.057 and 0.595 ranging from 2 to 13.8 µm by changing the thickness of layers.\cite{76} For experiments, the \(\text{Al}/a-\text{WO}_3/\text{Ta}_2\text{O}_5/c-\text{WO}_3/\text{Al}\) grid all-solid-state structure was fabricated which realized an emissivity modulation of 0.19.\cite{77} Different regulation mechanisms were found in MIR when using single and double grid electrodes in devices, in which the former changed the reflectance but the latter altered the substrate emission. The single grid electrode was shown to have a better \(\Delta\varepsilon\), which provided a standard of reference when choosing electrodes. To improve the intercalation efficiency of
ions and to further promote the EC properties, Viana et al.\cite{76} selected the WO$_3$·H$_2$O powder instead of c-WO$_3$ because of the widely open structure and embedded it into a porous plastic matrix. $\Delta \varepsilon$ finally reached 0.3 upon intercalation of 0.65 Li per tungsten. It worth noting that this flexible assembly not only provides a simple but efficient method for the WO$_3$-based devices but also allows testing of materials other than WO$_3$·H$_2$O.

For a-WO$_3$, the change in molecular vibration between bleaching and coloration states leads to dynamic regulation of emissivity. Kislov et al.\cite{77} deposited WO$_3$ on polyimide (PI) and Si substrates to facilitate thermal management in spacecraft, which realized $\Delta \varepsilon$ of 0.31 and 0.24, respectively. Furthermore, a protective layer was introduced\cite{78} to ensure the safety of the devices in space. The protective layer was additionally aimed at acting as an anti-reflective layer to promote the regulation ability. After that, Demiryont et al.\cite{79} prepared an all-solid WO$_3$ device named EclipseVED with Li compound as the electrolyte, which shows a great performance of $\Delta \varepsilon$. Within 7–12 $\mu$m and 4–26 $\mu$m, the modulations of 0.8 and 0.7 were achieved while the mass density and power consumption were only 5 g m$^{-2}$ and 0.1 mW cm$^{-2}$, respectively. Thermal imagery of the bleaching and coloration states also showed a clear contrast caused by the huge modulation of emissivity. These results reveal a great potential of the all-solid WO$_3$ device in satellite thermal management, although there are still some drawbacks, including the lack of inclusion of adequate details. (Figure 7A). Currently, a-WO$_3$ exhibits a bigger $\Delta \varepsilon$ compared to c-WO$_3$, since the amplitude of conductivity variation between the bleaching and coloration states is limited for c-WO$_3$. Thus, a-WO$_3$ seems to be superior to c-WO$_3$ when just consider $\Delta \varepsilon$. For a direct comparison, we also fabricated a-WO$_3$ and c-WO$_3$ based ECDs with the same glass/ITO/NiO$_x$/LiTaO$_3$/WO$_3$/ITO structure, whose $\Delta \varepsilon$ are indicated in Figure 7B.\cite{80} a-WO$_3$ ECD exhibited a much better tunability in contrast to c-WO$_3$, providing experimental evidence for the conclusion.

Besides the conventional inorganic EC materials, Yang et al.\cite{81} demonstrated Li$_4$Ti$_5$O$_{12}$ (LTO) based ECDs with super broadband EC properties from visible to MIR regions. Upon Li$^+$ intercalation, LTO changed from a wide band-gap semiconductor (Li$_4$Ti$_5$O$_{12}$) to a metal (Li$_7$Ti$_5$O$_{12}$), resulting in a broadband transformation from reflection to absorption for LTO nanoparticles on metal. The tunability of solar reflectivity, emissivity in 3–5 $\mu$m and 8–13 $\mu$m was observed as 0.74, 0.68, and 0.30, respectively. The promising cycling stability, and excellent capability that can switch between solar heating and radiative cooling under different sky conditions, made it a rising star for thermal regulation and camouflage in MIR. Meanwhile, another kind of inorganic material, samarium nickel oxide (SmNiO$_3$), was also found the ability to change optical properties in response to electric stimulations, over an ultra-broad spectral range from 400 nm to 17 $\mu$m.\cite{82} When electrons were inserted, the fourfold degenerate (including spin) $e_g$ manifold was occupied by two electrons and, the strong intra-orbital Coulomb repulsion between electrons opened a bandgap as large as 3 eV, resulting in the suppression of the free carrier absorption. This novel mechanism can be exploited to design various active photonic devices.

Inorganic EC materials have been studied extensively in recent years, however, there still lacks enough attention on emissivity in MIR. The ECDs based on WO$_3$ now have an excellent $\Delta \varepsilon$, but the performance still requires to be enhanced given their long response time. This can be improved by designing the nanostructure of the WO$_3$ layer in the way that promotes the efficiency of ions transportation or through a proper doping and composite process to ameliorate the performance. Some technologies that have been used in other applications, such as fabricating the WO$_3$ nanowires\cite{83} may also help to improve its

![Figure 7. A-a) Photograph of heat dissipation test module. b) Emittance spectra of typical EclipseVED in high-e and low-e states. B) Emissive power curves of ECDs a) a-WO$_3$ ECD and b) c-WO$_3$ ECD. A) Reproduced with permission.\cite{79} Copyright 2009, Elsevier B.V. B) Reproduced with permission.\cite{80} Copyright 2019, Elsevier B.V.](image-url)
properties. Novel inorganic EC materials like LTO and SmNiO$_3$ still need further promotion and enough practical tests to be qualified for commercial applications. Apart from EC properties, a huge challenge still exists in processing, which requires an urgent solution when it comes to the commercial practical stage.

### 3.2. Organic Electrochromic Materials

Unlike inorganic EC materials, organic EC materials change their infrared emissivity by relying on polaron generation and elimination from redox reaction. At present, polyaniline (PANI) is the widely studied organic EC materials in MIR. The EC properties of PANI are discussed in this chapter.

As a member of conductive polymers (CPs), PANI films can achieve different color conversion. In addition, PANI can also achieve conversion between high infrared emissivity and high infrared transmittance by applying different voltage, hence have the potential for use in optics and thermal management. Chandrasekhar et al.\[84\] first studied the infrared emissivity regulations of PANI and designed a PANI-based ECD. The response time of the fabricated device was less than 2 s, and the emissivity in 2.5–45 µm changed from 0.32 to 0.79, which greatly enhanced the $\Delta \varepsilon$ of a flexible ECD. Later, they\[85\] used poly(aniline-co-diphenyl amine) with a long-chain polymeric dopant as the conducting polymer. Aimed at serving for spacecraft thermal control, they proposed four methods to improve the overall EC performance. The addition of IR-transparent, solar-reflective semiconductor coatings and the removal of electrochromically inactive material from the CP matrix significantly lowered $\alpha$ and enhanced $\Delta \varepsilon$ drastically. As a result, $\Delta \varepsilon$ exceeded 0.5, while other EC performance got promoted as well. The research covers almost everything when applying conducting polymers (PANI) to spacecraft thermal control, which set the standard for other materials on the road to practical applications. Differently, Jia et al.\[86\] fabricated a novel EC film based on the copolymer of aniline and o-anisidine, and attained a $\Delta \varepsilon$ of 0.408 in 8–14 µm.

To further improve the EC abilities of PANI, doping with an acid constitutes one of the most efficient methods, which has been widely studied. A broadly recognized theory, which explains the mechanism, suggests that some $\pi$ electrons became delocalized and the number of delocalized electrons varies as well in PANI doped with protic acid. Thus, the $\Delta \varepsilon$ is significantly improved given the change in electron concentrations. Our group has been making a series of advances on acid-doping enhancement approaches including device designs, regulation mechanisms, fabrications, as well as, characterizations in the past years. For the first time, we will introduce several universal and intrinsic factors with great influence on the regulation ability in MIR of the PANI films. A further understanding was proposed suggesting that the existence and elimination of polarons and bipolarons delocalized on PANI chains are the direct and most critical factors for realizing emissivity modulation (Figure 8 A).\[87\] Besides, the surface morphology of PANI films is also critical in determining the thermal radiance properties in MIR. Actually, we can obtain diverse radiation regulation capabilities through tailoring the surface morphology adjusted by modulating the concentration of the monomer in the electro-polymerization system.\[88\] We anticipate that basic research will be geared to the promotion of PANI-based
devices and even the entire EC field. In practical experiments and designs, tremendous achievements have been made using either organic or inorganic acids. For organic acids, dodecylbenzene sulfonate acid (DBSA) doped PANI film was synthesized in situ on an Au/porous flexible substrate and ITO substrate respectively via electrochemical deposition. The $\Delta \varepsilon$ of the former device reached 0.183, 0.388, and 0.315 in the wavelength ranges of 3–5, 8–12, and 2.5–25 $\mu$m, respectively. Moreover, the regulation mechanism of the DBSA-doped PANI film on ITO substrates was further explained. The change in the MIR transmittance of the PANI film at different states realized the modulation of emissivity when the thickness of PANI was within a certain value, however, the pseudo-metallic behavior of the PANI film dominated this process when the thickness overran. (Figure 8B) For inorganic acids, an HClO$_4$ doped PANI porous film with excellent emissivity regulation abilities was in-situ fabricated on an Au/microporous substrate, and the emissivity changed from 0.316 to 0.735 in MIR under different voltages. Besides, an H$_2$SO$_4$-doped PANI film was fabricated on an Au deposited nylon 66 porous substrate with an excellent $\Delta \varepsilon$ of 0.4 and 0.3 at 8–14 and 2.5–25 $\mu$m, respectively. Moreover, the regulation mechanism of the DBSA-doped PANI film on ITO substrates was further explained. The change in the MIR transmittance of the PANI film at different states realized the modulation of emissivity when the thickness of PANI was within a certain value, however, the pseudo-metallic behavior of the PANI film dominated this process when the thickness overran. (Figure 8B) For inorganic acids, an HClO$_4$ doped PANI porous film with excellent emissivity regulation abilities was in-situ fabricated on an Au/microporous substrate, and the emissivity changed from 0.316 to 0.735 in MIR under different voltages. Besides, an H$_2$SO$_4$-doped PANI film was fabricated on an Au deposited nylon 66 porous substrate with an excellent $\Delta \varepsilon$ of 0.4 and 0.3 at 8–14 and 2.5–25 $\mu$m, respectively. The IR images of the device at different states exhibited its potential clearly on a honeycomb structure composed of hexagons. Unlike in the traditional materials where the electrons move according to the Schrödinger equation, electron excitations in graphene obey the Dirac Hamiltonian equation. (Figure 9A-a,b) Given the unique band structures of graphene, intraband and interband transitions result in different absorption positions, which dominate in visible to IRs and terahertz. The absorption of single layer graphene in MIR can reach up to ~2.3% at normal incidence, which can be tuned to near zero via the electrical tuning process. In detail, the Fermi-level $E_F$ and carrier density of graphene can be adjusted through electrolyte gating or doping process, which affect the interband transition process to attain tunability of emissivity in MIR. (Figure 9A-c)

However, absorption of the single layer graphene is relatively small to attain a large tunability. Therefore, multilayer graphene is a promising candidate instead. Kocabas et al. used multilayer graphene that served as the EC layer into fabricating a novel ECD. The highlight apart from the structure of the conventional ECD shown in Figure 6 indicates that the multilayer graphene was placed on top of the device to avoid the influence of electrode or other functional layers on $\Delta \varepsilon$. Besides, room-temperature liquid (RTIL) was selected as the electrolyte held by a porous polyethylene (PE) membrane, and the Au substrate served as the electrode. Under voltage bias, RTIL intercalated into the graphene layers, increasing carrier density and a blue-shift of the Fermi-level, which finally suppressed emissivity from 0.8 to 0.3. The process was confirmed by monitoring the peaks of N and F elements in the XPS spectrum by adjusting the positive bias voltage from 0 to 4 V. A “HELLO” thermal image pattern was generated by designing a composed device with different voltage configurations, which was confirmed as a feasible candidate for novel communications. (Figure 9B) Later, flexible adaptive textiles were fabricated using a similar mechanism, in which a conductive fabric, and 1-butyl-3-methylimidazolium hexafluorophosphate replaced the Au substrate and RTIL to act as the electrode and electrolyte, respectively, while multilayer graphene was maintained. Meanwhile, a similar trend of emissivity in response to different bias was observed, which was observed in the practical test when applied in a t-shirt. An additional practical examination showed that this device exhibits a high endurance and flexibility when experiencing mechanical and washing tests. (Figure 9C) This study provides the foundation for graphene-enabled adaptive optical textiles, which can attain multifunctional performance given the highly maneuverable feature of this structure.

In addition, graphene has been an excellent choice for the plasmonic materials in terahertz to IRs since the traditional plasmonic materials like noble metals worked mainly in visible to near IRs. By designing a metasurface structure, graphene could exhibit its outstanding plasmonic performance. Considering the higher absorption in the terahertz region than MIR due to Pauli blocking, great emphasis is also placed on this region in the graphene applications in tuning optical properties, which has been widely explored, in imaging, spectroscopy, and communications areas. It is worth mentioning that these structures applied in the terahertz region may provide feasible references for those in MIR, since the absorption band could be moved to MIR by doping or other processes.

3.3. Novel Electrochromic Materials

3.3.1. Graphene

Graphene has remained as the most superior material since it came out given its unprecedented surprising physical properties. It is made out of a single layer of carbon atoms arranged on a honeycomb structure composed of hexagons. Unlike in the traditional materials where the electrons move according to the Schrödinger equation, electron excitations in graphene obey the Dirac Hamiltonian equation. (Figure 9A-a,b) Given the unique band structures of graphene, intraband and interband transitions result in different absorption positions, which dominate in visible to IRs and terahertz. The absorption of single layer graphene in MIR can reach up to ~2.3% at normal incidence, which can be tuned to near zero via the electrical tuning process. In detail, the Fermi-level $E_F$ and carrier density of graphene can be adjusted through electrolyte gating or doping process, which affect the interband transition process to attain tunability of emissivity in MIR. (Figure 9A-c)

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3.3.2. Quantum Well Structures

A basic quantum well structure refers to a three-layer structure A/B/A, which consists of an alternating arrangement of
two different semiconductor materials. The thickness of the middle potential well layer B is smaller than the electron de Broglie wavelength. In this structure, the wave functions of the electrons are localized in one dimension, where the conduction band and valence band split into sub bands in the vertical direction, resulting in a step shape instead of a conventional parabolic profile of the relationship between the state density of carriers and energy. This implies, that some new absorption peaks will be seen due to electron transitions at these energy levels called intersubband transition, which can be applied in an infrared laser\[101\] and quantum cascade laser device. Similar to the mechanism of graphene mentioned above, electronic energy and density of quantum well structures can be changed by applying a reversible bias to obtain a tunable emissivity.

Noda et al.\[102\] first designed a quantum well structure, with a layer of the n-type GaAs/Al\(_{0.3}\)Ga\(_{0.7}\)As quantum wells sandwiched in the p-type GaAs, intrinsic GaAs layers, and a bottom n-type GaAs layer. Besides, a 2D photonic crystal structure was introduced to the upper GaAs layer and GaAs/Al\(_{0.3}\)Ga\(_{0.7}\)As layer for efficient light coupling to the intersubband transition. By adjusting structural parameters, the emissivity at around 9 \(\mu\)m reached 0.81 without an applied bias, but dropped to 0.12 with a reversible bias of 8 V. The reversible bias raised the electron potential further above the Fermi energy, depleting the electron density of the quantum wells, finally cutting off the intersubband transition. Evaluation of the influence of width and doping density of quantum wells on emissivity,\[103\] provided a reference for selecting appropriate parameters for dynamic modulations.

Considering the lack of electrical controllability at high temperature, Noda et al.\[104\] designed a photonic crystal thermal emitters structure containing the GaN/AlGaN multiple quantum wells inside the p–n GaN junction, with the potential to operate at high-temperature, whose \(\Delta \varepsilon\) reached 0.15 at 4 \(\mu\)m when the temperature was 500 °C. The study provided insights into the enhancement of the selectivity and sensitivity of spectroscopy applications even in extremely hot conditions. Besides the structures above which concentrate on MIR, in other literature,\[105–107\] quantum well-based multilayer structures were designed to modulate emissivity in the THz region which can
be applied in electrically modulated incandescent sources and cascade laser devices. This provides novel ideas for emissivity modulation in MIR.

Structures based on the quantum well combined with photonic crystal structure have realized a large $\Delta \varepsilon$ at a certain narrow wavelength that can be adjusted by changing the doping type, level, and the width of the potential well and barrier layers. The structure can be improved further by constructing a superlattice structure by reducing the thickness of the barrier layer or introducing quantum dots. These methods might attain a coupling effect, with different types of quantum effects to realize a broadband tunability. Moreover, a practical test should be performed in the future systematically.

3.3.3. Reversible Metal Electrodeposition Structures

Reversible metal electrodeposition, which involves the deposition and dissolution of metals on conductive substrates, provides an effective platform to manipulate metals for dynamic MIR modulation.[108] Typical reversible metal electrodeposition structures are similar to conventional ECDs, and Liu et al. proposed a structure with excellent adaptive performance.[109] They chose nanoscopic Pt films as the absorption film, and Ag was chosen as the variable functional material through the deposition and dissolution process, to reflect MIR waves. Primarily, when Ag was not electrodeposited, the nanoscopic Pt films had high MIR absorption, and partial MIR transmission could also be transformed to absorption by the IR-absorbing gel electrolyte layer, so that the device exhibited high emissivity. After electrodepositing, the formed Ag electrodeposited Pt films would convert the high absorption to high reflection in MIR, causing a huge tunability of emissivity. (Figure 10B) To have a more intuitive perception, devices were attached on a 50 °C hot plate to record their real-time MIR images, which MWIR and LWIR represented the wavelength from 3 to 5 $\mu$m and 7.5 to 13 $\mu$m, respectively. (Figure 10C) After electrodepositing, the apparent temperature of devices decreased a lot accompanying by their reduced emissivity. For other performance, the switching time (around 15s), stability, and reversibility (steadily operate up to 350 fully reversible cycles) were also comparable. (Figure 10D,E)

Meanwhile, they thought that the difficulty to find electrodes with both high MIR transmission and conductivity blocked the applications of the reversible metal electrodeposition devices in MIR.[108] To solve this problem, inspired by graphene and CNT—based transparent electrodes that have been used in various electronic devices, they fabricated proper graphene-based electrodes by transferring graphene to modified polypropylene (PP) film and the barium fluoride (BaF$_2$) substrates, respectively. As a result, the two kinds of graphene-based electrodes satisfied the basic requirements that applying to MIR dynamic regulation in reversible metal electrodeposition devices. Overall, the reversible metal electrodeposition devices have shown unbelievable potential in regulating thermal radiance dynamically even though there are still few relevant researches focusing on MIR. The devices can be enlarged, colored, and...
flexible easily according to practical needs, and the emissivity tunability is also fantastic. By exploring better electrodes and structure designs, the performance is totally possible to be further promoted.

Actually, the primary advantage of EC materials constitutes the active control, which can realize a more operable regulation. Conventional EC materials are usually fabricated into classic ECDs, and the emissivity in MIR can be tuned on a varying wide range, which is suitable for thermal management and camouflage. The novel EC materials and structures such as graphene and quantum well structures regulate in a narrow band mainly according to the change of electronic density and Fermi level, which have a full of potential in thermal sensing, imaging, and spectroscopy. It is worth noting that the doping modification process significantly enhances the tunability performance in MIR. Further development of these materials and structures should be destined as inseparable from the development of doping technology. The reversible metal electrodeposition devices are more compatible with diverse needs but need more attention in MIR and comprehensive tests for applications. How to fabricate large-area and reliable devices is also a problem on the road to practicality.

### 4. Other Smart Materials

Apart from thermochromic and EC materials which have been studied for years, there are some other novel smart materials which can also regulate emissivity in MIR dynamically in response to mechanical and humid stimulations. Meanwhile, their dynamic regulation process mainly relies on the reversible structural changes, so that we conclude them all together in this chapter.

#### 4.1. Mechanically Responsive Materials

Most mechanically responsive materials used in dynamic regulation of thermal radiance are inspired by living organisms, therefore, we will introduce some basic and relative bio-inspired knowledge first. Natural selection endows animals with amazing skills. Therein, visual camouflage is a hotspot among these abilities given its direct and dazzling visual effects. The production of color in nature is widely understood as the effect of combined pigments and microstructures. The former could adsorb light at a certain wavelength range, and the microstructures are able to reflect the light in diverse ways. Chameleons and cephalopods evade natural enemies by changing the optical response in visible region, providing bio-inspired approaches for scientists to regulate the electromagnetic waves in MIR. Recently, by applying mechanical stimulations to change the morphology or structure, there are some researches that have achieved the goal.

On land, the excellent color-changing ability of chameleons has been widely and extensively studied. Casanovas et al. designed a corrugated nickel-based stretchable emitter that modulates emissivity in MIR dynamically by combining the dynamic modification of optical properties of chameleons with an understanding of the unique morphology of the ant-hair structures showing as periodic triangular crests and troughs. Emissivity difference between the two states of nickel from corrugated to stretched state was caused by the enhanced multiple scattering effects when nickel was corrugated. Although \( \Delta \varepsilon \) of the structure needs further improvement, the concept provides a novel approach to dynamic thermal radiation regulation. (Figure 11A) By replacing Ni with smart materials indicated above, it is entirely possible to attain a combined control method for mechanical and other stimulations, such as thermal or electronic signals.

Under the sea, cephalopods possess two types of cells called pigment cells and iridocytes which are arranged alternatively to control the color change process through a biochemical signaling cascade. This phenomenon additionally opens a new avenue for tuning emissivity adaptively. Gorodetsky et al. designed an intriguing free-standing structure combined with an infrared-reflecting nanostructured copper film and infrared-transparent styrene–ethylene–butylene–styrene polymer. Through adjusting the uniaxial strain, the coverage of the polymer matrix by the infrared-reflecting copper film was changed, leading to the tunability of the infrared optical properties (Figure 11B). The structure was utilized to tune the infrared emissivity largely when the infrared-transparent matrix was replaced with a high-absorption one. Apart from this structure, another novel structure was also designed, which could respond to double electromechanical stimulations and, translated many key natural abilities of cephalopods from visible to MIR. The structure was conceptualized from a parallel plate capacitor type comprising a proton-conducting bottom electrode, a dielectric elastomer membrane, a proton-conducting top electrode, and an infrared-reflecting coating. The surface wrinkling was introduced to attain mechanical actuations. Moreover, the specular-to-diffuse reflectance ratios and the active area were introduced to explain the difference between emissivity and reflectivity before and after mechanical and electrical actuations, which showed a great potential of utilization in applying in dielectric elastomer based artificial muscles, pneumatic automation, energy generation, and adaptive optics. Later, they conceived a tri-layer device, in which an elastomer layer was sandwiched between two highly conductive membranes. Under electromechanical actuation, the device could adjust the specular-to-diffuse transmittance ratios by fourfold in MIR, which provided a new approach of camouflage and photothermal regulation (Figure 11C). We believe that the devices may afford new possibilities for various applications although the optimization of mechanical actuation strategies or the reduction of the associated operating voltages is required.

Apart from these bio-inspired materials, Cui et al. proposed that thermal radiation is the primary heat dissipation way in typical indoor environments heat for humans, which plays an important role in the design of clothes (Figure 11D-a). They fabricated a smart flipping textile structure which successfully regulated thermal radiation to realize personal thermal management. The structure comprises a bilayer thermal emitter which has different emissivity inside a nanoporous polyethylene (nanoPE) textile. Carbon was chosen as the material for the high emissivity side in the emitter and faced out in the cooling mode, whereas copper was selected as the low emissivity material which faced out in the heating mode. The
thickness of the nanoPE textiles was also tuned across the flipping process to change the thermal conduction between human skin and the emitter, and the combined transformations ensured that the temperature of skin maintains between 32 and 36 °C under a dynamic ambient temperature variation of 9 °C. (Figure 11D-b–d) It can be predicted that a wide range of materials could be processed in a similar approach to improve the performance and reduce the cost given the simplicity of the structures.

Overall, mechanically responsive materials have made significant breakthrough on stretchable and flexible devices for regulation of thermal radiation recently. The excellent compatibility and simplicity of the regulation mechanisms provide broad potentials for the combination with other smart materials and allow further improvements. When it comes to commercial applications, the protective packaging must be considered to ensure sufficient service time. To weaken the effect of packaging on the regulation process, the mechanical along with the optical performance of the packaging should meet stringent requirements but, less relevant research has been done. It can be predicted that effective enhancements in mechanically responsive materials will provide innovative technological and scientific opportunities across various fields.
4.2. Humidity Responsive Materials

Referring to humidity responsive materials, different from the flipping mechanism for personal thermal management as aforementioned, Wang et al. [1] effectively regulated infrared radiation by more than 35% in response to the relative humidity of the underlying skin. By coating triacetate-cellulose bimorph fibers with a thin layer of carbon nanotubes as the textile, a distance-dependent electromagnetic coupling between the neighboring coated fibers in the textile yarns was credited to the modulation. The yarn would make the concentration of the metal elements on the neighboring fibers to induce resonant electromagnetic coupling, promoting heat dissipation through radiation from the human body. (Figure 12A) The research first developed the technology of wearable personal thermal management textiles, constructing a more intelligent life, as well as expanding our abilities to adapt to demanding environments. Another approach was proposed by Yang et al. [118] which realized simple but dramatic modulation. They used intrinsic non-absorptive porous polymer coatings as the matrix and took advantage of the change in the refractive index contrast across the polymer-pore boundaries when the air in the pores was replaced by proper liquids, to realize the dynamic regulation finally. For regulation in MIR, they structured PE into a hierarchically porous form, which had about 40% porosity and about 0.1 µm pore sizes. When it was dry, it showed high transmittance but when it was wetted with MIR-absorptive alcohol, the transmitted waves were almost completely absorbed, showing a huge Δε of 0.64 in 8–13 µm. The design provides an inexpensive and scalable paradigm for dynamic regulation of light and heat with proper fluid pumping and collection systems, and a promising selection to more sophisticated conversion paradigms. (Figure 12B)

The above studies also open two different pathways for developing novel thermal management systems. It should be highlighted that, the technologies are both readily compatible with commercial processes due to the out-bound replaceability and machinability of materials. Nevertheless, detailed practical tests for abilities such as cycling performance, abrasion resistance, and so on, need to be completed to evaluate its practicality as well.
5. Summary and Perspective

In this review, we provide a state-of-the-art account of recent developments of smart materials for dynamic thermal radiation regulation and their emerging applications. Four kinds of functional materials and structures with engineered emissivity properties have been introduced, which are considered as part of the most promising candidates for realizing the dynamic regulation of thermal radiation in complex environments. Passive and active control of thermal radiation based on thermochromic and EC materials can be applied in different appropriate phenomena according to diverse needs. In addition, some advanced materials with adaptive thermal radiation in response to mechanical and humid stimulations have been intensively investigated, which opened up new directions for attaining dynamic regulation of thermal radiation.

Despite these great advances, research on these materials for practical applications is still in its early stages and there are numerous challenges hindering advancements on the road to commercial applications. Primarily, thermochromic materials can only change the infrared emissivity based on the temperature, which belongs to the passive control materials that have not yet achieved the potential of intelligent thermal management compared with other smart materials. In the future, thermochromic systems for dynamic thermal radiation modulation may use additional control aids such as electronic stimulations to realize the combined and accurate regulation. Second, EC materials are always assembled into ECDs to achieve the regulation process; therefore, the compatibility of each primitive material must be considered, making the designing process difficult and cumbersome. Moreover, the packaging technique is necessary when assembling ECDs into commercial applications to ensure the lifetime of employment, but the contradiction occurs due to the influence on the ability of thermal radiation regulation of it. Further studies should focus on constructing structure designing criteria, proposing mature packaging methods and the enhancement of EC properties. Finally, for mechanically and humidity responsive materials, the better compatibility of these materials compared to others should be fully utilized, such as redesigning structures with other smart materials, to realize multi stimuli-responsive regulations of thermal radiation to meet more complex needs. Practical tests of the overall performance are also needed urgently to apply for further validation.

Opportunities and challenges always coexist. The remarkable progress in the past decades has provided a robust foundation for potential applications of numerous smart materials with regulated thermal radiation. The trend of intelligence is inevitable in rapid development of science and technology across the globe. These advances imply that, smart materials with integrated functions will be more widely used in the future. Therefore, development of these adaptive smart materials will yield unlimited opportunities and continue to inspire research in various fields, including material science, physics, nanoscience, nanotechnology, and beyond.

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Conflict of Interest

The authors declare no conflict of interest.

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