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Review

Effectiveness of Daytime Radiative Sky Cooling in Constructions

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Abstract: In this paper, we have carefully studied the scientific literature dealing with the use of passive radiative surfaces within the construction industry. The aim of this paper is to highlight technologies and materials for daylight radiative cooling under study today—or already on the market—and to report their main characteristics, performance and, where possible, costs. Following a review of the available scientific literature, the advantages and limitations of such an option were highlighted, seeking to capture opportunities and future lines of research development. This review also provides the physical laws that evaluate the energy balance of passive radiative surfaces as well as the criteria to quantify all the terms of these equations.

Keywords: passive radiative cooling; buildings; sub-ambient temperature; urban heat island

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1. Introduction

1.1. Background of the Review

The planetary emergence of climate change requires the search for innovative strategies and technologies, with reduced anthropogenic impact, to limit the effects of global warming. The European Directive 2018/844 states that buildings contribute to 36% of greenhouse gas emissions and that 50% of final energy consumption in the European Union is used for heating and cooling [1]. The latter is widely considered a challenging issue, simply due to the constraints of the second law of thermodynamics [2]. Furthermore, in hot climates, cooling is becoming more and more a driver of the electric energy demand. Much attention is being regarded worldwide to passive radiative materials, which provide a path to dissipate thermal energy from surfaces toward the ultracold extra-terrestrial space [3]. The idea of passive cooling of surfaces to sub-ambient temperatures, using the night sky as an effective heat sink dates to the earliest studies by Granqvist et al. [4]. Such cooling capacity has been exploited for climatization, since ancient times, in tropical areas [5]. A similar behaviour has been observed not only in artificial structures, but also in butterflies that regulate the wing temperatures using radiative cooling [6], and in nano-structured wild moth cocoon fibres [7], providing effective radiative cooling for the moth pupae by controlling optical reflection as well as radiative heat transfer. Finally, Shi et al. have demonstrated that Saharan silver ants [8] (*Cataglyphis bombycine*) efficiently dissipate heat back to the surroundings due to the high emissivity for wavelengths higher than 2.5 μm, and high reflectivity in the wavelength range of solar radiation.

If, on the one hand, night-time radiative cooling has been extensively studied so far [9], daytime cooling would indeed represent a challenging option to face peak cooling demand (mainly occurring during the day) [10] as well as heat island effects [11] and other similar challenging issues regarding the anthropogenic footprint due to energy consumption. Figure 1 summarizes the many interactions between radiation emitted by the Sun with the atmosphere and the Earth's surface [12–16]. Incident solar radiation (at low wavelengths) undergoes absorption, reflection and scattering phenomena as it interacts with the atmosphere and the Earth's surface. At the same time, the Earth's surface emits electromagnetic radiation at higher wavelengths (in the infrared range) towards the atmosphere. This radiation can be again scattered, absorbed or reflected, or can even be transmitted through the atmosphere to free space. All these phenomena contribute to the overall thermal balance of the Earth's surface and regulate its average temperature. Passive cooling may thus represent an interesting opportunity for sustainable development, mitigating both the causes and the effects of global warming, offering a source of off-grid energy and even a water source by night cooling of surfaces below the dew point temperature [17].

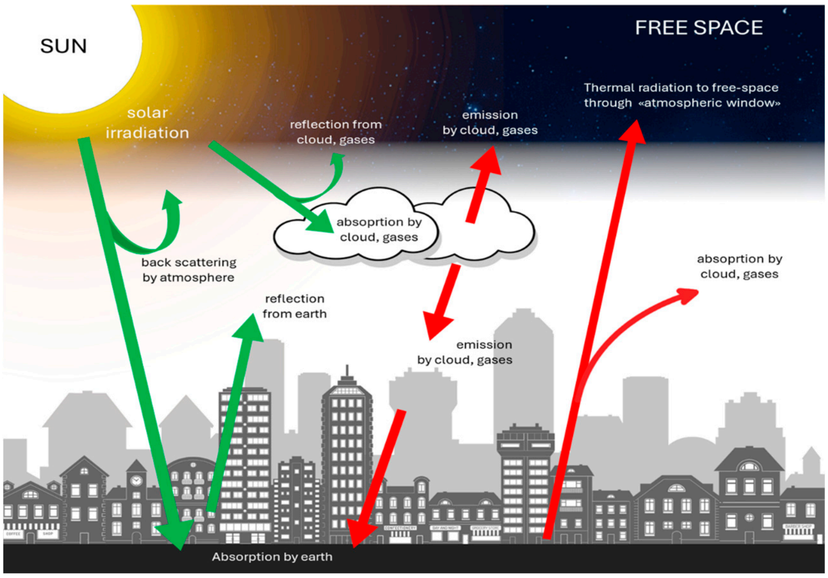

Figure 1. Energy exchange at the Earth's surface. The interactions of solar radiation and terrestrial radiation with the earth's atmosphere and surface are finely balanced to regulate the temperature of our planet.

1.2. Problem Statement and Motivation

A fundamental watershed in the research field regarding passive radiative coolers is undoubtedly represented by Aaswath P. Raman's seminal paper published in Nature in 2014 [18], which paved the way for research on radiative heat dissipation systems operating during daytime hours, exposed to solar radiation. This was a fundamental step, opening up new opportunities for the exploitation of heat dissipation. This paper aims to review the recent investigations in the field, with special reference to the construction sector, especially from that year to the present. This review may be useful to a wide audience of students, researchers and professionals who are interested in the effectiveness of new strategies to increase energy efficiency in buildings. With this aim, we have tried to identify the most suitable strategies to introduce radiative surfaces in buildings and to achieve significant energy savings in summer air conditioning operation. To this end, we took special consideration of publications that appeared after Aaswath P. Raman demonstrated, for the first time—supporting the assumption with an experimental activity—that it is possible to achieve sub-ambient temperature surfaces, even in the presence of solar radiation during daylight hours. This means that passive strategies may be exploited to achieve effective heat rejection without using energy. This is an important issue, especially in urban contexts, where urban heat islands represent more and more of an open issue [19].

1.3. Objective and Structure

This review is mainly devoted to gather the most relevant investigations about daytime passive coolers' technologies for the construction sector, within the time interval that separates us from the publication of Aaswath P. Raman's seminal paper published in Nature in 2014 [20], which fostered research relating to radiative heat dissipation systems operating during daytime hours. Hereafter, the design principles, the most investigated materials, and main applications of radiative sky cooling will be reviewed, with reference to the construction sector, with the intention of studying the effectiveness of such technologies, to ensure the reader's awareness of the benefits and limits of these technologies, with a highly quantitative approach. The structure of this review paper consists of an introduction reporting a background of the review, the problem statement and motivation faced in this activity, and the objective and structure of the manuscript; a short methodology section; principles of radiative cooling; a wide literature review section for building integration of radiative cooling surfaces; a part regarding switchable materials and systems applied to radiative sky cooling in buildings; and the concluding remarks, containing limitations and future directions for this investigation.

2. Methodology

For the reasons stated above, most of the publications reviewed in this investigation date from 2014 to 2024, beyond those strictly necessary to explain the principles underlying the design and physics of (passive and active) radiative systems. In the text, the main works that regarding building integration of radiative systems are reported, with special reference to materials, modes of operation, and cost, when the literature in the field also makes such elements available. We found the articles reported here by querying the Scopus database, using the most recurrent keywords in articles published in this field of investigation. Moreover, a table has been created, reporting the main technologies investigated in the current state of the art of building integrated radiative surfaces and the relevant figures of merit that express their performance.

3. Principles of Radiative Cooling

Though it was anticipated already in the 1980's, only in the last decade has passive radiative cooling been experimentally demonstrated by the seminal studies reported by Raman and co-workers [18]. This means that a passive cooling strategy may allow daytime cooling of structures to temperatures below ambient air, even in the presence of the Sun radiation. Such surfaces would be able to operate without any external energy, in a "passive" mode. In fact, the atmosphere of our planet shows a relatively wide transparency window for electromagnetic waves, in the infrared (IR) wavelength range between 8 µm and 13 µm (Figure 2b), due to the very low atmospheric emission in that spectral region [21]. This fact leads us to find suitable ways to exploit such a special feature of the atmosphere composition for the purpose of heat dissipation either from buildings or cities and industrial plants [22]. The existence of such "open window" paves the way towards the possibility to cool objects at an ambient temperature (≈300 K), by means of thermal radiation taking place between bodies on the Earth's surface and the extra-terrestrial space, roughly at ≈3 K. Coincidentally, according to Planck's law, the thermal radiation of a blackbody at 300 K shows its peak of radiation, precisely, at about 10 µm. In this way, the emitted radiation might escape to the extra-terrestrial space, which can be considered an outstanding heat sink. For daytime applications, the surface of a cooler must show selective features; at the same time, it should absorb as little solar radiation as possible but also emit the maximum radiation within the atmospheric window, using the extraterrestrial space as a thermal sink. This can be achieved by maximizing the reflectance of the cooler in the wavelength range from 250 nm to 2.5 μm (Figure 2a) and maximizing the emissivity in the wavelength range from 8 μm to 13 μm (Figure 2b). Structures capable of simultaneously working as broadband mirrors for the solar radiation (solar reflectors) and strong thermal emitters in the atmospheric window (IR radiators) may effectively act as daytime radiative coolers: achieving sub-ambient temperatures (for the whole day and night) may represent a milestone for engineering and materials science. Moreover, daytime cooling would match with the profile of peak energy uses for cooling in buildings and other applications.

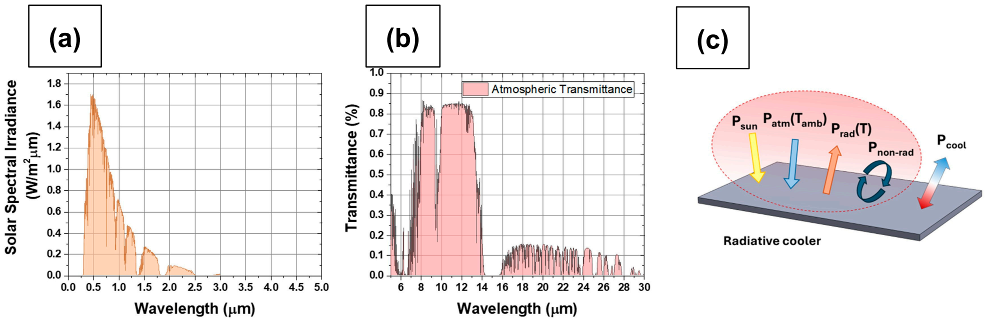

Figure 2. (**a**) Example of solar spectral irradiance at mid-latitude under a cloudless sky at sea level. (**b**) Atmospheric transmittance: the atmosphere shows high transmittance in the wavelength range between 8 and 13 μm. (**c**) Energy balance of a radiative cooler's surface: P_{sun} and P_{atm} represent the absorbed solar irradiation power and the absorbed atmospheric radiation power, respectively. Prad is the thermal radiation power from the surface, and $P_{non-rad}$ is the non-radiative heat transfer between the surface and the environment; all these terms contribute to the net cooling power P_{cool}, as expressed by Equation (1).

In essence, radiative coolers should maximize the radiative term of their full energy balance (Figure 2c), which is expressed as follows [20]:

$$P_{cool}(T) = P_{rad}(T) - P_{atm}(T_{amb}) - P_{sun} - P_{non-rad} \tag{1}$$

which not only takes into account the radiative term (P_{rad}) but also the one concerning non-radiative (convective/conductive) thermal exchange ($P_{non-rad}$), the absorbed solar irradiation (P_{sun}) and the absorbed power due to atmospheric thermal radiation (P_{atm}). Consequently, the term P_{cool} represents the net cooling power of a given structure that can be considered a radiator providing practical cooling only when the radiated power exceeds the sum of all the negative (absorbed) terms in Equation (1), which relates the net output power of a surface to its temperature. If $P_{cool} > 0$ when the ambient temperature equals the surface temperature, the surface may act as a daytime passive cooler. On the other hand, if Equation (1) is solved for $P_{cool} = 0$, it is possible to find the surface steady-state temperature, which must be lower than T_{amb}, to obtain effective radiative cooling [20]. The term $P_{rad}(T)$ is calculated as follows:

$$P_{rad}(T) = A \cdot \int_0^{\frac{\pi}{2}} (2\pi \cdot sin\theta \cdot cos\theta \cdot d\theta) \cdot \int_0^{\infty} \frac{2hc^2}{\lambda^5} \cdot \frac{1}{\left[e^{\left(\frac{hc}{\lambda k_B T}\right)} - 1\right]} \cdot \epsilon(\lambda, \theta) \cdot d\lambda \tag{2}$$

which integrates the spectral radiance of a blackbody at absolute temperature T, according to Planck's distribution law, embodying the angular integral over a hemisphere. For radiative sky cooling, it is generally acceptable to consider horizontal surfaces [23] and assume azimuthal symmetry. The term h represents Planck's constant, k_B is Boltzmann's constant, c is the speed of light in the vacuum and λ is the wavelength. On the other hand, $\varepsilon(\lambda, \theta)$ is the surface spectral angular emissivity, which is considered to vary only with the zenith angle θ and, according to the assumptions of Kirchhoff's law [24], replaces the surface absorptivity.

The term $P_{atm}(T_{amb})$ represents the absorbed power due to incident atmospheric thermal radiation, which can be calculated using the spectral angular emissivity of the atmosphere and the spectral radiance of a blackbody at temperature T_{amb} as follows:

$$P_{atm}(T_{amb}) = A \cdot \int_0^{\frac{\pi}{2}} (2\pi \cdot sin\theta \cdot cos\theta \cdot d\theta) \cdot \int_0^{\infty} \frac{2hc^2}{\lambda^5} \cdot \frac{1}{\left[e^{\left(\frac{hc}{\lambda k_B T_{amb}}\right)} - 1\right]} \cdot \varepsilon_{atm}(\lambda, \theta) \cdot \varepsilon(\lambda, \theta) \cdot d\lambda \tag{3}$$

where again the surface absorptivity is replaced by the emissivity. To quantify the spectral atmospheric radiation, the spectral directional emissivity, $\varepsilon_{atm}(\lambda, \theta)$, of the atmosphere is used, which is defined as the ratio between the atmospheric spectral radiance and the blackbody spectral radiance calculated at the air temperature (T_{amb}) near the ground. This is because the downward atmospheric thermal radiation comes mostly from the lowest few hundred meters of the atmosphere for those wavelengths where water vapor and carbon dioxide are strongly absorbing [25–27]. The atmospheric emissivity is angle-dependent and is generally given by the following expression:

$$\epsilon_{atm}(\lambda, \theta) = 1 - t(\lambda)^{\frac{1}{cos\theta}} \tag{4}$$

where $t(\lambda)$ is the atmospheric transmittance in the zenith direction. The values of the $t(\lambda)$ depend mainly on the concentration of some gases (H_2O, CO_2, O_3, CH_4, N_2O) and aerosols in the stratigraphy of the atmosphere and on the related temperature profile. To model the atmospheric transmittance, commercial software can be used (e.g., MODTRAN version 6) which draws the radiative properties of individual gases from specific databases (e.g., HITRAN). It has been observed that the cooling effect is boosted in dry climates with clear sky, as clouds and humidity may drastically reduce the value of P_{cool} [11,28].

The P_{sun} term integrates the incident solar irradiance, considering the spectrum corresponding to a value of 1.5 for Air Mass ($I_{AM1.5}$). and again, the spectral absorptivity equal to the spectral emissivity.

$$P_{sun} = A \cdot \int_0^{\infty} I_{AM1.5} \cdot \varepsilon_{atm}(\lambda, \theta_{sun}) \cdot d\lambda \tag{5}$$

Furthermore, the term reporting thermal power lost by non-radiative heat transfer is lumped as follows:

$$P_{non-rad}(T, T_{amb}) = h_c \cdot A \cdot (T_{amb} - T) \tag{6}$$

where h_c is a suitable heat transfer coefficient that considers both the convective heat exchange with air and the conductive heat exchange with external surfaces, in contact with the radiative cooler.

To achieve high values of $P_{cool}(T)$, the thermal emissivity of the cooler structure must be as high as possible within the atmospheric window, and, at the same time, its absorption should be very low throughout the wavelength range of the solar spectrum. Consequently, a correct design of passive cooling structures aiming at dissipating thermal energy during daytime hours minimizes the negative terms of the equation.

4. Literature Review for Building Integration of Radiative Cooling Surfaces

Several approaches have been explored towards the design of daytime radiative coolers, as reviewed in several works [29]. An effective approach is represented by one-dimensional photonic films obtained by depositing alternating layers of materials with different refractive index, deposited on top of a highly reflective material substrate [30]. With this approach, Raman et al. [20] cooled their structures about 5 °C below the ambient temperature, providing experimental evidence of the feasibility of daylight cooling. Chen et al. [31] theoretically showed that ultra-large temperature reductions to 60 °C below ambient can be achieved minimizing the parasitic heat losses (conduction and convection) by means of a vacuum chamber evacuated to a pressure of about 1.333×10^{-4} Pa. Their structure consisted of layers of silicon nitride, amorphous silicon, and aluminium, with thicknesses of 70 nm, 700 nm and 150 nm, respectively. A current trend of research for daytime passive cooling involves polymers. Zhai et al. [32] demonstrated the passive radiative cooling power of 93 W/m^2 of glass–polymer hybrid polymethylpenthene (TPX) membranes, embodying silicon dioxide microspheres, directly involved in the thermal emission. The highly transparent polymer reflects solar irradiation when backed with a silver thin film, deposited by E-Beam evaporation. Wang et al. [33] adopted the electrospinning technique to fabricate polyvinylidene fluoride/tetraethoxysilane (PVDF/TEOS) fibres with nanopores inside and silicon dioxide microspheres distributed on their surfaces. An average radiative cooling power of 61 W/m^2 was obtained, in May, in Shanghai. A radiative cooling structural material was developed by Li et al. [2], who demonstrated a highly resistant cellulose-based material embodying cellulose nanofibers capable of backscattering solar radiation and can emit in infrared wavelengths, providing continuous daytime and nocturnal cooling. More recently, Chen et al. reported the fabrication of a cellulose/SiO_2 bulk material, with significant passive cooling properties (sub-ambient temperature decline of about 7 °C) and mechanical properties. Current research trends also reported the use of nanophotonic structures, reviewed by Ko et al. [29]. This review reports an exhaustive list of best practices and research activities dealing with daytime radiative cooling applied to the construction sector.

The main limit to practical applications of cooling materials is represented by the low energy density provided, compared with design requirements. Apart from the intrinsic spectroscopic properties, cooling performance is dramatically affected by location, weather conditions, cooling profiles, cost of materials and maintenance, etc. Nevertheless, this field of investigation is widely recognized as an intriguing technological challenge [34,35].

Energy consumption in buildings is a relevant topic with regards to energy transition and reduction of environmental impacts of the construction sector responsible of 40% of total energy use in developed countries, where most of this consumption is related to HVAC (heating, ventilation, and air conditioning) systems. The impact of completely passive technologies for heat dissipation would be welcome both in terms of energy saving and in terms of CO_2 emissions reduction. In fact, in Zhao et al. [23], the adjective “passive” refers to technologies with zero energy input (i.e., with no fans or pumps to enhance cooling power).

Generally, the use of passive cooling in buildings can be achieved by exploiting passive and active approaches. The main difference is represented by the possibility of controlling performance according to seasonal or operation requirements, which is only possible in active systems. On the other hand, lower cost and complexity are the main advantages of passive systems.

4.1. Passive Cooling Surfaces from Traditional “Cool Roofs” to Daytime Radiative Coolers

Large rooftop surfaces are ideal candidates to host passive cooling surfaces. Cooling loads are compatible with values in the order of 100 W/m^2, as reported by Pacheco et al. [36]. With regards to passive technologies for buildings, cool roofs can be considered indeed an energy efficient solution [37,38]. Roof materials can be considered “cool” if they show—at the same time—high reflectance (or albedo) in the solar range of wavelengths and high emissivity in the atmospheric window; two simultaneous figures are then required to achieve acceptable performance in cool roofs [39], which can be considered highly selective materials.

As reported by Zhao et al. [23], cool roofs, in the form of coatings, tiles and other components, affect building performance by potentially reducing cooling loads, lowering electricity consumption, extending roof lifetime, and eventually reducing building impact on the heat island effect. According to ASHRAE [40], a cool roof must demonstrate a *solar reflectance index (SRI)* of 78 or higher. This figure of merit was defined by ASTM E1980 [41], as follows:

$$SRI = 123.97 - 141.35 \cdot \chi + 9.655 \cdot \chi^2$$

where the parameter χ depends on solar absorptance (α), on thermal emissivity (ε) and on the convective heat transfer coefficient (h_c) as well: the latest is evaluated for three wind conditions.

Energy saving associated with building integrated cool roofs have been studied in detail in several experimental and numerical works [42–44]. Akbari et al., in their study [42], reported that raising the solar reflectance of conventional dark roofs by 25% can reduce building cooling energy consumption by more than 10% and results in a lower ambient temperature. On the other hand, they found that raising roof reflectivity to 0.60 may reduce cooling energy use for buildings by about 20%.

A new prototyped cool clay tile on a traditional residential building was tested by Pisello et al. [45] to quantify summer benefits and winter penalties associated to the use of cool roofs in a temperate climate. The yearly analysis showed that the proposed technology achieved a decrease in indoor overheating by 4.7 °C, whereas the winter overcooling reduction is 1.7 °C. The substantial cooling benefits in summer are predominant with respect to the penalties in the winter season. Maximum year-round benefits were found for Palermo, in Southern Italy, with numerical simulations, corresponding to 14 kWh/m^2 per year. In fact, this technology may find application at low latitudes, in cooling dominated countries, where heating may be considered a lower concern for energy consumption in buildings.

A 67 µm thick roof surface under the mid-summer sun was fabricated by Gentle and Smith [46], suitable for large-scale production. Spectral selectivity of such materials allows for very high solar reflectance and emissivity, in the atmospheric window, to obtain net radiative power towards the clear sky. They met both of those criteria using specially chosen polyesters, deposited on a silver layer (200 nm). Such surface remained sub-ambient (2 °C) throughout a hot summer day (solar irradiance of 1060 W/m^2), with ambient air at 27 °C and high infrared intensity from the atmosphere of 400 W/m^2. Further numerical simulations showed that the reduction of cooling energy achievable using this new material would be 91 kWh/m^2 in Orlando (FL, USA).

Cool roofs with high reflectance may also produce visual discomfort, like glare. For this reason, cool-coloured roof tile coatings have been developed, with visible properties in the visible range (0.4–0.7 µm), with almost typical colour, like those of standard roofs but with much higher reflectance in the infrared wavelengths (0.7–2.5 µm).

Passive radiative cooling is well known to provide optimal figures in nocturnal hours, though the peak cooling load in buildings occurs in the daytime. Better performance than traditional cool roof materials can be achieved through recent results from photonics and optics, which enable the chance to use nanomaterials to improve both solar reflectance and infrared emissivity, with a useful diurnal net cooling power. With this regard, Baniassadi et al. [47] studied the effectiveness of engineered spectral properties of "super-cool" roofs showing reflectivity and emissivity values greater than 0.96 and 0.97, respectively, applied to a building rooftop in a numerical simulation activity in eight US cities. They claimed that the temperature rooftop remained lower than the ambient air temperature throughout the year, producing an average daily sensible flux of 30–40 W/m^2. Moreover, they found that this new technology could double the attainable cooling energy saving, compared to typical white roofs. At the basis of their simulation activities, they used the spectral properties of super-cool surfaces demonstrated by Jyotirmoy Mandal et al. [48]. They proposed hierarchically porous poly(vinylidene fluoride-co-hexafluoropropene) coatings with a high passive daytime radiative cooling capability: hemispherical solar reflectance $R_{sol} = 0.96 \pm 0.03$ and long-wavelength infrared emissivity $\varepsilon_{LWIR} = 0.97 \pm 0.02$, with maximum sub-ambient temperature drops of ~6 °C and cooling powers of ~96 with 750 W/m^2 solar irradiance.

The approach used in daytime radiative coolers so far could be reconsidered according to Wang et al. [49], in terms of real cooling potentials, depending on location and real atmospheric conditions. If in a dry, sunny winter day in California, the multi-layered cooling system designed by Raman et al. [20] reported radiative cooling to nearly 5 °C below the ambient air temperature; numerical simulations by Lu et al. showed that when h_c equals 6.9 W/(m^2K) in Bangkok, the temperature reduction in summer was as low as 0.1 °C, with very low passive radiative cooling performance in the mid-latitudes. The same surface may perform even worse in damp tropic zones due to the reduced transparency of the atmospheric window, associated with water vapor. The above-reported considerations suggest that new radiative coolers should be customized according to location and climatic conditions. Moreover, photonic radiators generally require nanoscale-precision fabrication, based on physical vapor deposition techniques which may act as a limiting factor in terms of cost and mass production.

Photonic structures requires multilayer optical calculations [50] as well as complex and expensive fabrication processes. Raman's cooler consisted of seven alternate layers of HfO_2 and SiO_2, whose thicknesses were obtained after extensive numerical optimization. Similar structures adopted other dielectric materials, like Ta_2O_5 or TiO_2 [29,30]. The availability of simple, bottom-up processes, based on chemical approaches, would be more compatible with large scale production with lower production costs.

Wang et al. [33] reported a high-performance flexible hybrid membrane radiator based on polyvinylidene fluoride/tetraethyl orthosilicate, with 61 W/m^2 and a temperature decrease up to 6 °C, under a surface solar irradiance of 1000 W/m^2. Such a flexible hybrid membrane reflected ≈97% of solar radiation and exhibited an infrared emissivity higher than 0.96.

Zhai et al. [32] embedded 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 due to phonon-enhanced Fröhlich resonances of the microspheres. They deposited silver on one side of the membrane, obtaining a noon-time radiative cooling power of 93 W/m^2 under direct sunshine. The described fabrication process is highly compatible with roll-to-roll manufacturing of this novel technology. Chen et al. [51] reported a membrane containing delignified biomass cellulose fibres and inorganic SiO_2 microspheres.

4.2. Integration of Passive Radiative Surfaces in Buildings and HVAC Systems

Daytime radiative cooling may represent a reliable mitigation strategy to counterbalance the impact of urban heat islands, using materials with high reflectivity [8] and chromogenics [52]. Daytime coolers can be fabricated in the form of multilayered photonic stacks, 2D–3D photonic structures—both require a top-down fabrication approach—paints or polymer structures embedding nanostructures and fabricated using a bottom-up approach. In theoretical terms, a surface area of 1 m^2 emits a maximum thermal power of 459.3 W, with a maximum radiation peaked at 9.67 μm, according to Wien's displacement law [53]. The amount of thermal power emitted by a blackbody at 300 K in the spectral range of the atmospheric window is roughly 32% of the total emitted power, i.e., 148 W. The latter represents the ideal reference value of the thermal power that can be emitted by a body at ambient temperature with a $\varepsilon = 1$. After Raman's seminal work [18,20], sub-ambient daytime radiative coolers have been demonstrated that they are capable of reaching 4 °C below ambient temperature when exposed to direct daylight and even 60 °C theoretical maximum temperature reduction. Nevertheless, external conditions dramatically affect the performance of a radiative cooler, apart from the amount of solar radiation impinging on the dissipating surface. The P_{atm} term of the energy balance may be dramatically influenced by the relative humidity of ambient air. In fact, experiments carried out in low humidity conditions or desert conditions in Israel have reported optimal results [54]. Atmospheric transmittance spectra were accurately studied by Berk et al. since the first decade of this century [55]. Thermal power emitted by the atmosphere may in fact be transmitted to the cooler surface according to its emittance properties, according to Kirchhoff's law.

Furthermore, the operation conditions of a radiative cooler should consider the great variability of the convective term, i.e., the $P_{non\,rad}$ term: the convective heat power could cancel out the radiative benefit if the air temperature and the convective heat transfer coefficient are high, depending on wind speed. To reduce convective heat gains, wind covers and windshields have been proposed in several works worldwide [49].

Carlosena et al. [56] fabricated and tested daytime radiative materials consisting of a Vikuiti substrate (0.97 reflectivity and 0.89 emissivity) covered with a 2 μm thick film of polymethylsesquioxane with embedded silica nanoparticles, which have a competitive cost of 0.3 €/m^2. The surfaces reached 7.32 °C temperature reduction in daytime conditions in moderate weather conditions, which is quite different from those used for experiments in ideal settings (no convection and low relative humidity). They demonstrated that only scalable and effective daytime radiative materials may be relevant in the context of future applications in constructions.

Radiative Sky Cooling (RSC) is used to reduce indoor thermal loads in building envelopes, both passively and actively. In active systems, unlike passive applications, a certain amount of energy is required to utilize free cooling. This is achieved using fans, pumps, or a combination of both in hybrid systems combined with radiative sky surfaces. Active application may involve integrating RSC directly into HVAC systems to improve overall cooling capacity and system efficiency. This emerging strategy demonstrates the significant potential of RSC technology in various building applications [34]. Typically, panels or surfaces that emit thermal radiation in the long-wavelength infrared spectrum are used in Active Radiative Sky Cooling systems (ARSC). The process of radiative cooling occurs during both day and night, but it is most effective at night: in both cases, the sky acts as a natural heat sink. By utilizing more effective technologies, ARSC systems may offer a sustainable and energy-efficient cooling method reducing active energy building loads.

A growing array of active cooling strategies has been proposed to enhance the efficiency of RSC applications within roofing systems. Active cooling roofs generate cold water or cold air through RSC mechanisms and subsequently convey it into indoor spaces for cooling in alignment with the specific requirements of the building. Bergman [57] demonstrated that spectrally selective surfaces for passive cooling could effectively match cooling loads, surface area for heat rejection and increase the amount of thermal power transferred from Earth to space. He adopted energy balances and heat transfer rate equations to predict of the performance of a novel active daytime radiative cooling concept, proposing the use of spectrally selective surfaces in conjunction with air conditioning and refrigeration systems.

Kousis et al. [58] discussed potential strategies and current progress in materials development of daytime radiative coolers, highlighting challenges and roadmaps to achieve effectiveness of their real-life applications. This gives rise to the need to design materials capable of achieving high performance at reasonable costs, thanks to advanced nanomanufacturing and synthesis processes.

Yuan et al. [59] demonstrated a daytime radiative cooling application using a selective polymer-based metamaterial to passively cool a full-scale model house, achieving a roof surface temperature of 2–9 °C below the ambient, continuously, for 72 h. Moreover, they claimed a further result: the indoor air temperature was also consistently below the ambient during the daytime.

Liu et al. [60] recently proposed a dual-layer film consisting of ethylene-tetra-fluoroethylene (25 μm) and silver (200 nm thick Ag layer), showing solar reflectivity of 0.94 and average total emissivity of 0.84, capable of reaching 1.6 °C below ambient air at daytime in Hefei (China).

Lim et al. [61] proposed high-energy band gap calcium carbonate ($CaCO_3$) for all-day radiative cooling, without any metal reflector. They adopted $CaCO_3$ microparticles with a diameter of 20–30 μm. The authors claimed cooling power of 93.1 W/m^2 and a sub-ambient temperature of 3.38 °C in daytime.

Huang et al. [62] reported a newly designed scalable-manufactured magenta-coloured daytime radiative cooler (60 cm wide and 500 cm a long) fabricated by a roll-to-roll deposition technique. Average temperature drops of 2.6–8.8 °C during the daytime were reported.

Yu et al. [63] fabricated a self-sustained insulated cooler with two features: daytime sub-ambient passive cooling (−3.3 °C in the field tests) and, on the other hand, the surface can harvest atmospheric water at night.

4.2.1. Air-Based Cooling Systems

A simple method of integrating RSC embodying a building cooling system is to use an air-cooling system, where air acts as the heat transfer medium. Such integration may be achieved through a simple air-based cooling system. This system includes an RSC surface, a propelling fan, and a connecting loop. The cooling process is facilitated through natural ventilation or fan-induced airflow, which directs the air through an RSC surface, positioned atop the building. The effectiveness of the air-based cooling systems depends on a restricted air passage beneath the radiator and a significant surface area, with the aim of maximizing the cooling of the exchanged air [49]. Moreover, the efficiency of these systems is usually determined by radiative cooling surface properties and climate conditions (e.g., ambient air temperature, humidity, wind speed).

According to Zhao et al. [23] three different air-based cooling system classes are currently reported in the literature (**Error! Reference source not found.**). The first class (Figure 3a) represents a relatively simple air-based system, using the roof volume as a cooling sink, either directly into the room or via a duct system. The net cooling power of air-based systems is typically low, ranging from 20 to 40 W/m^2 [49]. The second class (Figure 3b) represents an active strategy combining HVAC hardware with an air-based system of ducts. The figure reports only daytime systems, though the first investigation of effective radiative heat coolers dates to the 1970’s and is performed during night time. Some milestones in such activities have been reported hereafter.

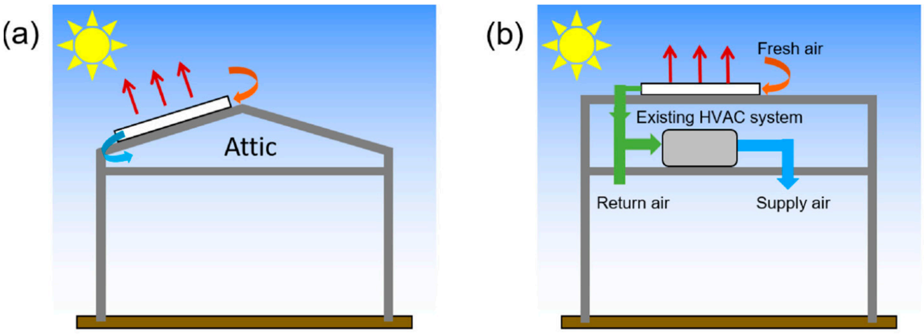

Figure 3. Active and passive strategies to exploit radiative coolers to cool fluids generally used in HVAC systems. (**a**) Air-based radiative sky cooling system using the roof as a radiator, (**b**) system integrated with HVAC system.

In 1977, Givoni introduced one of the first air-based applications named Roof Radiation Trap system. This system uses solar energy to heat buildings in winter and nocturnal radiation to cool them in summer [64]. This innovative approach involved the placement of a white-painted corrugated metal sheet on the roof to function as a nocturnal radiative cooler. The intervening space between the cooler and the roof was utilized for air storage. These corrugated metal sheets served the dual purpose of shielding against solar radiative heat during the day and cooling the air during the night. The interspace functioned as a cold reservoir, contributing to the cooling of the roof in subsequent days. Some vents connected the roof volume to the tested room. The results indicated that the roof radiation trap had the potential to yield a cooling capacity ranging from 29.7 to 55.8 W/m^2 under climatic conditions characteristic of Italy. The night sky radiant cooling performance of duct-type heat exchangers under different surface material and weather conditions was investigated by Liu et al. [65]. The differences between the inlet and outlet temperature of the night sky radiation heat exchanger resulted in a drop of 6.8 °C.

Along this line, Paker et al. [66] introduced the innovative "NightCool" roof concept designed to cool residential buildings. This approach involves establishing an attic area beneath a metal roof, with the internal building being interconnected or isolated based on airflow requirements within this space. The fan facilitated the airflow mechanism. The findings indicate that the "NightCool" roof resulted in an average cooling power of 5 to 10 W/m^2 overnight, particularly in the Florida climate.

Kimball et al. [67] have developed an air box convector using RSC technology. This system consists of a fan combined with two heat exchangers and is designed for cooling and dehumidification in tropical climates. Empirical results show that the innovative configuration using RSC has a potential energy saving of between 14% and 18% in the management of latent heat loads, contributing to the achievement of an optimal indoor environment.

Furthermore, Hollick [68] performed a series of performance tests on a nocturnal RSC roof. In this configuration, a sky radiative cooler was placed on the roof, and an air cavity was added underneath to aid air cooling. Cold air was then circulated into the room at night using a fan. The results showed that the RSC roof could lower the air temperature by approximately 4.7 °C compared to the ambient temperature.

Khedari et al. [69] designed and implemented four variants of roof radiators within an air-based system designed for a solar-powered school dormitory. Their experiments showed that during the night, the temperature of the roof radiators showed a reduction of 1 to 6 °C compared to the ambient air temperature, considering the prevailing weather conditions in Thailand.

Hu et. al. [70] introduced an innovative passive air conditioning module that integrates RSC and indirect evaporative cooling to boost efficiency. Results show that the system reduces the supply air temperature by 0.88 °C compared to the indirect evaporative cooling-only system. This corresponds to an 11.91% and 9.94% improvement in dew point efficiency and cooling energy gain, respectively.

Proper thermal insulation is also crucial to enhance the efficiency of ARSC system. Insulating materials prevent the reabsorption of heat from the surroundings, ensuring that the radiative cooling process remains effective [65].

Galvez et al. [71] tried to optimize the efficiency of an air-based RSC by analysing the performance of an air-based low-energy night-time radiative cooling system in Chile. The system is composed of a series of specialized radiative air collectors, a mechanical ventilation system, and a thermal storage wall, which is part of the indoor environment. The radiative air collector is cooled by radiative cooling due to radiative interaction with the sky. At night time, the fan is activated, and the cooled air is sent indoor to the gravel mass. At daytime, the fan is switched off and the gravel mass absorbs thermal energy that is accumulated indoor due to the internal loads and irradiation. Though this cannot be considered a daytime cooler, this technology is designed to operate during the daytime. This system aims at meeting the cooling demands of a building solely through natural ventilation or fans. Moreover, given the need for a narrow air duct and a large radiative cooling surface area, this air-based system is more suitable for use in detached houses or on the top floor of multi-storey buildings.

On the other hand, the cooling effect in daytime conditions is strongly affected by season (results presented in the first paper dealt with sunny days in winter conditions and in low humidity conditions [20]), radiation, location, humidity and air conditions. The non-radiative term of $P_{non\text{-}rad}$ is strongly affected by air speed. If the net nocturnal cooling of air systems reach values higher than 100 W/m^2 [9,72], the high convective heat transfer coefficients could hinder the performance in daytime conditions. Pollution also has a negative effect on coolers' performance since particulate emission absorbs (or emit) radiation, decreasing their cooling potential. According to Cui et al. [73], it is important to assess the influence of weather and geographical location on coolers' performance as well as to design radiative coolers capable of reducing the detrimental effects of wind, vapor, dirt, rain, and other external factors.

Zhao et al. [74] demonstrated the effectiveness of daytime cooling applied to a 1.08 m^2 system built using a wood framework and an aluminium plate (Figure 4). The cooling surface was protected with a polyethylene film acting as a convective shield. This prototype coupled radiative sky cooling with attic ventilation for temperature reduction: sub-ambient temperature reductions were between 5 and 8 °C, at nighttime, and between 3 and 5 °C during daytime hours. Daytime effective cooling technologies, compatible with passive air systems were demonstrated by Fu et al. [75] and by Torgerson et al. [76]. Wang et al. [77] reviewed typical materials and designs with adequate daytime radiative cooling capability: they can be grouped in several approaches, including nanophotonic materials obtained depositing alternating layers with suitable refractive properties, nano- and microparticle-based radiative materials, polymer-based radiative materials, and other radiative cooling designs.

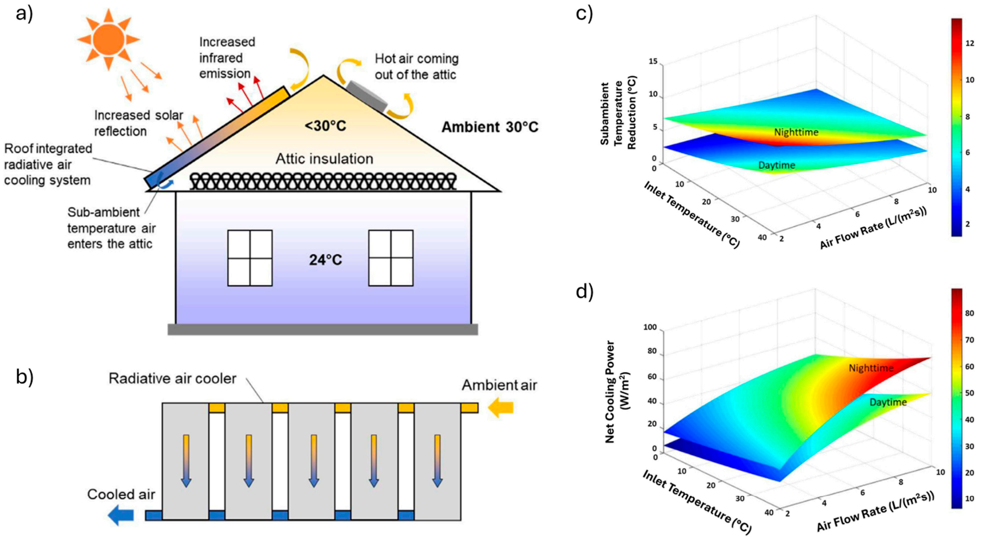

Figure 4. Radiative air coolers integrated atop a building (**a**,**b**); sub-ambient temperature reduction (**c**) and net cooling power attainable (**d**). [74].

Regarding the ideal component devoted to building integration of passive radiative coolers, roofs have generally been considered the most eligible surface to host such components. Nevertheless, Wu et al. [78] observed that roofs are generally responsible for only 10% to 20% energy consumption and such impact tends to be lower in high-rise buildings.

Passive radiative systems show limited effectiveness, highly depending on weather conditions, which may significantly harness their performance. Switchable properties may enhance their cooling capacity. In fact, if hot arid areas may benefit from passive coolers with static spectral properties almost throughout the year, due to high temperatures, their seasonal applicability is often hindered by lower temperatures and higher expenditures for heating in winter. Moreover, if the term regarding atmospheric power (P_{atm}) is strongly dependent on climate and weather conditions, the non-radiative term may be effectively attenuated by means of convective shields ($P_{non\ rad}$).

4.2.2. Water-Based Cooling Systems

Other systems use water as a heat transfer fluid, with higher specific heat capacity compared to air, using a cold storage unit, with net cooling power typically double, in the order of 40–80 W/m^2 [23].

Water-based cooling systems can be divided into two main types: open-loop and closed-loop. The open-loop water system typically involves a shallow roof pond as a key component, facilitating heat transfer to the environment through mechanisms such as convection, radiation and evaporation from the roof immersed in the pond water [79–82]. They have been largely investigated and used in arid areas of the planet. Conversely, the closed-loop water system differs from its open-loop counterpart by using water as the heat transfer fluid, with heat dissipation achieved through a flat plate radiator [69,83–85]. The heat carrier—water, in this case—flows in pipes embedded in a flat-plate and the system also includes an insulated water tank, a heat pump and the radiative plate.

The thermal energy derived from night-time radiative cooling, particularly in the form of chilled water, has the potential to be used as a cooling resource during the day. However, the typical low supply temperature of chilled water from conventional building air conditioning systems, such as 7 °C, may render the water from the radiative sky cooling system insufficiently chilled for direct use. Possible remedies include integrating the water-based cooling system with a radiant floor/ceiling system, which does not require an extremely low supply water temperature, typically in the range of 15–18 °C. Alternatively, the use of radiantly cooled water to pre-cool the heat transfer fluid before it enters the chiller is a viable solution.

Spanaki et al. [81] presented twelve different configurations of rooftop pools, providing a comprehensive analysis of their advantages and disadvantages, and discussed the criteria relevant to the design of rooftop pools.

Raeissi and Taheri [86] have shown that the implementation of a water-based open-loop system can lead to a significant reduction in the cooling load of the air conditioning system, through night-time radiative cooling, amounting to a 52% reduction during the summer season for a single-story house of 140.6 m^2 in Iran.

Meir et al. [87] proposed a radiative cooling system using water as a heat carrier, circulating in flat plate radiators. The system was equipped with a 280 L water reservoir. The cooling radiator consisted of sheets of polyphenylene oxide resin, arranged in twin-wall sheets. This system could cover a significant fraction of the cooling demand of a single-family house in Oslo (Norway).

Compared to the open-loop system, the closed loop results in higher efficiency. Zhou et al. [88] used an RSC system in conjunction with a heat exchanger to manage fresh air within the building environment. Cold water was generated using the radiative cooling panel and then fed to the heat exchanger to cool the fresh air. Cold storage significantly increases the drop in indoor air temperature, up to 12.7 °C. Any excess cooling capacity was stored in the thermal storage tank, not only meeting immediate cooling requirements but also providing additional thermal storage capacity.

Wang et al. [89] carried out numerical simulations for the HVAC system of a typical medium-sized office building integrating the use of the photonic radiative cooler. With reference to the cooling season, the free energy from the radiator addressed about 10% of the cooling load in Miami. A photonic radiative cooler encased in a polyethylene film in the air conditioning (AC) systems was designed to cool office buildings. Inside the cooler, water pipes were strategically placed to cool the water. The sky radiative cooler was positioned at the top of the building and connected to a water storage tank to form the RSC loop. The distance cooling loop, including the chiller, pump and cooling connections, were integrated with the RSC loop by heat exchange within the storage tank. This arrangement facilitated the adjustment of operating modes by means of valve switching (Figure 5).

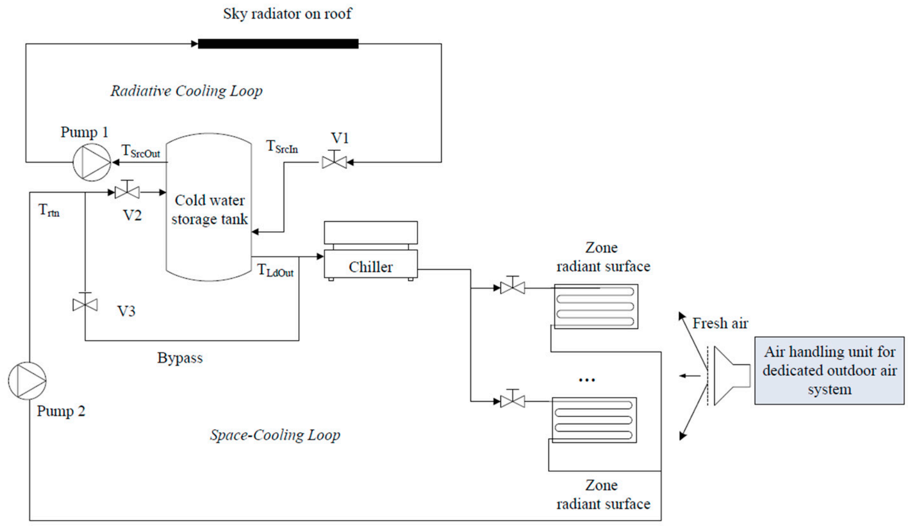

Figure 5. Schematic design of the integrated radiative cooling system [89].

A particularly promising roadmap for the application of RC modules is their integration with air conditioning systems to increase operational efficiency. Various studies have been carried out to explore the integration of either night or daytime RC structures with HVAC or other cooling systems. Within these hybrid systems, the use of chilled water from a radiative cooler helps to improve the efficiency of the air conditioning system by acting as a coolant for the cooling coils. Jeong et al. [10] described the design of an integrated radiative cooling, HVAC system with two different cooling coils—one supplied by radiative cooling and the other conventional. In this proposed cooling configuration, the conventional chillers used in the refrigeration cycle are replaced by an RC structure. The proposed cooling system has the potential to achieve a remarkable 35% reduction in energy consumption by complementing conventional space cooling equipment. Another study by Zhang et al. [90] investigated the integration of cold-water storage with radiative cooling to accumulate cooling energy. In addition, nighttime radiative coolers can be synergistically combined with evaporative cooling systems to facilitate pre-cooling, thereby increasing the overall systematic cooling efficiency. In this design, the radiative cooler generates cold water during the night, and during the day this cold water passes through the cooling coils to pre-cool the hot outdoor air before being subjected to a direct evaporative cooling process [91].

Recently, Yoon et al. [92] proposed a hybrid HVAC system that integrates a solar thermal collector and a radiative cooling panel as the heat source and heat sink, respectively. Annual power consumption is reduced by 3~29% as compared to a solar-assisted heat pump or radiative-cooling-assisted heat pump system.

With the spread of daytime passive radiative cooling, several studies [74,93] have shown that integrating such panels into an air conditioning system, known as a Radiative Cooling Assisted Heat Pump system, can reduce the electricity consumption in summer by 9–45%.

Along this line, Jia et al. [94] proposed a hybrid system that combines a ground source heat pump and all-day RSC radiators to improve the energy efficiency across China. It was found that the average annual cooling potential varies from 149.7 W/m^2 to 484.6 W/m^2 in all regions of China, with the highest cooling potential of 336.5 W/m^2 in cold northern China and the lowest cooling potential of 178.3 W/m^2 in tropical southern China.

In contrast to the air-based system, water-based implementations improve operability and controllability, thereby offering increased feasibility and efficiency. These systems can provide a cooling capacity tailored to the specific requirements of the building. However, their structural complexity is slightly increased, and their deployment is constrained by the available roof space for placement of the coolers.

Zhao et al. [93] reported a kilowatt-scale innovative module for radiative cooling named RadiCold, designed to cool water to 10.6 °C below ambient at daytime, and also investigated the effect of different weather conditions on its performance. The system surface area was 13.5 m^2 and a maximum cooling power of 1296 W was reported.

Goldstein et al. [95] reported their panels that harness radiative sky cooling to cool fluids 5 °C below the air temperature. Over three days of testing, we show that the panels cool water up to 5 °C, with a heat rejection power of 70 W/m^2. The authors also showed results of modelling activities, reporting that radiative surfaces, integrated on the condenser side of the cooling system of an office building, in a hot dry climate, reduced electricity consumption by 21% for cooling during the summer.

Table 1 shows that there are several technologies and materials that could lead to relevant results in terms of heat rejection. The determining factor, in the context of applications for the construction sector, will undoubtedly be that of cost (materials, installation, maintenance, disposal). According to Yu et al. [96], it is reasonable to expect that polymer-based porous structures and systems embodying randomly distributed particles (possibly without reflective silver metal layers) may perform well, being a promising approach for low-cost radiative cooling applications also in the construction sector, rather than nanophotonic-fabricated surfaces with a nanophotonic approach. For example, the cost of the RadiCold modules is estimated at about $25/$m^2$ [97]. Several technologies are still at a laboratory scale, and costs are only partially predictable. In general terms, polymers with a chemical-based bottom-up approach represent a viable alternative to expensive fabrication processes and will have more chances for building integration purposes. Apart from cost of materials, a consistent benefit related to radiative cooling technology is to save electricity used for cooling. A wide discussion of potential barriers to market adoption of radiative cooling materials has been reported in [98]. Their analysis revealed that the incremental cost of all components of the passive radiator should not exceed 8.25 $/$m^2$ to 11.50 $/$m^2$ of the total building floor area. It is quite easy to infer that materials with simple design criteria may cut fabrication costs. For example, Felicelli et al. [99] reported a low-cost, dual-layer system, comprising of a cellulose-based substrate as the bottom layer and a thin $BaSO_4$-based layer paint as the top layer. In the work by Zhang et al. [100], they estimated 26–46% saving of electricity consumption per year compared to split air conditioners in San Francisco, with a simple payback period of 4.8–8.0 years, and maximum acceptable incremental costs of 50.0–78.9 $/$m^2$. Papers reviewed during the preparation of this work reported limited information about costs of the radiators due to the low level of technology readiness generally at a laboratory scale. Nevertheless, some works show that potential benefits may be compatible with building integration. Furthermore, it should be observed that polymer-based structures may be more prone to scalability, inherently lightweight, and easy to install.

Table 1. Main state of the art technologies and figures of merit of their performance.

Reference	Technology Adopted	Adaptiveness	Main Features
Raman et al. [20]	Integrated photonic solar reflector/thermal emitter (seven layers of HfO_2 and SiO_2).	No	R = 97% of incident sunlight; high selective emittance in the atmospheric transparency window. Exposed to direct sunlight >850 W/m^2 cools to 4.9 °C below ambient T_{air}; cooling power of 40.1 W/m^2 at T_{air}.
Pisello et al. [45]	Prototyped cool clay tile.	No	Tiles decrease summer peak indoor temperature of the attic by up to 4.7 °C. Winter maximum temperature reduction was 1.2 °C
Gentle et al. [46]	Birefringent polymer pairs, with high index and one with low index, for example poly-ethylene terephthalate (PET)/naphthalene	No	For a 1000 $W \cdot m^{-2}$ incident, around 30 W/m^2 of solar energy is absorbed. Average thermal emittance of 0.96 from 7.9 to 14 µm. In the absence of a convective barrier, $T_{amb} - T_{roof}$ value is equal to 3

	dicarboxylate and polyethylene naphthalate.		°C for peak midday conditions on a clear summer day, and to 7 °C at night.
Wang et al. [33]	300 μm thick flexible hybrid photonic membrane radiator. Polyvinylidene fluoride/ tetraethyl orthosilicate fibres with randomly distributed SiO_2 microspheres.	No	Average infrared emissivity > 0.96 and $R_{sol} \approx 97\%$. Average radiative cooling power of 61 $W\cdot m^{-2}$ and a temperature decrease up to 6 °C under solar intensity of 1000 W/m^2.
Zhai et al. [32]	Resonant polar dielectric microspheres randomly embedded in a polymeric matrix, backed with silver coating.	No	Daytime radiative cooling power of 93 W/m^2 under direct sunshine and economical roll-to-roll manufacturing of the metamaterial.
Zhang et al. [90]	Switchable radiative cooler composed of a radiative cooling coating and a temperature-responsive part.	Yes	The prepared radiative cooler shows $R_{sol} \approx 96\%$ and 95% infrared emission in the atmospheric transmittance window (8–13 μm). The temperature responsive part consists of nickel–titanium alloy springs working as a thermal switch, showing low thermal resistance (2.7 $K\cdot W^{-1}$) in the ON state. The heat is blocked to escape the indoor space since a high thermal resistance (20 $K\cdot W^{-1}$) is created when the thermal switch is in the OFF state.
Deng et al. [101]	Electro-controlled polymer-dispersed liquid crystal.	Yes	The device reaches near/sub-ambient temperature when the solar irradiance is below 400 W/m^2 and can dynamically manage daytime cooling efficiency by applying an external bias.
Carlosena et al. [56]	Vikuiti substrate covered with 2 um thick film of polymethylsesquioxane + SiO_2 microparticles.	No	Daytime radiative cooler with a cost of 0.3 €/m^2. >7 °C sub-ambient temperature in moderate weather conditions.
Zhao et al. [74]	"RadiCold" metafilm on top of an aluminum sheet. Polyethylene-based convective shield.	No	Sub-ambient temperatures of 3–5 °C during daytime.
Yuan et al. [59]	Polymer-based spectrally selective metamaterial; R_{sol} about 96%.	No	When solar irradiation is 720 W/m^2, a surface temperature of the model house of 2–9 °C below the ambient during a 72 h experiment period is achieved.
Liu et al. [60]	Dual-layer film consisting of ethylene-tetra-fluoro-ethylene (25 μm) and silver.	No	$R_{sol} = 0.94$ and average total emissivity of 0.84, capable of reaching 1.6 °C below ambient air.
Lim et al. [61]	Single layer of a $CaCO_3$ composite without any metal reflector	No	Daytime sub-ambient temperatures of 3.38 °C and cooling power of 93.1 W/m^2.
Huang et al. [62]	Polymer–Tamm photonic structure.	No	Found theoretical thresholds for sub-ambient cooling through coloured coolers. Temperature drop of 2.6–8.8 °C during the daytime and 4.0–4.4 °C during the nighttime is achieved.
Yu et al. [63]	Porous polyethylene film at the top, an air layer in the middle, and poly(vinyl	No	$R_{sol} = 0.91$; $\varepsilon_{LWIR} = 0.96$; daytime sub-ambient cooling ~3.3 °C in the field tests.

	alcohol) hydrogel with lithium bromide at the bottom.		
Wang et al. [89]	The photonic radiative cooler consists of seven alternating layers of two thin oxides, a couple of metal layers, and a silicon wafer substrate.	No	HVAC system integrating the use of the photonic radiative cooler was proposed and modelled using the whole energy simulation program, EnergyPlus. During the cooling season, the passive cooler addressed about 10% of the cooling load in Miami, 17–36% in Las Vegas, and 61–84% in Los Angeles.
Jia et al. [94]	Hybrid system that combines ground source heat pump and all-day radiative sky cooling radiators.	No	Annual average cooling power provided by radiative sky cooling radiators ranges between 149.7 and 484.6 W/m^2 across all regions of China.
Zhao et al. [93]	Polymer-based hybrid film (50 μm); silver (200 nm); adhesive (90 μm); and polycarbonate (0.5 mm).	No	A 10.6 °C sub-ambient cooling of a large mass of water in real experiments.
Goldstein et al. [95]	Visibly reflective extruded copolymer mirror (3M Vikiuiti ESR film) to achieve sub-ambient temperatures under sunlight on top of a silver reflective surface.	No	Panels cooling water down to a 5 °C sub-ambient temperature with water flow rates of 0.2 L/(min·m^2), resulting in an effective heat rejection flux of 70 W/m^2.

Radiators with a non-dynamic behaviour allow passive radiative heat dissipation to be easily removed in the winter season since they could have undesirable effects in the winter season, leading to increased heating consumption. Energy savings attained in the cooling season may be counterproductive if the radiator is also used during winter. This aspect may be relevant according to the location where radiators are installed. Wu et al. [78] clearly reported that the location has a great impact in this balance between energy saving and increase in winter losses due to the radiators. They observed that in relatively high-temperature areas, the loss in winter is significantly lower than the energy benefits observed in summer; conversely, in most regions, the loss in winter may be even greater than the energy saved in summer. The location and season may dramatically affect the performance of radiators. Lu et al. [100] demonstrated that the maximum temperature depression of the radiator designed by Raman et al. may underperform in the mid-latitude region of Shanghai and work even worse in the hot and damp tropic areas.

5. Switchable Materials and Systems Applied to Radiative Sky Cooling in Buildings

The persistent thermal radiation of cooling materials during winter seasons may increase the heating cost and consequently affect indoor thermal comfort. For this reason, great attention is being paid to the design of switchable radiative cooling technologies, to dynamically cool or heat objects, according to changing external conditions, to address internal requirements throughout the year time. They have been classified according to the external *stimuli* that activate their operation [102]. Switchable cooling technologies should possess a switching ability between cooling and heating (or even intermediate behaviours) modes: high solar reflectance and high infrared emissivity during summer and low solar reflectance and emissivity during cold seasons, as shown in Figure 6. An exhaustive review about switchable radiative cooling surfaces was also proposed by Myung Jin Yoo et al. [103] in 2023. Different mechanisms for switchable radiative cooling were investigated thoroughly: wetting/drying switching mechanism, mechanical switching mechanism, thermochromic switching mechanism and electrochromic switching mechanisms. Novel technologies make it possible to dynamically adjust the optical characteristics of materials surfaces, enabling smart thermal management.

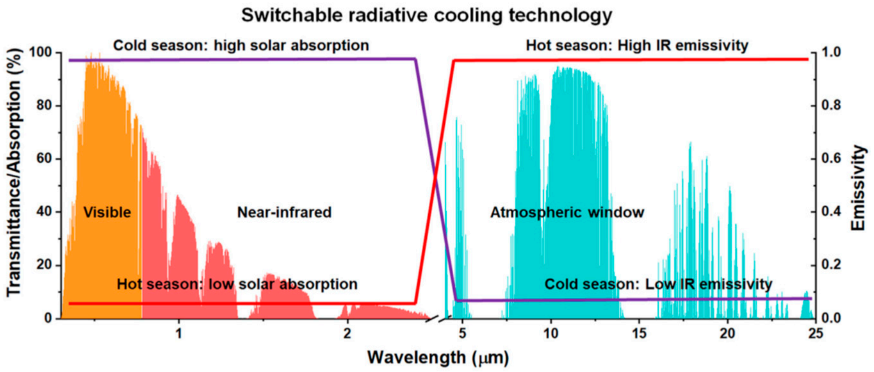

Figure 6. Ideal adaptiveness of spectral properties in selective radiative coolers.

The emittance modulation ($\Delta\varepsilon_{LWIR}$) is due to the change of the intrinsic molecular structure of materials: Yoo et al. [104] showed that some molecular bonds, namely C–O–C (peaked in the wavelengths 7936–9009 nm), C–OH (8071–9709 nm), and C–F_3 (8711 nm) affect vibrational energy resonance within the long-wavelength infrared range and cause an increase in infrared absorbing (emittance) features of the material. For example, the high value of ε_{LWIR} typically observed in polydimethylsiloxane at 9,813 nm and 11,455 nm is due to the resonating molecular bonds Si–O and Si–CH_3, respectively.

At high latitudes, a switching operation of roof properties would be welcome, with the ability to change reflectance properties when buildings switch from cooling to heating mode. Self-adaptive or smart radiative cooling materials should be designed for this purpose. Cool roofs, in fact, may unwantedly increase heating energy in winter. This point was accurately discussed by Testa et al. [104]. According to their studies, coatings with effectively switchable reflectance can improve annual energy savings by up to 6% compared to a static cool roof. Though static materials may produce overall energy savings in several climate conditions, switchable reflectance coatings may offer larger benefits, when applied to both roofs and opaque exterior walls.

Innovative dual-mode devices with both heating and cooling capacities can save energy of 236 GJ/year, 1.7 times more than cooling-only and 2.2 more than heating-only materials [102]. In this roadmap, passive adaptive cooling would be ideal to reduce maintenance and production costs. For example, the temperature-dependant behaviour of refractive indexes of VO_2 [105] would be compatible with the required operation of switchable passive coolers. Materials with stimulus-dependant characteristics represent a suitable field for further investigation. Such highly customized materials would enable adaptive regulation of IR emissivity and solar reflectance, creating an all-season energy-saving technology. In other words, switchable cool roofs should have the ability to change reflectance throughout the year, according to changes in external conditions.

Zhang et al. [106] proposed a switchable radiative cooler composed of a radiative cooling coating and a temperature-responsive part, based on nickel–titanium springs as temperature-responsive actuators, capable of changing thermal resistance from 2.7 K/W in the “on” state to 20 K/W in the “off” state, with possible temperature drops of 11 K in daytime.

Deng et al. [101] proposed a switchable polymer-dispersed liquid crystal to design a smart window showing on-demand passive radiative cooling efficiency that was designed and prepared by incorporating mid-infrared emitting monomers into the material matrix. They demonstrated the effectiveness of their device during a daytime experiment performed in Beijing, in spring.

In conclusion, the goal of an efficient radiative thermal management is related to the capability of a simultaneous, effective control of R_{sol} and ε_{LWIR}, and to avoid any unwanted performance in precise seasonal conditions. If reflectance control may be associated with a decrease in transmittance, one further benefit attainable may be the improvement of indoor visual comfort. The scattering observed in hydroxypropylcellulose and similar hydrogels, for example, may reduce high glare effects, in addition to increasing reflectance and emittance in hot and sunny summer days [107].

6. Conclusions

This work aims to quantify the effectiveness of radiative systems applied to the construction sector, with reference to their operation during daytime. This review provides the physical laws that evaluate the energy balance of passive radiative surfaces and provides the tools to quantify all the terms of these energy balances. Above all, the materials and technologies that allow—according to the current state of the art—for the production of passive radiative surfaces operating in daytime conditions and therefore under incident solar radiation, are reviewed, considering the effectiveness of the various technologies available today, both on the market and still at a laboratory scale. Different approaches in the fabrication of radiative systems have been reviewed, including photonic and polymeric membranes containing nanoparticles resonant with infrared radiation between 8 and 13 μm. Furthermore, different ways of integrating passive radiative systems inside buildings are shown to achieve air or water cooling in different system configurations. The most recent and high impact works appeared in this field of investigation were considered, with special attention to applications of switchable materials. Some references to the costs of available products are also provided, when available. The great scientific interest aroused by the possibility of producing surfaces intended for heat rejection, even under daylight, bodes well for the availability, in a few years, of several materials for applications in various fields. A separate discussion has been dedicated to the development of adaptive materials, which will give further degrees of freedom to a technology already endowed with disruptive potential. A driving element, in this intriguing roadmap, will be the cost of these materials, particularly in the construction sector, as well as the benefits that can be achieved. Indeed, in this review paper, we have reported the performance and cost of several materials, some of which are already patentable and commercially available, while others are still at a laboratory development level, with advantages and disadvantages. Some considerations have also been made in this aspect, when available in the scientific literature. Not every research group has reported cost considerations, and this represents a limit of this review but also of the field investigated, as well as the limited availability of LCA analysis on these types of materials and systems. These limitations, duly pointed out here, could be a warning to increase the level of information in the articles produced in this area of research.

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References

1. EU Parliament. *Directive (EU) 2018/844 of the European Parliament and of the Council of 30 May 2018 Amending Directive 2010/31/EU on the Energy Performance of Buildings and Directive 2012/27/EU on Energy Efficiency*; EU Parliament: Strasbourg, France, 2018.
2. Li, T.; Zhai, Y.; He, S.; Gan, W.; Wei, Z.; Heidarinejad, M.; Dalgo, D.; Mi, R.; Zhao, X.; Song, J.; et al. A Radiative Cooling Structural Material. *Science* **2019**, *364*, 760–763. https://doi.org/10.1126/science.aau9101.
3. Granqvist, C.G.; Hjortsberg, A. Surfaces for Radiative Cooling: Silicon Monoxide Films on Aluminum. *Appl. Phys. Lett.* **1980**, *36*, 139–141. https://doi.org/10.1063/1.91406.
4. Granqvist, C.G.; Hjortsberg, A. Radiative Cooling to Low Temperatures: General Considerations and Application to Selectively Emitting SiO Films. *J. Appl. Phys.* **1981**, *52*, 4205–4220. https://doi.org/10.1063/1.329270.
5. Givoni, B. Options and Applications of Passive Cooling. *Energy Build.* **1984**, *7*, 297–300. https://doi.org/10.1016/0378-7788(84)90075-6.

6. Tsai, C.C.; Shi, N.; Pelaez, J.; Pierce, N.; Yu, N. Butterflies Regulate Wing Temperatures Using Radiative Cooling. In Proceedings of the 2017 Conference on Lasers and Electro-Optics, CLEO 2017—Proceedings 2017, San Jose, CA, USA, 14–19 May 2017; Volume 2017-Janua, pp. 1–2. https://doi.org/10.1364/CLEO_QELS.2017.FTh3H.6.
7. Shi, N.N.; Tsai, C.C.; Craig, C.; Yu, N. Nano-Structured Wild Moth Cocoon Fibers as Radiative Cooling and Waveguiding Optical Materials. In Proceedings of the 2017 Conference on Lasers and Electro-Optics, CLEO 2017—Proceedings 2017, San Jose, CA, USA, 14–19 May 2017; Volume 2017-Janua, pp. 1–2. https://doi.org/10.1364/CLEO_SI.2017.STh4I.2.
8. Shi, N.N.; Tsai, C.C.; Camino, F.; Bernard, G.D.; Yu, N.; Wehner, R. Keeping Cool: Enhanced Optical Reflection and Radiative Heat Dissipation in Saharan Silver Ants. *Science* **2015**, *349*, 298–301. https://doi.org/10.1126/science.aab3564.
9. Hossain, M.M.; Gu, M. Radiative Cooling: Principles, Progress, and Potentials. *Adv. Sci.* **2016**, *3*, 1500360. https://doi.org/10.1002/advs.201500360.
10. Jeong, S.Y.; Tso, C.Y.; Zouagui, M.; Wong, Y.M.; Chao, C.Y.H. A Numerical Study of Daytime Passive Radiative Coolers for Space Cooling in Buildings. *Build. Simul.* **2018**, *11*, 1011–1028. https://doi.org/10.1007/S12273-018-0474-4/METRICS.
11. Ulpiani, G.; Ranzi, G.; Feng, J.; Santamouris, M. Expanding the Applicability of Daytime Radiative Cooling: Technological Developments and Limitations. *Energy Build.* **2021**, *243*, 110990. https://doi.org/10.1016/j.enbuild.2021.110990.
12. John, A.; Duffie, W.A.B. *Solar Engineering of Thermal Processes*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2013.
13. Swinbank, W.C. Long-Wave Radiations from Clear Skies. *Q. J. R. Meteorol. Soc.* **1963**, *89*, 339–348.
14. Bliss, R.W. Atmospheric Radiation near the Surface of the Ground: A Summary for Engineers. *Sol. Energy* **1961**, *5*, 103–120. https://doi.org/10.1016/0038-092X(61)90053-6.
15. Martin, M.; Berdahl, P. Summary of Results from the Spectral and Angular Sky Radiation Measurement Program. *Sol. Energy* **1984**, *33*, 241–252. https://doi.org/10.1016/0038-092X(84)90155-5.
16. Berdahl, P.; Martin, M. Emissivity of Clear Skies Permalink. *Energy Environ. Div.* **1984**. https://doi.org/10.1016/0038-092X(84)90144-0.
17. Ahmad, M.I.; Jarimi, H.; Riffat, S. *Nocturnal Cooling Technology for Building Applications*; Springer: Singapore, 2019; ISBN 9789811358340. https://doi.org/10.1007/978-981-13-5835-7
18. Rephaeli, E.; Raman, A.; Fan, S. Ultrabroadband Photonic Structures to Achieve High-Performance Daytime Radiative Cooling. *Nano Lett.* **2013**, *13*, 1457–1461. https://doi.org/10.1021/nl4004283.
19. Santamouris, M.; Yun, G.Y. Recent Development and Research Priorities on Cool and Super Cool Materials to Mitigate Urban Heat Island. *Renew. Energy* **2020**, *161*, 792–807. https://doi.org/10.1016/j.renene.2020.07.109.
20. Raman, A.P.; Anoma, M.A.; Zhu, L.; Rephaeli, E.; Fan, S. Passive Radiative Cooling below Ambient Air Temperature under Direct Sunlight. *Nature* **2014**, *515*, 540–544. https://doi.org/10.1038/nature13883.
21. Fan, S.; Raman, A. Metamaterials for Radiative Sky Cooling. *Natl. Sci. Rev.* **2018**, *5*, 132–133. https://doi.org/10.1093/nsr/nwy012.
22. Heo, S.Y.; Lee, G.J.; Kim, D.H.; Kim, Y.J.; Ishii, S.; Kim, M.S.; Seok, T.J.; Lee, B.J.; Lee, H.; Song, Y.M. A Janus Emitter for Passive Heat Release from Enclosures. *Sci. Adv.* **2020**, *6*, eabb1906. https://doi.org/10.1126/sciadv.abb1906.
23. Zhao, D.; Aili, A.; Zhai, Y.; Xu, S.; Tan, G.; Yin, X.; Yang, R. Radiative Sky Cooling: Fundamental Principles, Materials, and Applications. *Appl. Phys. Rev.* **2019**, *6*, 021306. https://doi.org/10.1063/1.5087281.
24. Greffet, J.-J.; Bouchon, P.; Brucoli, G.; Sakat, E.; Marquier, F. Generalized Kirchhoff Law. *arXiv* **2016**, arXiv:1601.00312. https://doi.org/10.1103/PhysRevX.8.021008.
25. Ji, M.; Xu, Y.; Mo, Y.; Zhang, Y.; Zhou, R.; Zhu, S. Land Surface Temperature Retrieval Method Based on UAV Thermal Infrared Remote Sensing and Synchronized Atmospheric Profiles. *J. Geo-Information Sci.* **2023**, *25*, 2456–2467, doi:10.12082/dqxxkx.2023.230351
26. Vall, S.; Castell, A. Radiative Cooling as Low-Grade Energy Source: A Literature Review. *Renew. Sustain. Energy Rev.* **2017**, *77*, 803–820. https://doi.org/10.1016/j.rser.2017.04.010.
27. Zhao, B.; Hu, M.; Ao, X.; Huang, X.; Ren, X.; Pei, G. Conventional Photovoltaic Panel for Nocturnal Radiative Cooling and Preliminary Performance Analysis. *Energy* **2019**, *175*, 677–686. https://doi.org/10.1016/j.energy.2019.03.106.
28. Lim, X.Z. The Super-Cool Materials That Send Heat to Space. *Nature* **2020**, *577*, 18–20. https://doi.org/10.1038/d41586-019-03911-8.
29. Ko, B.; Lee, D.; Badloe, T.; Rho, J. Metamaterial-Based Radiative Cooling: Towards Energy-Free All-Day Cooling. *Energies* **2019**, *12*, 89. https://doi.org/10.3390/en12010089.
30. Kecebas, M.A.; Menguc, M.P.; Kosar, A.; Sendur, K. Passive Radiative Cooling Design with Broadband Optical Thin-Film Filters. *J. Quant. Spectrosc. Radiat. Transf.* **2017**, *198*, 1339–1351. https://doi.org/10.1016/j.jqsrt.2017.03.046.
31. Chen, Z.; Zhu, L.; Raman, A.; Fan, S. Radiative Cooling to Deep Sub-Freezing Temperatures through a 24-h Day-Night Cycle. *Nat. Commun.* **2016**, *7*, 13729. https://doi.org/10.1038/ncomms13729.
32. Zhai, Y.; Ma, Y.; David, S.N.; Zhao, D.; Lou, R.; Tan, G.; Yang, R.; Yin, X. Scalable-Manufactured Randomized Glass-Polymer Hybrid Metamaterial for Daytime Radiative Cooling. *Science* **2017**, *355*, 1062–1066. https://doi.org/10.1126/science.aai7899.
33. Wang, X.; Liu, X.; Li, Z.; Zhang, H.; Yang, Z.; Zhou, H.; Fan, T. Scalable Flexible Hybrid Membranes with Photonic Structures for Daytime Radiative Cooling. *Adv. Funct. Mater.* **2020**, *30*, 1907562. https://doi.org/10.1002/adfm.201907562.
34. Yan, T.; Xu, D.; Meng, J.; Xu, X.; Yu, Z.; Wu, H. A Review of Radiative Sky Cooling Technology and Its Application in Building Systems. *Renew. Energy* **2024**, *220*, 119599. https://doi.org/10.1016/J.RENENE.2023.119599.

35. Hu, M.; Zhao, B.; Suhendri; Ao, X.; Cao, J.; Wang, Q.; Riffat, S.; Su, Y.; Pei, G. Applications of Radiative Sky Cooling in Solar Energy Systems: Progress, Challenges, and Prospects. *Renew. Sustain. Energy Rev.* **2022**, *160*, 112304. https://doi.org/10.1016/J.RSER.2022.112304.
36. Pacheco, R.; Ordóñez, J.; Martínez, G. Energy Efficient Design of Building: A Review. *Renew. Sustain. Energy Rev.* **2012**, *16*, 3559–3573. https://doi.org/10.1016/j.rser.2012.03.045.
37. Jia, S.; Weng, Q.; Yoo, C.; Xiao, H.; Zhong, Q. Building Energy Savings by Green Roofs and Cool Roofs in Current and Future Climates. *Npj Urban Sustain.* **2024**, *4*, 23. https://doi.org/10.1038/s42949-024-00159-8.
38. Feng, J.; Saliari, M.; Gao, K.; Santamouris, M. On the Cooling Energy Conservation Potential of Super Cool Roofs. *Energy Build.* **2022**, *264*, 112076. https://doi.org/10.1016/J.ENBUILD.2022.112076.
39. Chan, Y.H.; Zhang, Y.; Tennakoon, T.; Fu, S.C.; Chan, K.C.; Tso, C.Y.; Yu, K.M.; Wan, M.P.; Huang, B.L.; Yao, S.; et al. Potential Passive Cooling Methods Based on Radiation Controls in Buildings. *Energy Convers. Manag.* **2022**, *272*, 116342. https://doi.org/10.1016/j.enconman.2022.116342.
40. ASHRAE. *Advanced Energy Design Guide for Small to Medium Office Buildings 50%*; ASHRAE: Peachtree Corners, GA, USA, 2014; ISBN 9781936504053.
41. ASTM. *ASTM E1980-11(2019)*; Standard Practice for Calculating Solar Reflectance Index of Horizontal and Low-Sloped Opaque Surface. ASTM: West Conshohocken, PA, USA, 2019; Volume 04.04. https://doi.org/10.1520/E1980-11R19.
42. Akbari, H.; Berdahl, P.; Levinson, R.; Wiel, S.; Miller, B.; Desjarlais, A; 2006. Cool-Color Roofing Material. California Energy Commission, PIER Building End-Use Energy Efficiency Program. CEC-500-2006-067.
43. Bamdad, K. Cool Roofs: A Climate Change Mitigation and Adaptation Strategy for Residential Buildings. *Build. Environ.* **2023**, *236*, 110271. https://doi.org/10.1016/j.buildenv.2023.110271.
44. Hernández-Pérez, I.; Xamán, J.; Macías-Melo, E.V.; Aguilar-Castro, K.M. *Reflective Materials for Cost-Effective Energy-Efficient Retrofitting of Roofs*; Elsevier Ltd.: Amsterdam, The Netherlands, 2017; ISBN 9780081011287.
45. Pisello, A.L.; Cotana, F. The Thermal Effect of an Innovative Cool Roof on Residential Buildings in Italy: Results from Two Years of Continuous Monitoring. *Energy Build.* **2014**, *69*, 154–164. https://doi.org/10.1016/j.enbuild.2013.10.031.
46. Gentle, A.R.; Smith, G.B. A Subambient Open Roof Surface under the Mid-Summer Sun. *Adv. Sci.* **2015**, *2*, 2–5. https://doi.org/10.1002/advs.201500119.
47. Baniassadi, A.; Sailor, D.J.; Ban-Weiss, G.A. Potential Energy and Climate Benefits of Super-Cool Materials as a Rooftop Strategy. *Urban Clim.* **2019**, *29*, 100495. https://doi.org/10.1016/j.uclim.2019.100495.
48. Mandal, J.; Fu, Y.; Overvig, A.C.; Jia, M.; Sun, K.; Shi, N.N.; Zhou, H.; Xiao, X.; Yu, N.; Yang, Y. Hierarchically Porous Polymer Coatings for Highly Efficient Passive Daytime Radiative Cooling. *Science* **2018**, *362*, 315–319. https://doi.org/10.1126/science.aat9513.
49. Wang, Z.; Liang, J.; Lei, D.; Jiang, C.; Yang, Z.; Yang, G.; Zhang, D.; Zhang, L.; Zhang, C.; Bai, Y. Temperature-Adaptive Smart Windows with Passive Transmittance and Radiative Cooling Regulation. *Appl. Energy* **2024**, *369*, 123619. https://doi.org/10.1016/j.apenergy.2024.123619.
50. Byrnes, S.J. Multilayer Optical Calculations. *arXiv* **2016**, arXiv:1603.02720.
51. Chen, Y.; Dang, B.; Fu, J.; Wang, C.; Li, C.; Sun, Q.; Li, H. Cellulose-Based Hybrid Structural Material for Radiative Cooling. *Nano Lett.* **2021**, *21*, 397–404. https://doi.org/10.1021/acs.nanolett.0c03738.
52. Cannavale, A.; Pugliese, M.; Giannuzzi, R.; Scarfiello, R.; Prontera, C.T.; Primiceri, V.; Mazzeo, M.; Martellotta, F.; Ayr, U.; Fiorito, F.; et al. Towards the Scale-up of Solid-State, Low-Emissive Electrochromic Films, Fabricated on a Single Substrate with Novel Electrolyte Formulations. *Sol. Energy Mater. Sol. Cells* **2022**, *241*, 111760. https://doi.org/10.1016/j.solmat.2022.111760.
53. Çengel, Y.A. *Introduction to Thermodynamics and Heat Transfer*; McGraw-Hill: New York, NY, USA, 2009; Volume 960.
54. Erell, E.; Etzion, Y. Analysis and Experimental Verification of an Improved Cooling Radiator. *Renew. Energy* **1999**, *16*, 700–703. https://doi.org/10.1016/S0960-1481(98)00255-9.
55. Berk, A.; Anderson, G.P.; Acharya, P.K.; Bernstein, L.S.; Muratov, L.; Lee, J.; Fox, M.; Adler-Golden, S.M.; Chetwynd, J.H., Jr.; Hoke, M.L.; et al. MODTRAN5: 2006 Update. *Algorithms Technol. Multispectral Hyperspectral Ultraspectral Imag. XII* **2006**, *6233*, 62331F. https://doi.org/10.1117/12.665077.
56. Carlosena, L.; Andueza, Á.; Torres, L.; Irulegi, O.; Hernández-Minguillón, R.J.; Sevilla, J.; Santamouris, M. Experimental Development and Testing of Low-Cost Scalable Radiative Cooling Materials for Building Applications. *Sol. Energy Mater. Sol. Cells* **2021**, *230*, 111209. https://doi.org/10.1016/j.solmat.2021.111209.
57. Bergman, T.L. Active Daytime Radiative Cooling Using Spectrally Selective Surfaces for Air Conditioning and Refrigeration Systems. *Sol. Energy* **2018**, *174*, 16–23. https://doi.org/10.1016/j.solener.2018.08.070.
58. Kousis, I.; D'Amato, R.; Pisello, A.L.; Latterini, L. Daytime Radiative Cooling: A Perspective toward Urban Heat Island Mitigation. *ACS Energy Lett.* **2023**, *8*, 3239–3250. https://doi.org/10.1021/acsenergylett.3c00905.
59. Yuan, J.; Yin, H.; Yuan, D.; Yang, Y.; Xu, S. On Daytime Radiative Cooling Using Spectrally Selective Metamaterial Based Building Envelopes. *Energy* **2022**, *242*, 122779. https://doi.org/10.1016/j.energy.2021.122779.
60. Liu, J.; Xu, C.; Ao, X.; Lu, K.; Zhao, B.; Pei, G. A Dual-Layer Polymer-Based Film for All-Day Sub-Ambient Radiative Sky Cooling. *Energy* **2022**, *254*, 124350. https://doi.org/10.1016/j.energy.2022.124350.
61. Lim, H.; Chae, D.; Son, S.; Ha, J.; Lee, H. $CaCO_3$ Micro Particle-Based Radiative Cooling Device without Metal Reflector for Entire Day. *Mater. Today Commun.* **2022**, *32*, 103990. https://doi.org/10.1016/j.mtcomm.2022.103990.

62. Huang, T.; Chen, Q.; Huang, J.; Lu, Y.; Xu, H.; Zhao, M.; Xu, Y.; Song, W. Scalable Colored Subambient Radiative Coolers Based on a Polymer-Tamm Photonic Structure. *ACS Appl. Mater. Interfaces* **2023**, *15*, 16277–16287. https://doi.org/10.1021/acsami.2c23270.
63. Yu, L.; Huang, Y.; Zhao, Y.; Rao, Z.; Li, W.; Chen, Z.; Chen, M. Self-Sustained and Insulated Radiative/Evaporative Cooler for Daytime Subambient Passive Cooling. *ACS Appl. Mater. Interfaces* **2023**, *16*, 6513–6522. https://doi.org/10.1021/acsami.3c19223.
64. Givoni, B. Solar Heating and Night Radiation Cooling by a Roof Radiation Trap. *Energy Build.* **1977**, *1*, 141–145. https://doi.org/10.1016/0378-7788(77)90026-3.
65. Liu, Z.; Tan, H.; Ma, G. Experimental Investigation on Night Sky Radiant Cooling Performance of Duct-Type Heat Exchanger. *Int. J. Vent.* **2017**, *16*, 255–267. https://doi.org/10.1080/14733315.2017.1299520.
66. Parker, D.S.; Sherwin, J.R. *Evaluation of the NightCool Nocturnal Radiation Cooling Concept: Annual Performance Assessment in Scale Test Buildings Stage Gate 1B*; Florida Solar Energy Center: Cocoa, FL, USA, 2008. https://doi.org/10.2172/1219078.
67. Kimball, B.A.; Idso, S.B.; Aase, J.K. A Model of Thermal Radiation from Partly Cloudy and Overcast Skies. *Water Resour. Res.* **1982**, *18*, 931–936. https://doi.org/10.1029/WR018I004P00931.
68. Hollick, J. Nocturnal Radiation Cooling Tests. *Energy Procedia* **2012**, *30*, 930–936. https://doi.org/10.1016/J.EGYPRO.2012.11.105.
69. Khedari, J.; Waewsak, J.; Thepa, S.; Hirunlabh, J. Field Investigation of Night Radiation Cooling under Tropical Climate. *Renew. Energy* **2000**, *20*, 183–193. https://doi.org/10.1016/S0960-1481(99)00104-4.
70. Hu, M.; Seng Lee, P. Performance Evaluation of a Passive Air Conditioning Module Integrating Radiative Sky Cooling and Indirect Evaporative Cooling. *Appl. Therm. Eng.* **2024**, *244*, 122608. https://doi.org/10.1016/J.APPLTHERMALENG.2024.122608.
71. Gálvez, M.; García, J.; Barraza, R.; Contreras, J. Parametric Analysis of an Air-Based Radiative Cooling System Coupled to a Thermal Storage Wall for a Low-Income Household. *Energy Build.* **2021**, *252*, 111364. https://doi.org/10.1016/J.ENBUILD.2021.111364.
72. Al-Zubaydi, A.Y.T.; Dartnall, W.J. Design and Modelling of Water Chilling Production System by the Combined Effects of Evaporation and Night Sky Radiation. *J. Renew. Energy* **2014**, *2014*, 1–8. https://doi.org/10.1155/2014/624502.
73. Cui, Y.; Luo, X.; Zhang, F.; Sun, L.; Jin, N.; Yang, W. Progress of Passive Daytime Radiative Cooling Technologies towards Commercial Applications. *Particuology* **2022**, *67*, 57–67. https://doi.org/10.1016/j.partic.2021.10.004.
74. Zhao, D.; Aili, A.; Yin, X.; Tan, G.; Yang, R. Roof-Integrated Radiative Air-Cooling System to Achieve Cooler Attic for Building Energy Saving. *Energy Build.* **2019**, *203*, 109453. https://doi.org/10.1016/J.ENBUILD.2019.109453.
75. Fu, Y.; Yang, J.; Su, Y.S.; Du, W.; Ma, Y.G. Daytime Passive Radiative Cooler Using Porous Alumina. *Sol. Energy Mater. Sol. Cells* **2019**, *191*, 50–54. https://doi.org/10.1016/j.solmat.2018.10.027.
76. Torgerson, E.; Hellhake, J. Polymer Solar Filter for Enabling Direct Daytime Radiative Cooling. *Sol. Energy Mater. Sol. Cells* **2020**, *206*, 110319. https://doi.org/10.1016/j.solmat.2019.110319.
77. Wang, C.; Chen, H.; Wang, F. Passive Daytime Radiative Cooling Materials toward Real-World Applications. *Prog. Mater. Sci.* **2024**, *144*, 101276. https://doi.org/10.1016/j.pmatsci.2024.101276.
78. Wu, Y.; Zhao, H.; Sun, H.; Duan, M.; Lin, B.; Wu, S. A Review of the Application of Radiative Sky Cooling in Buildings: Challenges and Optimization. *Energy Convers. Manag.* **2022**, *265*, 115768. https://doi.org/10.1016/j.enconman.2022.115768.
79. Hamza, A.; Ali, H. Passive Cooling of Water at Night in Uninsulated Open Tank in Hot Arid Areas. *Energy Convers. Manag.* **2006**, *48*, 93–100. https://doi.org/10.1016/j.enconman.2006.05.012.
80. Tang, R.; Etzion, Y. On Thermal Performance of an Improved Roof Pond for Cooling Buildings. *Build. Environ.* **2004**, *39*, 201–209. https://doi.org/10.1016/j.buildenv.2003.09.005.
81. Spanaki, A.; Tsoutsos, T.; Kolokotsa, D. On the Selection and Design of the Proper Roof Pond Variant for Passive Cooling Purposes. *Renew. Sustain. Energy Rev.* **2011**, *15*, 3523–3533. https://doi.org/10.1016/j.rser.2011.05.007.
82. Spanaki, A.; Kolokotsa, D.; Tsoutsos, T.; Zacharopoulos, I. Theoretical and Experimental Analysis of a Novel Low Emissivity Water Pond in Summer. *Sol. Energy* **2012**, *86*, 3331–3344. https://doi.org/10.1016/J.SOLENER.2012.08.017.
83. Hosseinzadeh, E.; Taherian, H. An Experimental and Analytical Study of a Radiative Cooling System with Unglazed Flat Plate Collectors. *Int. J. Green Energy* **2012**, *9*, 766–779. https://doi.org/10.1080/15435075.2011.641189.
84. Okoronkwo, C.A.; Nwigwe, K.N.; Ogueke, N.V.; Anyanwu, E.E.; Onyejekwe, D.C.; Ugwuoke, P.E. An Experimental Investigation of the Passive Cooling of a Building Using Nighttime Radiant Cooling. *Int. J. Green Energy* **2014**, *11*, 1072–1083. https://doi.org/10.1080/15435075.2013.829775.
85. Ferrer Tevar, J.A.; Castã No, S.; Marijuán, A.G.; Heras, M.R.; Pistono, J. Modelling and Experimental Analysis of Three Radioconvective Panels for Night Cooling. *Energy Build.* **2015**, *107*, 37–48. https://doi.org/10.1016/j.enbuild.2015.07.027.
86. Raeissi, S.; Taheri, M. Skytherm: An Approach to Year-Round Thermal Energy Sufficient Houses. *Renew. Energy* **2000**, *19*, 527–543. https://doi.org/10.1016/S0960-1481(99)00079-8.
87. Meir, M.G.; Rekstad, J.B.; LØvvik, O.M. A Study of a Polymer-Based Radiative Cooling System. *Sol. Energy* **2002**, *73*, 403–417. https://doi.org/10.1016/S0038-092X(03)00019-7.
88. Zhou, K.; Miljkovic, N.; Cai, L. Performance Analysis on System-Level Integration and Operation of Daytime Radiative Cooling Technology for Air-Conditioning in Buildings. *Energy Build.* **2021**, *235*, 110749. https://doi.org/10.1016/J.ENBUILD.2021.110749.
89. Wang, W.; Fernandez, N.; Katipamula, S.; Alvine, K. Performance Assessment of a Photonic Radiative Cooling System for Office Buildings. *Renew. Energy* **2018**, *118*, 265–277. https://doi.org/10.1016/j.renene.2017.10.062.
90. Zhang, K.; Zhao, D.; Yin, X.; Yang, R.; Tan, G. Energy Saving and Economic Analysis of a New Hybrid Radiative Cooling System for Single-Family Houses in the USA. *Appl. Energy* **2018**, *224*, 371–381. https://doi.org/10.1016/J.APENERGY.2018.04.115.

91. Pirvaram, A.; Talebzadeh, N.; Leung, S.N.; O'Brien, P.G. Radiative Cooling for Buildings: A Review of Techno-Enviro-Economics and Life-Cycle Assessment Methods. *Renew. Sustain. Energy Rev.* **2022**, *162*, 112415. https://doi.org/10.1016/J.RSER.2022.112415.
92. Yoon, S.; Kim, M.; Seo, J.; Kim, S.; Lee, H.; Lee, J.; Lee, B.J. Performance Analysis of a Hybrid HVAC System Consisting of a Solar Thermal Collector and a Radiative Cooling Panel. *Energy Build.* **2021**, *241*, 110921. https://doi.org/10.1016/J.ENBUILD.2021.110921.
93. Zhao, D.; Aili, A.; Zhai, Y.; Lu, J.; Kidd, D.; Tan, G.; Yin, X.; Yang, R. Subambient Cooling of Water: Toward Real-World Applications of Daytime Radiative Cooling. *Joule* **2019**, *3*, 111–123. https://doi.org/10.1016/J.JOULE.2018.10.006.
94. Jia, L.; Lu, L.; Chen, J. Exploring the Cooling Potential Maps of a Radiative Sky Cooling Radiator-Assisted Ground Source Heat Pump System in China. *Appl. Energy* **2023**, *349*, 121678. https://doi.org/10.1016/J.APENERGY.2023.121678.
95. Goldstein, E.A.; Raman, A.P.; Fan, S. Sub-Ambient Non-Evaporative Fluid Cooling with the Sky. *Nat. Energy* **2017**, *2*, 17143. https://doi.org/10.1038/nenergy.2017.143.
96. Yu, X.; Chan, J.; Chen, C. Review of Radiative Cooling Materials: Performance Evaluation and Design Approaches. *Nano Energy* **2021**, *88*, 106259. https://doi.org/10.1016/j.nanoen.2021.106259.
97. Fang, H.; Zhao, D.; Yuan, J.; Aili, A.; Yin, X.; Yang, R.; Tan, G. Performance Evaluation of a Metamaterial-Based New Cool Roof Using Improved Roof Thermal Transfer Value Model. *Appl. Energy* **2019**, *248*, 589–599. https://doi.org/10.1016/j.apenergy.2019.04.116.
98. Fernandez, N.; Wang, W.; Alvine, K.J.; Katipamula, S. *Energy Savings Potential of Radiative Cooling Technologies*; Pacific Northwest National Lab. (PNNL): Richland, WA, USA, 2015; Volume 72.
99. Felicelli, A.; Wang, J.; Feng, D.; Forti, E.; Azrak, S.E.A.; Peoples, J.; Youngblood, J.; Chiu, G.; Ruan, X. Efficient Radiative Cooling of Low-Cost $BaSO_4$ Paint-Paper Dual-Layer Thin Films. *Nanophotonics* **2024**, *13*, 639–648. https://doi.org/10.1515/nanoph-2023-0642.
100. Lu, X.; Xu, P.; Wang, H.; Yang, T.; Hou, J. Cooling Potential and Applications Prospects of Passive Radiative Cooling in Buildings: The Current State-of-the-Art. *Renew. Sustain. Energy Rev.* **2016**, *65*, 1079–1097. https://doi.org/10.1016/j.rser.2016.07.058.
101. Deng, Y.; Yang, Y.; Xiao, Y.; Xie, H.L.; Lan, R.; Zhang, L.; Yang, H. Ultrafast Switchable Passive Radiative Cooling Smart Windows with Synergistic Optical Modulation. *Adv. Funct. Mater.* **2023**, *33*, 2301319. https://doi.org/10.1002/adfm.202301319.
102. An, Y.; Fu, Y.; Jian-Guo, D.; Yin, X.; Lei, D. Switchable Radiative Cooling Technologies for Smart Thermal Management. *Cell Rep. Phys. Sci.* **2022**, *3*, 101098. https://doi.org/10.1016/j.xcrp.2022.101098.
103. Yoo, M.J.; Pyun, K.R.; Jung, Y.; Lee, M.; Lee, J.; Ko, S.H. Switchable Radiative Cooling and Solar Heating for Sustainable Thermal Management. *Nanophotonics* **2024**, *13*, 543–561. https://doi.org/10.1515/nanoph-2023-0627.
104. Testa, J.; Krarti, M. A Review of Benefits and Limitations of Static and Switchable Cool Roof Systems. *Renew. Sustain. Energy Rev.* **2017**, *77*, 451–460. https://doi.org/10.1016/j.rser.2017.04.030.
105. Cui, Y.; Ke, Y.; Liu, C.; Chen, Z.; Wang, N.; Zhang, L.; Zhou, Y.; Wang, S.; Gao, Y.; Long, Y. Thermochromic VO_2 for Energy-Efficient Smart Windows. *Joule* **2018**, *2*, 1707–1746. https://doi.org/10.1016/j.joule.2018.06.018.
106. Zhang, H.; Huang, J.; Fan, D. Switchable Radiative Cooling from Temperature-Responsive Thermal Resistance Modulation. *ACS Appl. Energy Mater.* **2022**, *5*, 6003–6010. https://doi.org/10.1021/acsaem.2c00421.
107. Cannavale, A.; Pugliese, M.; De Matteis, V.; Giannuzzi, R.; Mancarella, F.; Valenzano, V.; Ayr, U.; Liuzzi, S.; Maiorano, V.; Berardi, U.; et al. Multifunctional Hydrogel-Based Electrolytes for Thermoelectrochromic Devices. *J. Appl. Polym. Sci.* **2023**, *140*, e54330. https://doi.org/10.1002/app.54330.