

天空辐射制冷技术的制备及其应用研究进展

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摘要

辐射制冷技术凭借其无额外能量输入、适应复杂工况、材料轻便等特点广受关注。辐射制冷理论源于光电、物理学交叉领域, 有力推动了辐射制冷行业的飞速发展。本文系统综述了辐射制冷基本原理, 归纳了制备辐射制冷材料的种类与制备方法, 分析材料与制备方法适配性、材料结构性能特征及应用范畴, 并简单介绍了辐射制冷膜在建筑、个人防护、农业领域的应用进展。最后, 探讨了辐射制冷技术将面临的挑战和未来的发展方向。

关键词

辐射制冷, 天空制冷, 功能材料, 制备方法, 热管理

Preparation and Application Advances in Sky Radiative Cooling Technology

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Abstract

Radiative cooling technology has attracted substantial attention owing to its ability to operate without external energy input, adapt to complex working conditions, and utilize lightweight materials. Rooted in the interdisciplinary integration of optoelectronics and physics, the theoretical foundation of radiative cooling has vigorously propelled the rapid advancement of this field. This article systematically reviews the fundamental principles of radiative cooling, summarizes the categories and fabrication strategies of radiative cooling materials, and analyzes the compatibility between materials and preparation methods, the structure-property relationships, and the corresponding application domains.

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In addition, recent progress in radiative cooling films for applications in buildings, personal protection, and agriculture is briefly highlighted. Finally, the challenges confronting radiative cooling technology and its prospective future directions are discussed.

Keywords

Radiative Cooling, Sky Cooling, Functional Materials, Fabrication Methods, Thermal Management

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1. 引言

近年来,全球气候变化异常、极端天气事件频发,传统的制冷方式难以满足建筑、工业和个人热管理领域的多元需求。传统制冷方式依赖制冷设备和大量电能驱动,设备制造需消耗大量金属资源,安装过程繁琐需投入大量人力物力,运行过程还会排放大量温室气体并产生热污染问题,与“绿水青山就是金山银山”的发展理念相悖。在此背景下,天空辐射制冷技术[1]-[3]以安装便捷、无额外能量输入、全天候运行、运行过程无温室气体排放和热污染等优势备受关注,被认为是极具潜力的绿色可持续降温新途径[4]-[6]。

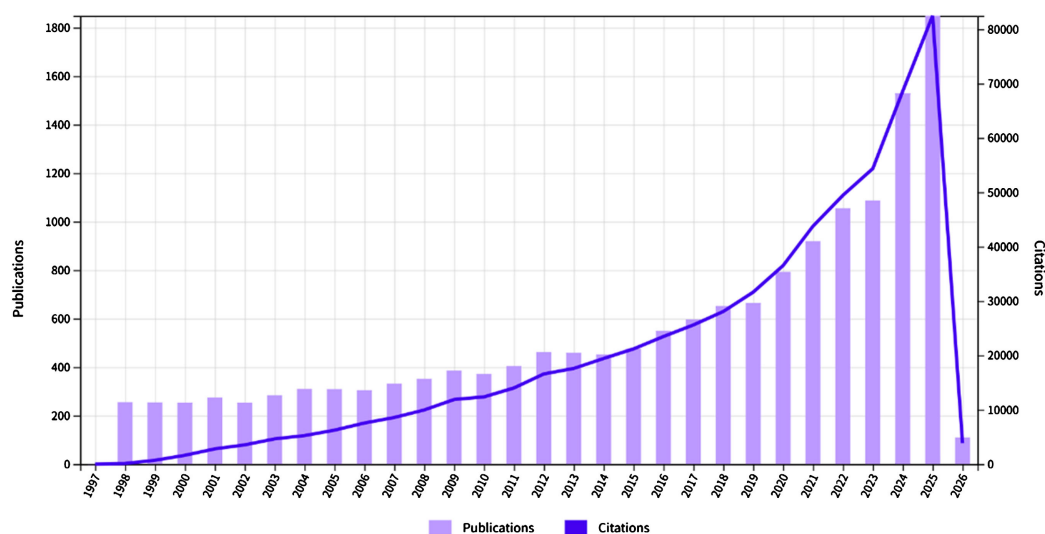
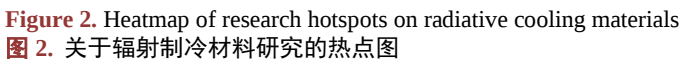


Figure 1. Relationship between the number of publications and citations of radiative cooling papers and the year (Topic = radiative cooling)

图 1. 辐射制冷论文的出版数量和引用次数与年份之间的关系(Topic = radiative cooling)

8~13 μm 红外波段具备热辐射性能[7],天空辐射制冷技术的核心降温机理是将物体表面这些中红外波段的光辐射到外太空,从而实现自身降温[8][9]。当光波波长处于太阳光谱(0.3~2.5 μm)范围内时,材料可反射该波段光线,降低日间太阳光吸收量,同时向低温空间辐射热量,达成被动冷却效果[10]。该技术可实现“无能量输入制冷”,在建筑、户外设备、纺织衣物等领域具有广阔的应用前景。近年来,辐射制冷逐渐成为研究热点[11]-[13],相关论文层出不穷。以“radiative cooling”为主题的文章检索结果达 15,998,



2. 国内外研究进展

热力学定律规定高于绝对零度的物体均会以电磁波形式向外辐射能量。天空辐射制冷的本质是对热辐射传热过程进行定向调控。地球大气层对 8~13 μm 波段光波的吸收系数较低, 该波段因此被称为“大气窗口”。在该波段内, 物体辐射的能量可直接透过大气层逃逸至外太空(图 3), 为被动辐射制冷技术奠定了理论基础[18]。

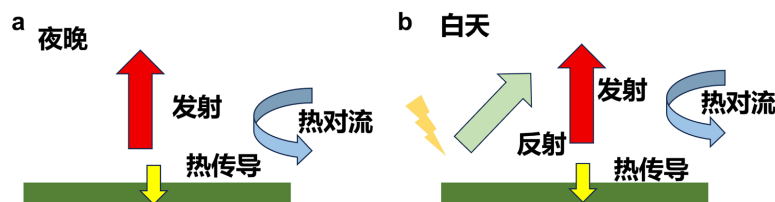


Figure 3. Schematic diagram of the principle of radiative cooling

图 3. 辐射制冷原理示意图

基尔霍夫热辐射定律[19]表明, 热平衡状态下, 物体在特定波长与方向上的发射率与吸收率相等, 即物体对某一波段光波的发射率越高, 但实际工况中, 绝大多数物体并非处于热平衡状态, 因此需通过合理的技术手段与精准的结构设计, 使材料具备特定光谱特性: 在 $0.3\sim 2.5\ \mu\text{m}$ 波段内具备高反射率, 同时在 $8\sim 13\ \mu\text{m}$ 大气窗口内具备高发射率[20]。

在实际环境中, 辐射制冷性能($P_{\text{cool}}(T)$)由多能量交换过程决定, 包括材料向天空的辐射散热($P_{\text{atm}}(T_{\text{amb}})$)、太阳辐射吸收(P_{sun})、大气反向辐射, 以及与周围环境的对流和传导换热($P_{\text{cond+conv}}$)。方程(1)描述了发射器的热流网络, 其净冷却功率由四部分构成, 其中仅有发射器的辐射功率 $P_{\text{rad}}(T)$ 为向外输出的能量流, 这意味着发射器仅能通过热辐射实现散热[21]。仅当 $T < T_{\text{amb}}$ (低于环境热平衡温度)时, 净功率为正值, 此时发射器可作为辐射冷却装置。它们之间的关系为:

$$P_{\text{cool}}(T) = P_{\text{rad}}(T) - P_{\text{atm}}(T_{\text{amb}}) - P_{\text{sun}} - P_{\text{cond+conv}} \quad (1)$$

在公式(1)中, 发射器辐射出的功率为

$$P_{\text{rad}}(T) = A \int d\Omega \cos \theta \int_0^\infty d\lambda I_{\text{BB}}(T, \lambda) \varepsilon(\lambda, \theta) \quad (2)$$

$$I_{\text{BB}}(T, \lambda) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1}$$

是温度为 T 的黑体的光谱辐射度, λ 是波长, h 是普朗克常数, c 是光速,

k_B 是玻尔兹曼常数。发射器从大气辐射中吸收的功率是

$$P_{\text{atm}}(T_{\text{amb}}) = A \int d\Omega \cos \theta \int_0^\infty d\lambda I_{\text{BB}}(T_{\text{amb}}, \lambda) \varepsilon(\lambda, \theta) \varepsilon_{\text{atm}}(\lambda, \theta) \quad (3)$$

角度依赖的发射率 $\varepsilon_{\text{atm}}(\lambda, \theta) = 1 - t(\lambda)1/\cos \theta$, 其中 $t(\lambda)$ 表示大气透射率, T_{amb} 表示环境空气温度。

发射器从太阳辐射和漫射阳光中吸收的能量是

$$P_{\text{sun}} = A \int_0^\infty d\lambda \varepsilon(\lambda, 0) I_{\text{AMsw1.5}}(\lambda) + A \int d\Omega \cos \theta \int_0^\infty d\lambda I_{\text{solar-diffuse}}(\lambda) \varepsilon(\lambda, \theta) \quad (4)$$

在方程式(5)中, $I_{\text{AM1.5}}(\lambda)$ 表示 AM1.5 太阳光辐照度, 其值为 $964\ \text{W}\cdot\text{m}^{-2}$ [8], 而 $I_{\text{solar-diffuse}}(\lambda)$ 表示朝向发射器的散射太阳辐射。由于热传导和对流而损失的功率为

$$P_{\text{cond+conv}}(T, T_{\text{amb}}) = Ah_c(T_{\text{amb}} - T) \quad (5)$$

此处, $h_c = h_{\text{cond}} + h_{\text{conv}}$ 表示发射体的综合非辐射热系数。

综上分析可知, 太阳辐射是影响白天制冷的核心因素。因此, 实现高效日间辐射制冷需同时满足两项光谱调控条件: 1、在太阳光谱范围内实现高效反射; 2、在红外大气窗口内具备接近两黑体的高发射率, 以增加热辐射能力[22]。近年来, 光子学和热辐射理论研究表明, 引入多尺度结构、折射失配界面以及光子带隙效应, 可以显著增强在特定波段的选择性辐射特性与反射性能[23]。例如: 多孔结构和纳米粒子散射可提升可见光波段的散射率, 分子振动模式和晶格声子共振则有利于增强中红外波段的发射能力[24]。

2.2. 辐射制冷材料

天空辐射制冷的核心在于辐射制冷材料种类的选择和结构的设计, 调控太阳光谱和红外光谱特性是实现辐射制冷性能的关键[25]。其中, 材料种类的选择是调控辐射制冷性能最有效的手段。近年来开发的辐射制冷材料不断涌现, 主要分为无机材料、聚合物和复合材料等[16], 下文将对这类材料展开简要分析。

无机辐射制冷材料以氧化物为主, 如 SiO_2 、 Al_2O_3 、 TiO_2 等[26]-[28]。此类材料化学性质稳定、中红外发射性能优异, 但柔性欠佳, 需以聚合物为支撑材料, 制备成薄膜或多层结构实现辐射制冷效果。Yang 等人制备的聚偏氟乙烯(PVDF)/ SiO_2 -PTFE 纤维膜, 可实现全天候辐射制冷, 将其贴于皮肤表面测试, 薄膜的温度比人体温度低 9.2°C 。该分级结构纤维膜在节能织物热管理领域表现突出, 为未来的被动辐射冷却纺织品的发展开辟了一条可持续发展道路[29]。

无机材料领域中, 人工合成材料在辐射制冷领域亦占据重要地位。例如: 4A 沸石经过 800°C 热处理后, 对太阳光的反射率可达 92%, 在 $8\sim 14\ \mu\text{m}$ 波段的发射率高达 0.94, 作为低成本材料, 其在未来辐射制冷材料的发展中极具潜力[30]。此外, 为适配实际应用中的外观需求, 研究人员制备出彩色辐射制冷材料。通过在材料中添加可见光波段具有窄带吸收的磷光材料或颜料, 可使材料兼具美观性, 且能在太阳光谱范围内保持较高反射率, 同时具备优异的红外波段发射性能[31] [32]。

光子晶体与超导材料可通过设计亚波长级别的微纳结构(如多层膜、光栅或随机分布散射体), 调控光与物质的相互作用, 实现光谱选择性反射和发射[33]。例如, 基于 SiO_2 、氧化铪(HfO_2)、Si 及 Ag 构建的多层结构, 可以实现高太阳反射率与大气窗口高发射率[34] [35]。光子晶体可以在可见光波段保持透明, 同时在红外波段实现选择性发射, 这一特性对透明辐射制冷材料(如辐射制冷窗)具有重要意义。相变材料与辐射制冷材料复合构建的混合被动冷却系统, 可提升系统冷却效能(约 $100\ \text{W}\cdot\text{m}^{-2}$)及控温精度[36]。

无机辐射制冷材料具有化学性质稳定高, 中红外发射能力强, 太阳光反射率与红外发射率高且成本低的优势。但其柔性欠佳, 需借助聚合物制成薄膜或多层结构方可发挥制冷作用。

除基本光学性能外, 实际应用中、导热性、耐久性和自清洁能力亦是关键性能指标。例如, 内部发热设备需采用高导热系数材料将热量辐射散出; 户外织物材料则需具备优良的抗紫外、耐酸碱、耐磨及自清洁性能, 以适配长期服役需求[37]。

采用聚合物制备辐射制冷材料, 兼具加工简便高效、性能优异、柔韧性好等优势, 已成为当前辐射制冷材料的首选制备路径[33] [38]。其制冷机理核心在于分子结构中含有 C-O、C-F、C-N、Si-O 等化学键, 这类官能团在中红外区域具有强烈的振动吸收, 具备较高的红外发射率[39]。例如, 多孔聚(4-甲基戊烯) (P-TPX) 薄膜和聚二甲硅氧烷(PDMS)基复合涂层均展现出优良的辐射制冷性能[32] [40]。高分子辐射制冷材料近年来发展迅速, 典型代表包括 PVDF、聚四氟乙烯(PTFE)、聚乙烯(PE)等[41]-[43]。这类材料对太阳光吸收率低、中红外发射率高, 且加工性能与环境耐久性优良, 尤其适合制备大面积柔性制冷薄膜, 在未来实际应用中前景广阔。

此外, 将高折射率的粒子(如 TiO_2 、 SiO_2)掺杂至聚合物基体(如 PVDF、PMMA)中也可强化材料辐射制冷性能[38] [44] [45]。复合辐射制冷材料通过将无机纳米粒子引入高分子基体, 实现性能协同优化。纳米粒子不仅能强化太阳光散射, 还可提升薄膜机械性能和环境稳定性。例如, 将 SiO_2 微球随机嵌入聚合物基体中, 可以制备出太阳光谱透明、大气窗口内发射率超过 0.93 的超材料[30]。例如, PVDF-HFP-Ag 薄膜可用于调控太阳入射和热发射行为[46]。

基于单一薄膜结构, 后期发展出多层薄膜结构, 其可利用不同介电常数和厚度的膜层产生干涉效应, 从而提升材料在特定波长范围内的反射率和发射率[33]。例如: 利用金属反射层(如 Ag) [47]和介质层(如 SiO_2 、 Al_2O_3) [48]制备成的多层材料, 可最大限度反射太阳光并向太空辐射热量。

随着可持续发展理念的深入，生物质基辐射制冷材料备受关注[49]。例如，纤维素、纤维和纳米纤维素等材料，这类材料具备生物相容性[33]。引入多孔结构可进一步提升其光谱调控能力，例如利用静电纺丝技术制备的纳米纤维膜可形成多孔结构，进一步提高辐射制冷性能[44][50]。聚合物辐射制冷材料兼具加工简便、柔韧性好，红外发射率高、太阳光吸收率低，环境耐久性佳，易制大面积柔性薄膜等优势，且可与无机粒子复合提升性能；其不足之处在于单一聚合物导热性有限，需复合改性方可满足需求(表 1)。

Table 1. Several representative radiative cooling materials and their performance parameters
表 1. 几种代表性的辐射制冷材料及其性能参数

材料类型	代表性材料	太阳光反射率	红外发射率 (8~13 μm)	特点与制备	文献来源
无机材料	800℃热处理的 4A 沸石涂层	92%	0.94	成本低，性能优异，通过热处理优化结构	[30]
聚合物复合材料	彩色 PS/PDMS/PECA 复合涂层	86.6%~92.8%	95.3%~96.3%	超疏水、耐用，通过喷涂和相分离法制备	[32]
聚合物复合材料	多孔聚(4-甲基-戊烯) (P-TPX) 薄膜	88.6%	88.11% (透射率)	高红外透明度，适用于非接触式冷却	[51]
超材料	聚合物基质中嵌入 SiO ₂ 微球	对太阳光谱透明	>0.93	背衬银涂层时，日间冷却功率达 93 W/m ²	[30]
彩色涂层	磷光染料涂层 (Y ₃ Al ₅ O ₁₂ :Ce 等)	≥0.90	≥0.90	可实现黄、绿、红等多种颜色，兼具美学与冷却性能	[31]
多层薄膜	J-MRC 薄膜(纳米多孔 PE/PEO/Ag 纳米线)	-	顶面高发射/ 底面低发射	Janus 光学特性，增强封闭空间冷却效果	[39]

2.3. 辐射制冷材料的制备方法

辐射制冷材料的制备方法具有多样性，不同制备工艺赋予材料各向异性结构和性能特征，以适应不同材料体系和应用场景，主要包括以下几种：

静电纺丝技术是制备聚合物复合材料的高效工艺[52]。该技术借助高压电场作用，将聚合物溶液或熔体拉伸为微米或纳米级纤维，形成多孔网状结构薄膜。例如，TiO₂-PVDF 纤维膜可通过电纺技术制备，具有分级结构和良好的辐射制冷性能[44]。近年来，电纺技术在辐射制冷领域展现出独特优势，具有可加工性强、成本低、性能高、易于批量生产的优点[50]。该方法可构筑三维交织纳米纤维网络结构，显著强化多重光散射效应，同时维持优异的中红外发射性能，为高性能柔性辐射制冷膜的制备提供了有效途径。

相分离法是制备多孔聚合物薄膜的简便低成本工艺，例如采用相分离法制备的多孔 PVDF 薄膜，可以实现高太阳反射率(95.6%)和大气窗口高发射率(99.1%) [38]。相分离技术可在聚合物膜中构筑均匀多孔结构，从而显著提高太阳反射率[53]。

通过电纺技术和相分离法制备的聚合物薄膜均具有多孔结构，可有效散射太阳光并增强红外发射，且成本相对较低，易于规模化生产。但电纺技术对溶液粘度、浓度等参数及环境温湿度较为敏感，导致

纤维直径均匀性难以控制。相分离法则存在多孔结构的孔径与孔隙率调控难度大、薄膜机械强度低、工艺周期较长等问题。

利用物理或化学气相沉积等技术构建多层薄膜体系,使不同折射率和厚度的介电材料层交替堆叠。通过精确设计各厚度及材料种类,可以构建出高效辐射制冷材料[33]。

将高反射率微米或纳米颗粒(如 TiO_2 、 SiO_2)与高红外发射率的聚合物基体(如 PVDF、PDMS)混合制备成涂料,然后通过喷涂、刷涂或刮涂等方式施加在物体表面[32][54]。例如,通过喷涂结合非溶剂诱导相分离法可以制备出多孔结构的复合涂层,其多孔结构有助于增强太阳光散射[32]。为实现规模化生产和应用,刮涂、喷涂和印刷等低成本、可扩展制备工艺正被积极开发[33],这类技术能将辐射制冷涂层或薄膜高效地应用于大面积的建筑表面,如聚合物薄膜喷涂工艺已在 2020~2022 年实现产业化[33]。溶液浇铸和喷涂工艺简单,适用于大面积制备,但对微结构的调控能力有限。

利用如嵌段共聚物、胶体颗粒等材料自身的物理化学性质,使用自组装技术使其在特定条件下自发形成有序微纳结构。例如,自组装的 SiO_2 纳米结构可以形成高效的辐射制冷层[55]。自组装方法能实现精细的多层光子结构,但存在工艺复杂、成本较高的不足。

对于部分无机材料,热处理是一种简单有效的改性方法。通过特定温度下的煅烧处理,可改变材料的晶相结构和微观形貌,进而优化其光学性能。例如,在 800°C 的条件下对 4A 沸石进行热处理,可促使其晶相转变,辐射冷却性能显著提升[30]。热处理的优势在于操作简单、效果显著,可调控无机材料晶相结构与微观形貌;缺点是高温煅烧能耗较高,对设备耐高温性能存在一定要求。

针对光子晶体和超材料,通常采用电子束光刻、紫外光刻、原子层沉积、溅射等精密的纳米制造技术,构建周期性或随机性纳米结构,以制备具有特定图案的表面结构[17][56]。这些方法可精确控制材料的光学性能,但成本较高。

对于聚合物基辐射制冷材料,可通过紫外光接枝聚合等化学合成方法制备功能性的薄膜。例如,通过紫外光接枝聚合可以制备出兼具超疏水、透明和辐射冷却性能的复合薄膜[37]。化学合成方法虽操作复杂,但可精准调控材料性质其优势在于可精准调控材料性质,制备兼具多重功能的复合薄膜,不足则是操作流程相对繁琐,对实验条件要求较高。

2.4. 辐射制冷材料的应用

天空辐射制冷材料已实现实验室突破,凭借其无耗能的独特优势,正逐步走入实际生活,在户外设备[57]、车辆[58]、建筑[59]、农业[60]等领域均具备潜在的应用价值,如图 4 所示。

辐射制冷材料在建筑领域应用最为广泛[61]。将辐射制冷涂料或薄膜用于建筑物屋顶及外墙,可有效反射太阳光能,降低表面温度,减少夏季空调使用次数,从而降低能耗,削减温室气体排放。研究表明,夏季高温环境下,在传统屋顶安装铺设制冷材料后,屋顶温度可显著降低,由 $50\sim 60^\circ\text{C}$ 降低到室温乃至室温以下。中国一项研究显示,具备辐射制冷功能的屋顶,可使年度制冷和供暖总负荷降低 84.9%、30.3% 和 2.4% 左右[62]。伊朗的测试结果表明,屋顶辐射制冷系统的冷却功率可达 96 W/m^2 ,该效果足以满足夏季住宅的制冷需求[63]。

全球人口增长引发粮食危机,加之粮食成熟期固定,产量分布不均,粮食存储成为关键课题。传统储粮多为粮仓顶部覆盖稻草,安装空调等,以降低粮仓内温度,延缓粮食霉变,但此类措施耗费大量人力、物力及电力资源,且稻草覆盖等方式存在防火安全隐患,而辐射制冷技术的出现为粮食仓储带来了曙光[64]。在杭州地区的测试显示,粮仓顶部铺设辐射制冷薄膜后,仓内温度降低 9.8°C ,粮仓本体温度下降 4°C 。若该类薄膜在全球范围内推广应用,全年可节约电力 573 G Wh,部分地区可完全替代空调实现低温储粮[65]。

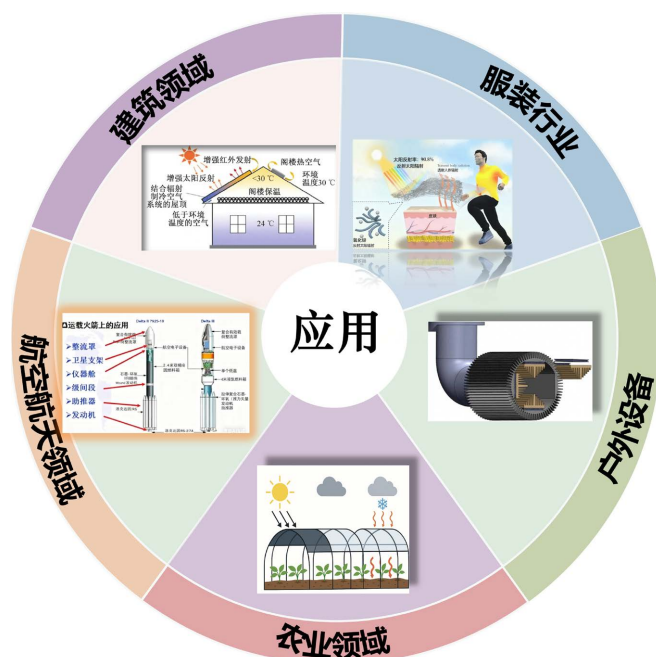


Figure 4. Application fields of radiative cooling materials

图 4. 辐射制冷材料的应用领域

高原和山区海拔高导致造成昼夜温差显著，当地居民着装繁琐，而采用辐射制冷功能衣物或在衣物表面涂覆相关涂料，可以缓解此问题。此类衣物能助力人体在高温环境下散热，提升穿着舒适度，减少对空调的依赖[32]。

电子设备、热电发电机、光伏组件的效率会随着温度的升高而降低，因此需降低器件表面温度，辐射制冷涂料和薄膜在此发挥关键作用。在光伏板表面、背面或其他设备表面设置辐射制冷层，能有效降低工作温度，提升发电效率并延长设备使用寿命[66] [67]。

天空辐射制冷技术还可用于室外设备箱冷却、汽车降温、航空航天领域及大气水资源收集等场景[68]。

3. 未来发展趋势

尽管辐射制冷技术已取得显著进展，但要实现未来广泛实际应用与商业化推广，仍面临一系列挑战，具体可围绕以下方面展开：

1) 提高冷却效率：目前实验室环境下辐射制冷功率密度约为 $100 \text{ W}\cdot\text{m}^{-2}$ [36]，但这一功率较低，限制了其实际应用。未来研究需进一步优化材料设计与结构，以提升冷却功率密度。

2) 新材料研发：开发性能更为优异的辐射制冷性能材料，如兼具低热导率和高发射率的聚合物、陶瓷或复合材料。生物质基辐射制冷材料作为环境友好型材料，在未来可持续发展领域具备广阔潜力。

3) 理论模型与仿真优化：建立更精确的辐射制冷热力学模型，结合先进仿真工具，为材料设计和系统优化提供理论支撑，加速新材料的研发进程。

4) 提升材料的耐久性与可靠性：全球气候变化异常，极端天气频发，臭氧层空洞造成的紫外线辐射，全球工业化造成的酸雨、灰尘污染等均会造成材料性能衰减。因此开发具有优异的环境耐候性、抗老化、自清洁性能和机械性能优异的材料是未来制备辐射自冷材料的首要任务。

5) 降低成本与实现规模化生产：当前多数辐射制冷材料存在制备流程繁琐、原料成本高，制约了材料的大规模应用。未来需大力发展低成本、低能耗、高利润、可拓展的先进制造技术推动规模化、商业

化的发展进程。

6) 研发多功能与美学化材料：传统辐射制冷材料多为白色、单色或镜面形态，单调的外观限制了其在建筑领域的进一步应用。开发色彩丰富、高辐射制冷性能的材料是未来材料制备领域的重要方向，可显著拓宽技术应用前景。

7) 增强气候适应性：辐射制冷性能受天气条件影响显著，高温高湿多云的天气会降低气窗口的透明度，进而减弱辐射制冷效果。未来需设计可在恶劣气候下稳定工作的材料，通过非互易红外窗口抑制低透明度大气的热辐射输入。

8) 系统集成与人工智能化：将辐射制冷技术与主动制冷技术结合，构建混合冷却系统，实现优势互补，能源综合利用降低能耗。此外，发展动态可调辐射制冷技术，依托人工智能根据环境变化调控材料光学特性，是未来的前沿发展方向，辐射制冷玻璃即为典型代表。

4. 结语

辐射制冷技术是一种绿色、可持续的降温手段，无需能量输入、安装操作简便，在应对未来能源危机和气候异常变化方面展现出巨大的发展潜力和应用前景。随着科技进步，对辐射制冷机理的认知不断深入、交叉学科持续发展，材料设计理念和制备手段逐步革新、材料性能及应用范围亦将不断拓展。未来辐射制冷技术将与多学科深度交叉融合、协同发展，推动材料从实验室迈向大规模商业化应用，在建筑、个人热管理、农业、医学等领域发挥日益关键的作用，进而助力实现革命性技术变革与碳中和目标。

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