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Selection of nano-particulate material for improved passive cooling skylight performance

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Abstract:

The passive radiative cooling (PRC) system cools objects without requiring external energy. Scientific interest has been growing in the use of thermal radiation via the atmospheric window (8-13μm) where the sky is transparent. This is most effective for nocturnal applications, but it is possible to obtain temperatures lower than the ambient under direct sunlight, thus allowing diurnal applications, using advancements in nanotechnology/metamaterials. With the aim to increase the cooling power, our research analyses the optimal properties and use of nanoparticles (NPs) based high solar irradiation-reflecting layer on the top surface of a skylight window as designed and tested at Åbo Akademi University (ÅAU). In this paper, the main purpose is to identify low-cost NPs (or mixes of these) for better performance during the daytime of PRC skylights. This involves distinct NPs materials produced through different procedures. It is expected that NP-based approaches can easily handle large surfaces, which is important for widespread use in PRC for building thermal control (or in vehicles as well). The strong reflection of solar radiation is certainly a prerequisite; the work of others has shown that NPs can actually tune absorption and emission in the atmospheric window by phonon resonance properties. The analysis presented here suggests that TiO_2 and SiO_2 NPs are most suitable for use with the ÅAU skylight. Furthermore, using a thermal imager, heat flux measurements were carried out experimentally on window glasses with and without NPs deposited on them. This established a relationship between (absorptivity/emissivity) for longwave radiation at two different temperatures.

Keywords:

Emissivity; Radiative Cooling Coating; Reflection; TiO_2 – SiO_2 nanoparticles; Thermal radiation.

1. Introduction

It is crucial to maintain a comfortable temperature for many domestic, commercial, and industrial applications, which makes cooling an important component. The following three considerations indicate the need for passive cooling solutions for the following issues. (i) Global demand for electricity (the cooling system alone uses a substantial amount of energy),(ii) Concerns regarding the security and consumption of water, and (iii) Chemicals used in synthetic working fluids in cooling equipment affect the environment negatively. An increase in energy sustainability awareness and environmental concerns has resulted in a greater interest in enhancing the efficiency of existing cooling systems and developing new alternatives [1]. The concept of passive radiative cooling (PRC) is capable of realizing temperatures below the ambient temperature without using any energy. Furthermore, it produces no CO_2 or other harmful chemicals. While traditional cooling systems reject heat to the air, water, and to other surfaces resulting in local and global warming, PRC rejects heat to the outer atmosphere and space above. The PRC phenomenon has become popular in recent years due to its potential use in many energy-saving applications such as the thermal management of buildings, spacecraft thermal control, vehicle manufacturing, thermoelectric cooling, and even the cooling of solar cells. [2].

The process of radiation cooling plays an important role in keeping the earth's temperature constant. The principle of PRC relies on the fact that the atmosphere transmits about 87% of the radiation emitted by the earth via a wavelength region called the *"atmospheric window"* (8 to13 μm) where the sky (if cloudless) is transparent [3]. For effective PRC during the daytime, >> 90% reflection is required (preferably > 97%) in the solar spectrum (0.2–3 μm) and high emission in the atmospheric window. Through the atmospheric window, radiative cooling sends thermal energy into the cold space (3 K). However, to obtain maximum solar reflection and thermal emission with PRC, simple building materials and standard window glass alone cannot fulfil both the reflection and emission requirements, thus the development of sophisticated materials is necessary. For successful thermal management applications, the use of PRC technology during daytime requires surfaces that have a high reflectance in the solar spectrum and a high emittance in the "atmospheric window" spectrum.

Therefore, coatings and other forms of deposited materials are used to modify the thermal radiative properties of surfaces to meet specific requirements [2,4].

There have been two types of PRC studies dealing with coatings and other deposits, addressing either daylight radiative cooling (diurnal) or nighttime radiative cooling (nocturnal), the latter excluding solar irradiation. There is evidence that it is possible to achieve nocturnal cooling at around 100 W/m^2 by developing spectrally selective emitters (solids or fluids) in the atmospheric window [5]. However, these devices and systems are less effective when exposed to direct sunlight during day-time (around noon) because a much larger cooling power up to 1000 W/m^2 may be required then, which means coolers are required to have both high emissivity in the "atmospheric window" and high reflectivity in the solar spectrum as shown in Fig.1. It is challenging to achieve these simultaneously.

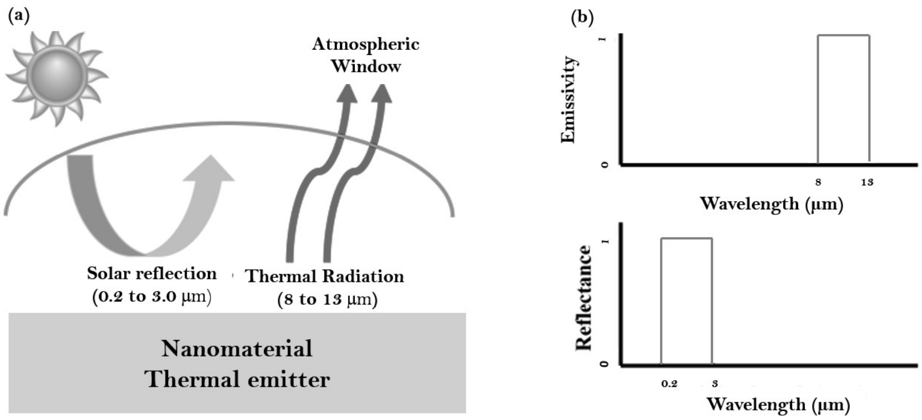

Fig. 1. (a) Radiative cooling: Schematic presentation. (b) Radiative cooling properties of materials for ideal reflection and emission. (Modified version after [6]).

Effective daytime radiative (DPRC) depends on three factors. First, the radiative cooler must reflect the maximum amount of sunlight away from an object. Second, the cooler should facilitate objects to radiate heat into space. In addition, the cooler has heat insulation capabilities to maintain the temperature difference with the surroundings. Controlling the inherent properties of the material and the target structure is crucial in achieving efficient daytime cooling. There is a need for further research as it is essential to design a new generation of radiative coolers that maximize net cooling performance always when needed. Furthermore, if this technology is to compete with active cooling systems, it needs to be cost-effective as well. Due to this, scalability and affordability are key for PRC objectives, rather than wavelength-dependent behaviour. In the future, thermally reflective coatings with excellent performance that are less expensive and easier to create will be most appealing. DPRC currently uses backscattering of solar radiation, thermal infrared pumping, phonon control, and surface coating enables it to produce a continuous cooling effect. Nano-particle (NP) based methods and materials are gaining much attention lately. The benefit of this method is that it can cover large surfaces with a relatively small amount of material, which is a major step toward the wide application of PRC [7].

Figure 2a shows a side view of the passive cooling skylight developed and tested for proof-of-concept at ÅAU [8,9]. Its performance is comparable to that of a roof paint or other covering material that not only reflects thermal radiation but also has a high emissivity in the wavelength range for the atmospheric window as shown in Fig. 2b. The skylight has the benefit of a larger heat transfer (per square meter) from the building envelope to the outside top surface governed by a convective circulation heat transfer inside the skylight that is stronger than conductive heat transfer through the material the building roof is made of. For the indicated heat flows $Q_{conv} >> Q_{cond}$ and eventually, the limiting heat flow will determine the heat radiation to the sky (Q_{rad}). Consequently, the passive cooling effect occurs due to the building's top surface having direct visual contact with the sky, thus taking more heat out of the building. (Besides that, the skylight brings light into the room). (Note that, in the future ÅAU skylight designs, the centre window will become obsolete, this work will be presented elsewhere soon [10].)

With the aim of increasing the cooling performance of the ÅÅ skylight and reflecting the solar irradiance effectively, this study involves synthesizing and testing several distinct NPs or (mixtures of these) through different procedures. In this current work, TiO_2-SiO_2 nanoparticles were selected (from twelve produced materials) for a single-layer radiative cooling coating or set of dispersed NPs on the ÅAU skylight top window to optimize its performance as a passive cooler and as well as a thermal insulator if needed. The purpose of this research is to select and possibly use multiple types of particles. The key here is that NPs must be deposited onto the window material in such a way that longwave heat radiation through the material is not obstructed, whereas separately deposited NPs would be necessary.

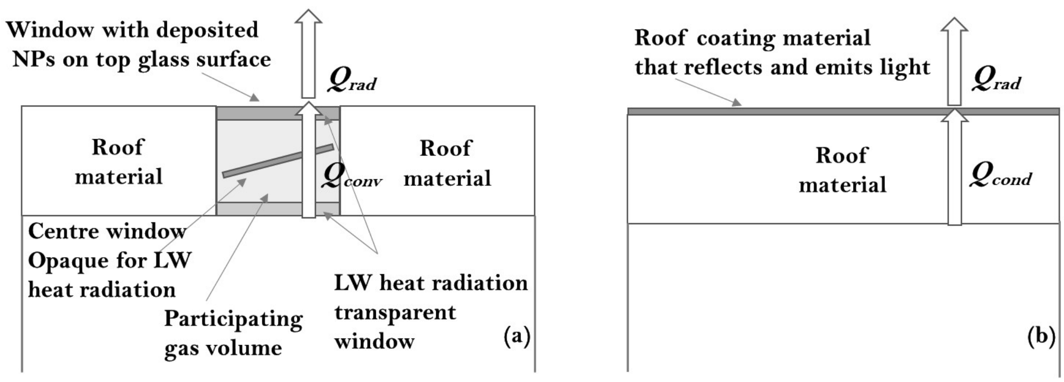

Fig. 2. (a) A skylight design with reflective NPs on a ZnS substrate and (b) compared with a rooftop reflecting and emitting coating material.

2. Principles of DPRC and theoretical cooling performance

Radiative heat transfer involves electromagnetic waves traveling between objects of different temperatures (from warmer to colder region). Earth radiates heat into cold space due to its relatively high temperatures (300 K) compared to space (3 K). The temperature of the Earth drops at night on the side facing away from the sun. In DPRC, the principle is that when the heat absorbed by the material deposited on a surface is less than the heat radiated to the cold space, the surface will remain cool even during the day - see Fig. 3a. Here, P_{net} represents the net cooling power, and $P_{coat,rad}$ represents the coating's radiative power. P_{atm} and P_{solar} are the absorbed powers from the atmospheric and solar irradiations, respectively. P_{nonrad} is the overall loss of heat energy caused by non-radiative heat transfer processes (convection and conduction, not shown in the Figure) between the NPs or dispersed particles and the surroundings.

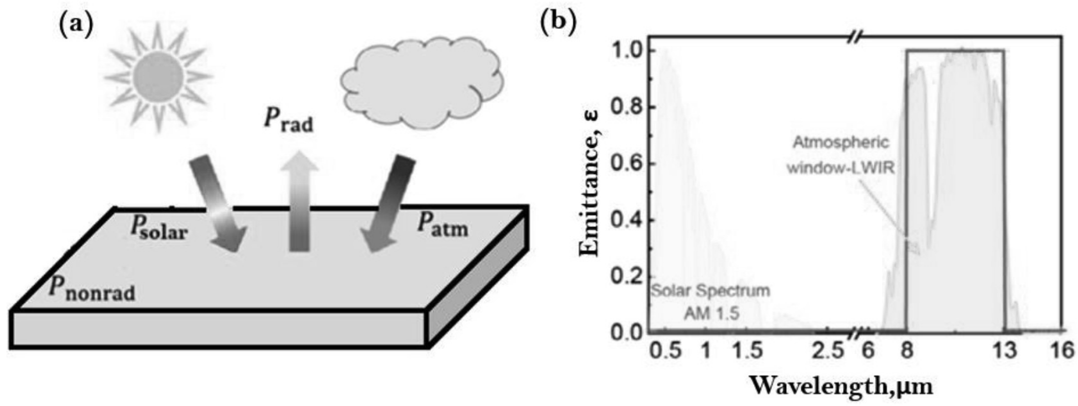

Fig. 3. (a) Diagram illustrating the heat transfer mechanisms of DPRC coatings. (b) The solar spectral intensity in yellow and LWIR atmospheric transparency in blue, respectively [10].

2.1. DPRC's solar irradiation and heat emittance

DPRC coatings have specific requirements and definitions for their optical performance over a broad range of wavelengths from ultraviolet to mid-infrared. The violet line in Fig. 3(b) shows the optimal spectrum for materials that offer DPRC: (a) ideally, short-wavelength absorption should be low (nearly 100% reflectance) in order to prevent heating by solar irradiation. (b) To radiate heat effectively from the atmosphere to space, the transmittance in the atmospheric long-wavelength infrared (LWIR) transmission window (8-13 μm) should be close to 1. (c) Outside the atmospheric window, (wavelengths 3–8 μm and > 13 μm) the material should have low absorption and high emissivity to minimize excess heating from atmospheric (diffuse) irradiation at temperatures above that of DPRC coatings.

Typically, the temperature difference between the ambient sky and dispersed DPRC coating is quite small (5–10°C). Within the range of wavelength λ= 0.2-3 μm, R_{Solar} represents the ratio of reflected solar irradiation with respect to total solar irradiation intensity [10]:

$$R_{Solar} = \frac{\int_{0.3}^{2.5} I_{Solar}(\lambda)\rho(\lambda)\, d\lambda}{\int_{0.3}^{2.5} I_{Solar}(\lambda)\, d\lambda} \quad (W/m^2) \quad (1)$$

In this equation, $I_{Solar}(\lambda)$ refers to the solar intensity spectrum and ρ(λ) represents the coating's spectral reflectance. Similarly, ε_{LWIR} is [10]:

$$\varepsilon_{LWIR} = \frac{\int_{8}^{13} I_{bb}(T,\lambda)\varepsilon(T,\lambda)\, d\lambda}{\int_{8}^{13} I_{bb}(T,\lambda)\, d\lambda} \quad (2)$$

Where $I_{bb}(T, \lambda)$ refers to the spectral intensity emitted by a blackbody at temperature T(K) and ε(T, λ) denotes the material's spectral emittance.

Materials that give surfaces or windows DPRC properties achieve their overall cooling performance during the day through a combination of (SW) solar radiation; SW reflection and LW emission by dispersed particles or a coating of NPs, atmospheric thermal radiation (SW and LW), and non-radiative heat transfer. See Fig. 3(a), [10]:

$$P_{net} = P_{coat,rad} - P_{atm} - P_{Solar} - P_{nonrad} \ (W/m^2) \quad (3)$$

DPRC has been a challenge due to the sun's continuous and powerful radiation, especially around noon (about 1000 W/m^2 at an air mass (AM) of 1.5). Certainly, radiators cannot compensate for the heat acquired from direct sunlight without high solar reflectivity besides emitting thermal radiation into the cold universe through the atmospheric window. Researchers are developing multilayer coatings and surface/integral structures with high solar reflectance across the entire solar spectrum, including metamaterials, photonic structures, and nanoparticle-doped materials capable of operating at sub-ambient temperatures. The following sections describe what strategies may be most effective in achieving DPRC and how to apply that to ÅAU skylights.

3. DPRC materials and surface structures

A number of PRC techniques have proven to be effective both throughout the day and at night. For instance, bulk materials (gypsum, painted metal), thin films (SiO, PbSe, ZnS, CdTe, MgO), and gaseous materials (ethylene, ethylene oxide, and ammonia) have all been used to study PRC systems. Later, for nocturnal radiative cooling, alternative energy-efficient radiators, such as colorful paints and functional films coated with silicon monoxide (SiO) or silicon nitride (Si_3N_4), were developed. A few research have also looked into the use of colored paints that are highly reflective in the solar spectrum but transparent in the atmospheric window, allowing the material to cool itself by thermal emission while absorbing solar radiation. Although these radiators emit high levels of radiation into the atmosphere, the reflectance of solar radiation is low, limiting their effectiveness during the day [11]. The advancement of advanced design and fabrication processes in recent years has enabled the development of new forms of selective infrared radiators, such as nanophotonic structures and metamaterials. Nanophotonic structures are becoming more adept at altering the thermal emission and reflection properties of bulk materials. These unique radiators have a high solar reflectivity while also emitting strongly within the atmospheric window, giving significant diurnal cooling effects.

3.1. Multiple layer nanophotonic radiators

A typical photonic radiator is a multilayer film composed of alternating layers of materials with different dielectric constants. For example, Raman et al. [12] investigated daylight radiative cooling to the sky with an integrated photonic thermal radiative cooler, yielding sub-ambient temperatures- see Fig. 4(a).

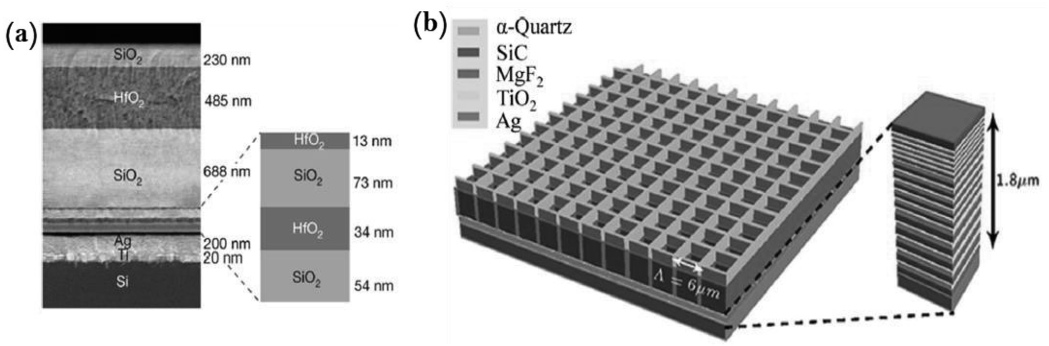

Fig. 4. (a) Multilayer nanophotonic radiator consists of alternating layers, (b) 2D photonic radiator with multilayers for solar reflection and thermal emission [12,13].

This radiative cooler is composed of seven optimized layers of silicon dioxide (SiO_2) and hafnium dioxide (HfO_2) on top of a silver (Ag)-coated silicon wafer with a thickness of 200 nm. The bottom four layers of SiO_2 and HfO_2 are thinner and intended to reflect solar radiation, whereas the top three layers are thicker and intended to reflect thermal radiation. This structure can reflect 97% of received sunlight while simultaneously emitting significant thermal radiation via the atmospheric window, resulting in the diurnal radiative cooling of 5°C below ambient temperature and an overall net cooling capacity of 40.1 W/m^2. Rephaeli et al. designed a metal-dielectric nanophotonic structure that enables DPRC. The photonic structure is seen in Fig. 4(b) is a two-dimensional (2D) periodic pillar array made of quartz and silicon carbide (SiC) as top and bottom layers, respectively, as well as a stack of high- and low-refractive-index dielectric materials on a silver substrate. The top two layers, quartz, and SiC showed higher emissivity in the atmospheric window range through phonon-polariton resonance, with a net cooling power of more than 100 W/m^2 during the day [13]. These photonic structures also exhibited high reflectivity and high emission in the solar spectrum and atmospheric window- see Figs. 5. (a) and (b).

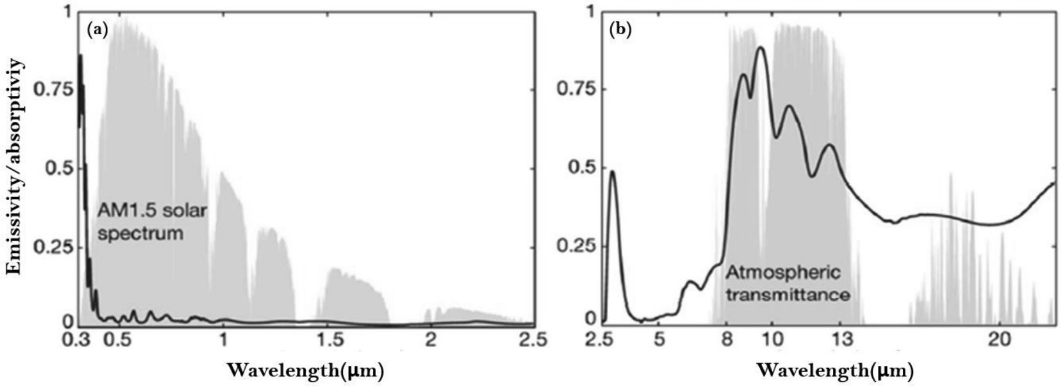

Fig. 5. (a) An emissivity of a solar spectrum photonic radiative cooler and (b) the photonic radiative Cooler's spectral emissivity in the mid-infrared range [12,13].

Hossain et al., on the other hand, provided a novel concept for a thermal emitter based on multilayer conical metamaterial pillar arrays. The pillars are made of alternate layers of aluminum (Al) and germanium (Ge). A coating of aluminum is 30 nm thick, while a layer of germanium is 110 nm thick. This structure has very high emissivity within the atmospheric window (8–13 μm), but low emissivity outside the atmospheric window [14]. Even though photonic structures are a promising solution for all-day radiative cooling, their cost, limited scalability, and intricate manufacturing techniques make them challenging to deploy in real-world circumstances. Most nanophotonic devices are fabricated in laboratories using time-consuming, expensive, and difficult technologies like nanolithography, electron beam lithography, and electron beam evaporation. As a result, complex three-dimensional (3D) structure production procedures are no longer available, limiting the complexity of producible nanostructures. As a result, complicated three-dimensional (3D) structure production processes remain unavailable, limiting the complexity of producible nanostructures.

PRC technology development was able to solve these problems by introducing random NPs-based material surfaces that are simple to construct and apply to any surface. It is straightforward to apply NP technologies to large areas, which is a significant step towards the widespread application of PRC technologies. In early studies, PRC successfully achieved temperatures up to 10°C below the ambient [15].

3.2. NPs based radiators

Radiative cooling has gained traction because of the photonic radiator's unique ability to modify spectrum characteristics for efficient diurnal cooling, which has enabled the development of sub-ambient radiative cooling. Nonetheless, as noted in the preceding section, photonic radiators confront several limitations. As a result, NPs-based radiators are a viable alternative for efficient PRC.

Gentle et al studies used a top layer of silicon carbide (SiC) and silicon oxide (SiO_2) chosen for their high emissivity in the atmospheric window, and a bottom layer of aluminum to reflect solar radiation - see Fig. 6(a). The addition of NPs increased the total emissivity from 0.35 to 0.95. Furthermore, using a reflective layer, this design can enable low-cost high-performance cooling (e.g., aluminum) [6].

As this trend gained popularity, Bao et al. proposed a scalable double-layer coating radiator – see Fig. 6(b).with selective radiative cooling properties. The top and bottom emissive layers of the radiator are composed of TiO_2 NPs and SiO_2 and/or SiC NPs, which reflect solar radiation and radiate heat to space through the atmospheric window. The combination of TiO_2+SiO_2 and TiO_2+SiC can theoretically achieve about 17°C below ambient at night and 5°C below ambient during daytime respectively. Huang et al. used a simple double-layer structure composed of acrylic resin, in which top and bottom layers include acrylic resin embedded with TiO_2 and carbon black particles, which are responsible for reflecting solar irradiation and emitting heat in the atmospheric window, respectively. TiO_2 particles of different sizes are tested for the top layer, and it was determined that a radius of 0.2 μm gives the best cooling performance.

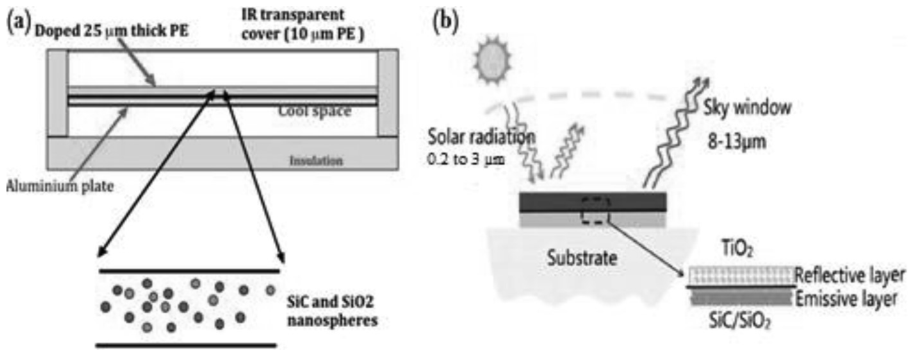

Fig. 6. (a) Two typical NP-doped polymer radiators [16] and (b) Two typical double-layer coatings based on NPs [17].

Applying a coating or adopting this design can significantly boost the emissivity of the surface. This random-particle embedded coating (in practice a dispersion of separate particles on the surface) reflected more than 90% of solar irradiation, and the average emissivity in the atmospheric window is > 0.9. The cooling power at ambient temperatures is more than 100 W/m^2 during the day and more than 180 W/m^2 at night. [16].

Further, Zhai et al developed a one-of-a-kind metamaterial - see Fig. 7. (a) - using randomized, glass-polymer hybrid metamaterials with SiO_2 microspheres randomly distributed in TPX material to exhibit efficient radiative cooling during the day and night. It has almost 0% loss in the solar spectrum with its polymer matrix metamaterial encapsulating SiO_2 microspheres (4 μm). This metamaterial emits significant amounts of thermal emission within the atmospheric window and low emissivity in the other infrared ranges due to its strong phonon resonance. The average emissivity of this thin film was greater than 0.93 during the day, with almost 96% of solar irradiance reflected by silver (Ag) as a reflective layer. The average radiative cooling power in a 72-hour experiment was 110 W/m^2. This device can cool to a temperature of more than 10 °C below the ambient, which is sufficient for commercialization. TPX is also resistant to mechanical and chemical attacks, making it suitable for outdoor applications [15].

For daytime cooling, Atiganyanun et al. developed photonic random media made of SiO_2 microspheres that outperform commercially available solar-reflective white paints - see Fig. 7. (b). Other than radiation, the desirable quality for daytime cooling is to significantly reflect or scatter sunlight to reduce solar heating. The low refractive index of these particles increases emissivity in the atmospheric window by reflecting or scattering incident sunlight. . Furthermore, under sun irradiation, SiO_2 microspheres can drop the temperature of a black substrate below the ambient level by up to 12°C without the use of costly silver coatings. The coating also reduced the surface temperature by 4.7°C below that of a commercial solar-reflective white paint during intense solar irradiation.

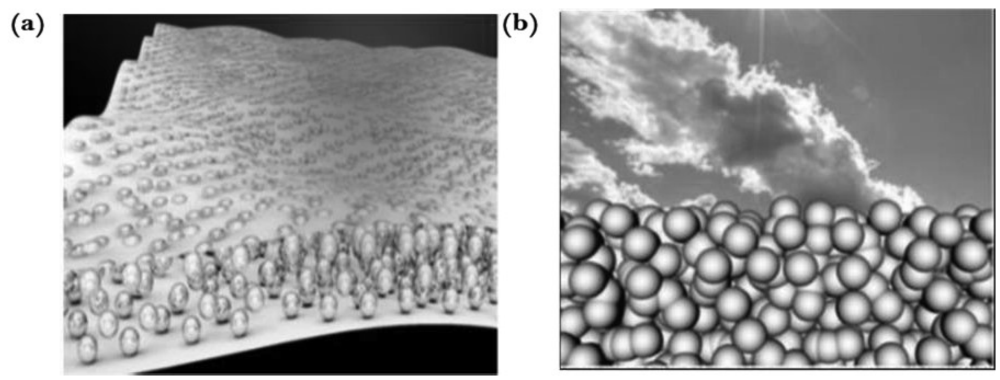

Fig. 7. (a) Random NP-based designs for radiative cooling using SiO_2 microparticles and (b) Photonic random media based on SiO_2 microspheres [15].

In contrast to expensive processing and materials, random particle-based methods do not require specialized materials or processing. These simple and scalable techniques could facilitate the application of low-cost, easy-to-apply coatings for radiative cooling [15].

4. Application to ÅAU skylight daytime passive cooling performance

4.1. Selection of NPs and preparation methods

The top window of the ÅAU skylight would be possible to modify using the materials described above such as quartz, SiC, HfO_2, MgF_2, Al, Ag, and other materials with variable dielectric constants. The most significant criterion for this application is that visible light (0.4 - 0.9 µm) can travel through it without interruption. Metallic nanoparticles are flexible nanostructures due to their ability to change their shape, size, composition, and structure during production. Metallic NPs also exhibit unique surface properties such as plasmon excitation, shape, and dielectric properties, making them useful in a variety of applications. According to the previous discussion, nanomaterials and nano/meta structures for radiative cooling are highly beneficial.

Cheng et al. demonstrated in their research that the combination of TiO_2 and SiO_2 would effectively reflect the incident sunlight, which is critical for improving the ÅAU skylight. An NP material that is suitable for large-scale applications (such as in buildings or the manufacture of vehicles) must comply with the following requirements: (1) Ideal emittance property. (2) Reasonable cooling effect. (3) The substrate must be rigid or flexible. (4) It can be mass-produced. (5) The price must be affordable [18] and specific here, and (6) In addition; the material deposited on the upper skylight window must not obstruct the LW radiation coming from below. Appendices 1 and 2 provide details on how to produce NPs and deposit them as discrete dispersed NPs on a glass surface, as could be carried out by our faculty at ÅAU.

4.2. Heat transfer experiments on window glass with dispersed NPs

The heat transfer measurements and calculations for radiative cooling of glass substrates having a TiO_2-SiO_2 particle mixture coating are discussed in this section. The experimental setup in the figure below is used to measure the temperatures of glass substrates with and without NPs particles deposited on the surface.

4.2.1 Equipment and test procedure

A glass beaker filled with hot water was maintained at temperatures of either 313 K or 333 K. A 2.5 cm glass sample (simple window glass thickness of thickness 2 mm) inserted into the cartoon, and a fluke Ti9 thermal imaging camera that captures infrared images (7.5 – 14 µm LW radiation) and measures the surface temperature are all part of the experimental setup. Smart view software can be used to process data from the camera later. The ambient temperature in the experiments was 292 K.

Procedure: A glass beaker with hot water was placed on the backside of the glass substrate in the experiment, allowing the water to radiate heat into the environment and pass through the glass. This sample has NPs on its surface facing the heat source, giving it direct visual contact with the heat source's radiation. Some heat traveling through the glass sample is absorbed and blocked by NPs. The thermal imager measures the heat passing the glass sample and records the temperature of the substrate surface. The experimental setup is depicted schematically below.

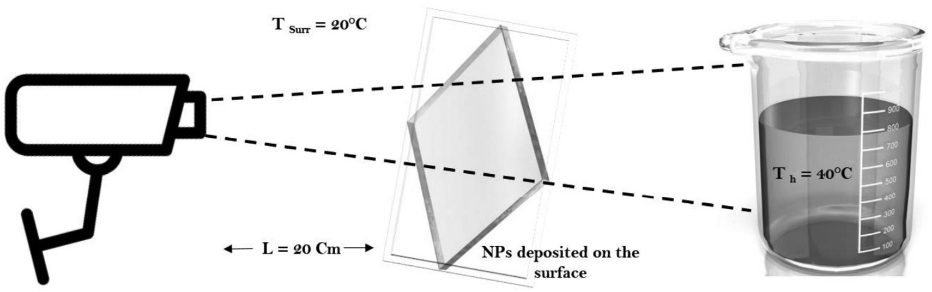

Fig. 8. Schematic representation of an experimental setup

4.2.2 Experimental results and calculation of (absorptivity/emissivity)

The heat camera (the Thermal Imager Ti9, Fluke, Everett, WA, USA, with a wavelength range of 7.5 - 14 µm) collects infrared images from a heat source (T_h), and (T_o) is the temperature of the camera, in principle the temperature of the laboratory, $T = T_o \sim 292K$. For determining the relation between absorptivity (α_s) and emissivity (ε_s) of a window, a substrate with NPs deposited on the surface and without NPs on the normal window glass. , A heat source (hot water at $T_h \sim 313$ K and 333 K) is used and passed through a window substrate, and the heat camera records thermal radiation. The thermal radiation detected by the heat camera is given by the heat balance equation:

$$Q'' = \varepsilon_h \cdot \sigma \cdot (T_h{}^4 - T_o{}^4) \cdot \tau_s + \varepsilon_s \cdot \sigma \cdot (T_s{}^4 - T_o{}^4) = (1-\rho_s) \cdot \varepsilon_h \cdot \sigma \cdot (T_h{}^4 - T^{\circ 4}) \quad (4)$$

which is the radiation from the (313 K and 333 K respectively) heat source transmitted with transmittance τ_s through the substrate + the radiation emitted by the substrate which has a temperature T_s, with $T^\circ < T_s < Th$, and substrate emittance ε_s. The substrate is considered to have a reflectance ρ_s, while the heat source has an emissivity = 0.98, as already acquired within the software database of Fluke Ti9 while processing the thermal images. The substrate has a temperature of $T_s > T°$ because of some heat absorption from the heat source. By rearranging the above heat balancing equation, with reflectance ρ_s for the substrate, $\rho + \alpha + \tau = 1$, the relationship between the absorptivity and emissivity can be obtained.

$$\frac{\alpha_s}{\varepsilon_s} = \frac{T_s^4 - T_0^4}{(T_h^4 - T_0^4)\varepsilon_h} \tag{5}$$

T_s, which represents the temperature of the substrate, is the only unknown parameter in equation (5). T_s values were determined experimentally using the thermal imager. Two sets of experimental tests were conducted in order to accomplish this. T_h = 313 K was initially specified as the heat source temperature. T_s appear automatically in the thermal imager once the heat source is projected onto the window substrate with NPs placed on the surface, using a test with a window without NPs deposited on the surface for comparison. The procedure was repeated after changing the heat source temperature to 333 K. The results are given in Figures 9 and 10, respectively.

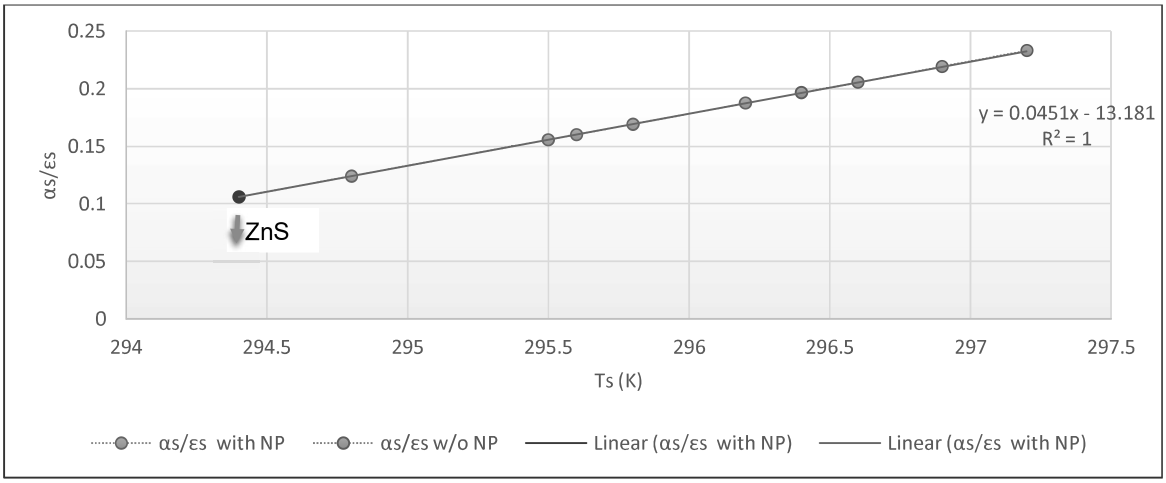

Fig. 9. The ratio between absorptivity and emissivity with and without NP's for T_h = 313 K.

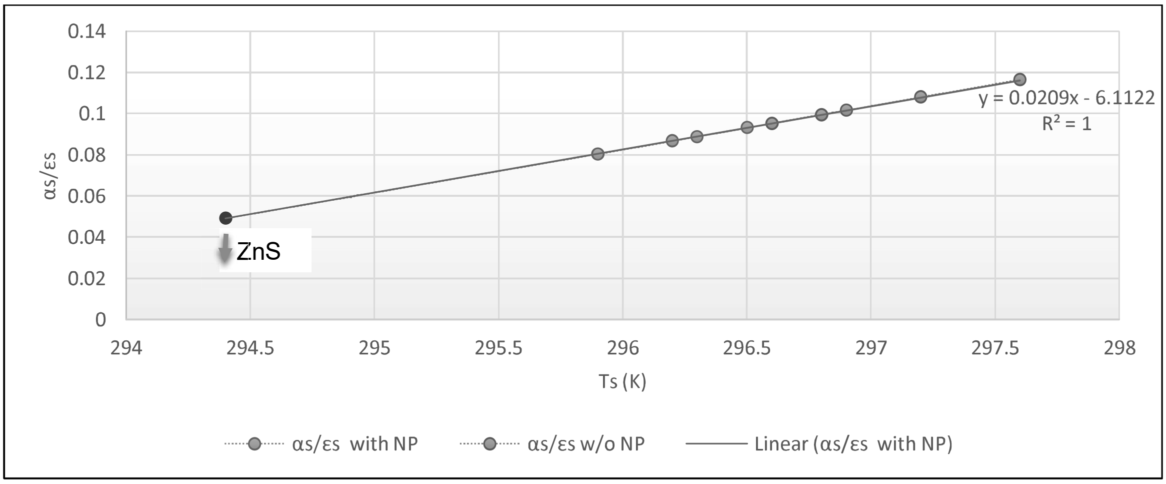

Fig. 10. The ratio between absorptivity and emissivity with and without NP's for T_h = 333 K.

Taking into account all the parameters in equation (5), it is now possible to plot substrate temperatures (T_s) against (α_s/ε_s). The graphs in Figs. 9 and 10 showed a linear relationship between T_s vs α_s/ε_s for window substrates having NPs on the surface and without NPs.

5. Conclusions

The majority of previous research studies focused on nocturnal radiative cooling using infrared selective radiators. In recent years, thanks to innovations in nanophotonics and metamaterials, a hot topic worthy of in-depth research has been the use of thermal radiation cooling, which provides a great cooling effect throughout the day. In spite of the development of various metamaterials to reduce the cost and scale of the radiator for diurnal radiative cooling, the design and manufacturing of large-scale cost-efficient radiators remain a key challenge for commercial applications. Thus, NP-based radiators are the preferred method for future commercialization because of their high production capacity, ease of fabrication, and adaptability. It is necessary to conduct more research into the selection of materials and optimization of NP size, $g/m^{2,}$ and filling fractions to build the most efficient radiative cooling device. This study proposes the use of NPs of TiO_2 and SiO_2, which will improve cooling by enhancing reflectivity in the region of the sun's spectrum, for future advancements in ÅAU skylights. Future experiments will include the study of at least a few NP materials, synthesized in the laboratory to achieve a strong reflection of solar radiation. Heat flux measurements of the window glasses with and without NPs deposited on them gave the relationship between the surface temperatures T_s and (absorptivity/emissivity) for long-wave radiation.

6. Future work

The past research indicated that single-layer radiative cooling coatings had the disadvantage of low cooling performance. We will nevertheless examine in more depth in the future considering the effect of particle diameter, volume fraction, filling factor, and thin-film thickness on the cooling performance of a single-layer radiative cooling with a mixture of TiO_2 – SiO_2 and sever other NPs in order to achieve the net cooling performance. The material selected for future study (ZnS Cleartran) is zinc sulfide. Both short- and long-wave heat radiation are transparent to this material, and it has a high mechanical strength suitable for containing the participating gas inside the ÅAU skylight. (ZnS) windows have a good IR transmission range of 8-14 µm and it has a good transmission range for the visible and mid-wave or LWIR, making it a good material for PRC applications. Besides LW radiation, testing will also involve SW radiation, focusing mostly on reflectivity.

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Appendix A: Materials and preparation methods for NPs

To investigate the solar reflectivity for the ÅA skylight used for PRC applications, the evaporation impregnation method (EIM) is the used method for synthesizing TiO_2-SiO_2 particles.

A.1. Using EIM to synthesize TiO_2-SiO_2 particles

Amount of SiO_2 used = 10 g + added 250 ml of distilled water. The initial pH was 6.75. After adding 3.79 grams of TiO_2 to it, the pH value changed to 5.76. A rotavapor apparatus in the laboratory was set up to attach a round-bottom flask filled with the solution to the rotavapor at 60 rpm and maintain a constant temperature of 60°C to obtain homogeneity so that we could begin the evaporation process after 24 hrs. The evaporation setup for this experiment was 80 mbar vacuum and 58 minutes duration time. Then, TiO_2-SiO_2 metal NPs were dried and calcined at the required temperatures starting at 25°C and then gradually increased up to 400°C shown in the below graph. The yield obtained after calcination of the material was 10.86 gm.

A.2. Characterization results of TiO_2-SiO_2 particles

A.2.1. Transition electronic microscopy

TiO_2 particles are spherical in shape, whereasSiO_2 particles are scattered over the surface shown in the graph below (see Fig. A.1). Thereby, an average particle size of 24.96 nm is determined for TiO_2.

A number of factors influenced the selection of TiO_2 and pure SiO_2 particles for radiative cooling: (i) Owing to the low extinction coefficient of TiO_2 particles (close to zero), and their refraction index greater than 2.5 in the solar spectrum, these particles may replace silver-reflectance layers in reflecting solar irradiation. (ii) Furthermore, for wavelengths greater than 10 µm, the extinction coefficient of TiO_2 particles steadily increases with wavelength, indicating that TiO_2 particles have a high emissivity in the atmospheric window. (iii) SiO_2, particles have a relatively high extinction coefficient in the atmospheric window. Therefore, SiO_2 coated with a radiative cooling coating gives excellent emissivity (iv). In the 10-12 µm wavelength range, SiO_2 particles exhibit low emissivity, lowering the emissivity of a radiative cooling coating, whereas TiO_2 as supplementary material can improve the emissivity of the radiative cooling coating at 10-12 µm wavelength. (v) Furthermore, SiO_2 particles also have a very low absorption coefficient, which allows them to scatter solar irradiation effectively and reduce the absorption of solar irradiation [19]. Therefore, TiO_2 and SiO_2 are the most commonly used metallic NPs in controlling thermal radiation, and they have shown to be quite effective in obtaining DPRC.

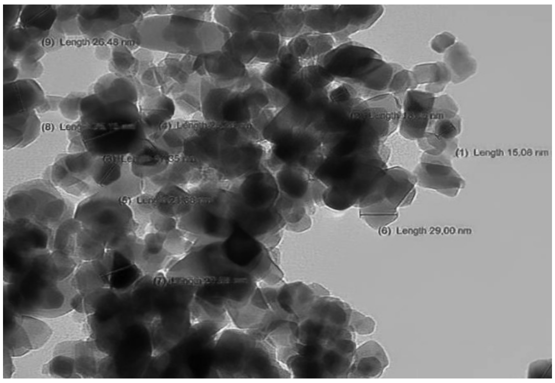

Fig. A.1. Transmission Electron Micrograph of catalyst TiO_2-SiO_2

A.2.2. SEM-EDXS results

SEM - EDXS detects the elemental arrangement of materials. EDXS analyses generate data in the form of spectra with peaks corresponding to the elements of the tested material. A non-destructive technology, EDX offers element distribution through mapping and is suitable for qualitative and semi-quantitative analysis. The results obtained are as follows, weight percentages of Ti and Si are 28.96% and 31.88%, and oxide percentages of 48.30% and 50.03%, respectively.

A.2.3. X-ray diffraction

XRD results confirm that the sample consists of both rutile and anatase TiO_2. They differ primarily in their appearance. While anatase TiO_2 is colorless, rutile TiO_2 is typically dark red in color. The TiO_2 in Rutile is optically positive and gives a high reflection of solar irradiation.

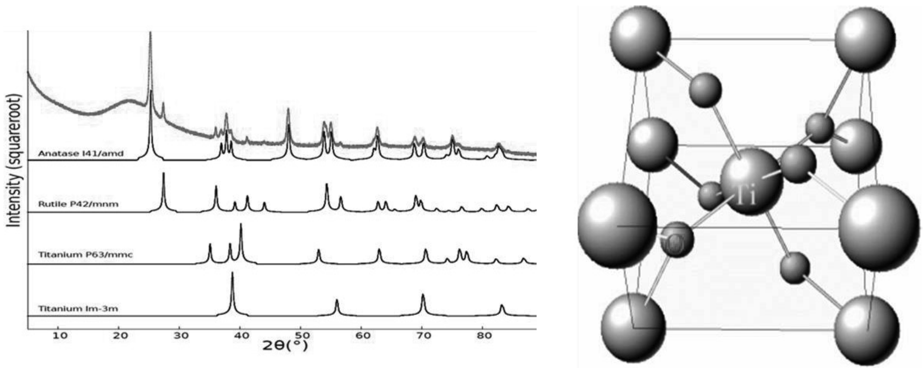

Fig. A.2. (a) The X-Ray Powder diffraction patterns for TiO_2 and Ti and, (b) Crystal structure of rutile TiO_2

Appendix B: Materials and preparation methods

B 2.1. Preparation of the single radiative cooling coating

In the coating process, 0.05 gm of TiO_2-SiO_2 NPs were dissolved in 10 gm of ethanol, followed by 0.2 gm of α- Terpineol, which helps bind the particles to the glass, and 0.016 gm of ethylcellulose to the precursor solution. After this, the magnetic stirring process continued vigorously for approximately two hours.

B.2.2. Methods for nano-coating fabrication

a) Spin coating: This entails placing a small quantity of nanofluid in the center of a substrate and spinning it at high speed. Nanofluid will spread to and eventually leave a thin film coating on the surface due to centripetal acceleration. Nanofluid characteristics (viscosity, drying rate, percentage of NPs, surface tension, etc.) and spin process parameters will determine the final film thickness. The parameters used for spin coating were speed: 3000 rpm, time: 45s, and acceleration: 3000 rpm (ramp up to 3000 rpm in one second). This spin coating process produced densely packed NP agglomerations (Substrate 1), for example, due to the fluid's high viscosity or non-homogeneity. The nano solution was prepared using 1 g of ethanol, and then an additional

10 gm of excess ethanol added to decrease agglomeration and increase transparency. A single-layer thin-film coating (Substrate 2) is then applied after altering the concentration of the solution. (see Fig. B.1).

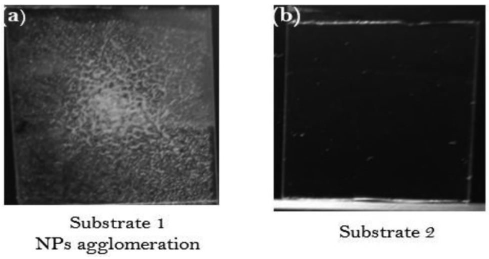

Fig. B.1. Spin coating mechanism substrates (a) with and (b) without NPs agglomeration

(b) ***Dip coating:*** This process involves dipping a substrate in a tank containing coating material, (TiO_2-SiO_2-EIM) removing it from the tank, and allowing it to drain. The coated piece can then be dried using force-drying or heat-treatment methods. In this procedure, optimization of withdrawal speed is essential to creating high-quality thin films. Thin films were, therefore produced at 85 mm/min (see Fig. B.2).

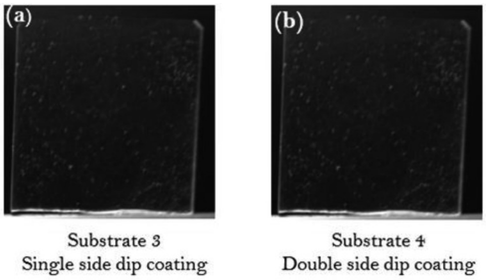

Fig. B.2.Dip coating mechanism substrates (a) Single-sided thin-film, and (b) Double-sided thin-film

One of the challenges in the implementation of ÅA skylight for PRC applications is to ensure the stability of coated NPs. Skylights are typically built on the top roof of the buildings. NPs must be robust and able to withstand harsh weather conditions when applied to the top surface layer of skylights. Thus, we used a process known as sintering to fix the particles on the substrate.

Nomenclature

AM	Air mass (-)
DPRC	Daytime passive radiative cooling
EDXS	Energy-dispersive X-ray spectrum
EIM	Evaporation Impregnation Method
I	Solar radiation intensity (W/m^2)
LWIR	Longwave infrared
NPs	Nanoparticles
P	Radiation intensity (W/m^2)
PRC	Passive radiative cooling
Q	Heat transfer (W)
SEM	Scanning electron microscopy
T	Temperature (K)
TEM	Transition electron microscopy
TPX	Methyl pentene copolymer matrix
XRD	X-ray diffraction
ÅAU	Åbo Akademi University

Greek symbols

α	Absorptivity (-)
ε	Emissivity (-)
λ	Wavelength (μm)
ρ	Reflectivity (-)

σ Stefan-Boltzmann constant ($5.67*10^{-8}$ $W/(m^2{\cdot}K^4)$)
τ Transmittance (-)

Subscripts and superscripts

atm Atmospheric radiation
coatrad Coatings radiative power
con Conduction
conv Convection
nonrad Non-radiative heat transfer process
net Net cooling power
Solar Solar

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