Daylong Sub-Ambient Radiative Cooling with Full-Color Exterior Based on Thermal Radiation and Solar Decoupling

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1. Introduction

In recent times, cooling demands have escalated due to economic advances and global climate change. The worst-case scenario suggests that electricity usage for space cooling will triple by 2050,[1] which is alarming. Of more concern is that the majority of the cooling systems currently in use rely on electric power generated by fossil fuels, leaving large carbon footprints. To break this vicious cycle, much attention has been paid recently to radiative cooling because it can achieve sub-ambient cooling without using electricity. Its physical principle is based on both the release of radiative heat into extraterrestrial space and near-perfect solar reflection.[2–6] Comprehensive studies have examined such cooling schemes including energy-saving buildings,[7,8] functional textiles,[9,10] and energy harvesting systems.[11,12]

In radiative cooling, however, extreme solar-reflecting conditions restrict the visual appearance of cooling surfaces to white,[4,7,11] ultra-bright,[16–19] or silvery.[20] Colors. Historically, visual discomfort by dazzling exteriors has been a great issue in building design,[19,21] so several countries legally regulate the use of solar reflective materials in buildings; particularly in Singapore where the solar reflection from glassy materials should be less than 20%.[22] In addition, lack of aesthetics of cooling surfaces may be objectionable in the commercial and social arena[21] despite the advantages of saving energy. Therefore, color diversity in radiative cooling is a practically important problem with no obvious solution.

A potential approach is to use thermally optimized spectral absorptance designs, which can suppress the solar thermal load while retaining the same color.[18,19,24–26] Nevertheless, studies have shown that the diminution of solar thermal load via wavelength selection is fundamentally insufficient to realize sub-ambient cooling for the majority of colors.[24,27] A different approach is to scatter light in different directions according to its wavelength.[28] This can achieve a colorful iridescent effect, but is not a viable solution when a consistent color is required or total reflectance is regulated. Yet another approach is photoluminescence, which recycles the absorbed photons for color exhibition rather than converting them to heat.[29–31] In a recent study, we revealed that sub-ambient cooling is possible for all colors based on the ideal photoluminescent process.[27] While this is also a promising approach, it requires the development of optimal photoluminescent colorants for each target color. It is still not clear whether it is possible to achieve sub-ambient cooling with any color using only currently available materials.

In the current study, we present a colored radiative cooling system that can appear in arbitrary exterior colors while cooling...
inside objects below the ambient temperature at all times of the day, based on a simple multi-layer stacking of available materials without need for vacuum insulation. The different sub-systems of the cooler cooperate with one another such that, collectively, they absorb only the absolutely necessary spectral range of the sunlight for desired coloration and emit efficiently in the mid-infrared atmospheric transparency window while maintaining a steep temperature gradient within the system. Especially, the intentionally induced non-equilibrium state between sub-systems allows the outer-most surface to contribute to cooling through convection in case of dark colors with large solar absorption. The end result is that the thermal emitter has a good radiative connection to the cold outer space but is radiatively and non-radiatively isolated from external heat sources such as the sun and atmosphere even in colored coolers. Thus, our radiatively intertwined non-equilibrium (RINE) system can resolve the conflict between color appearance and radiative cooling, in contrast to conventional radiative coolers. We experimentally show that vacuum-free RINE systems with dark colors (black and dark red are chosen as two examples) absorbing very large amount of solar power (646 and 672 $\text{W m}^{-2}$, respectively, under AM1.5 solar irradiation condition) accomplish sub-ambient cooling during daytime hours. Maximum temperature differences of 6.9 and 7.4 K and average differences of 3.5 and 3.7 K below the ambient temperature, respectively, were observed. Another notable aspect of the RINE system is that it exploits non-radiative heat exchange with the ambient air to improve its sub-ambient cooling performance, which is the opposite of conventional coolers whose sub-ambient cooling performances degrades from heat exchange with surrounding objects. Owing to this reversed ambient effect, the RINE system does not require additional wind covers or non-radiative shields on the exposed side, which are essential components in conventional designs to suppress non-radiative heat influx from the surrounding objects including ambient air.[33]

Thus, for sub-ambient cooling to occur, the solar absorption of the radiative surface (white arrows in Figure 1a) should be suppressed below $W_{\text{max,amb}}$ (black arrows in Figure 1a), which means that only $10\%$ of solar irradiance can be absorbed by the cooler. However, this conflicts with diversifying the colors of the coolers because dark colors require a significant amount of incident light to be absorbed, far exceeding the $W_{\text{max,amb}}$ limit.[24,27] Consequently, conventional radiative cooler design for sub-ambient cooling has to have a mirror-like appearance or if diffuse, be pure white, or some other very bright color, absorbing less than $W_{\text{max,amb}}$. For instance, a radiative cooler with a bright pink color (left in Figure 1a) can be cooled below a $T_{\text{amb}}$ of 300 K if its spectral absorbance is optimally designed to have a solar thermal load of 53 $\text{W m}^{-2}$, which is less than $W_{\text{max,300}}$ (Figure 1b). On the other hand, the dark reddish radiative cooler (middle in Figure 1a) never reaches sub-ambient temperature at noon owing to a large solar thermal load of 191 $\text{W m}^{-2}$ even with the optimal spectral absorbance that achieves the lower bound of the solar thermal load of that color by the metamer optimization algorithm (Note S1, Supporting Information). Investigation of the sub-ambient cooling possibility of all colors in the absorptive color space reveals that the color variety in the radiative surface horizontally placed on the ground is fundamentally limited to 5% of the total color space volume, if designed to achieve sub-ambient cooling at noon in mid-latitude summer (or 14% under AM1.5 conditions as described in ref. [27]) (Note S1, Supporting Information).

2.2. RINE System

We introduce a RINE system that exploits the thermal non-equilibrium between its color and mid-infrared emission parts for full-color sub-ambient cooling. The system in part is similar to previous novel radiative cooler designs that utilize a wavelength filter on top of a thermal emitter[14–36] or that place an IR-transparent solar panel above a vacuum-insulated thermal emitter.[37] However, previous approaches did not explicitly consider diverse color expression. Also, the use of ultra-high vacuum may limit its application to such cases in which the associated cost with vacuum maintenance can be justified.

Our system comprises an outer-most spectrally selective filter (SSF), a selective heat transfer layer (SHTL) in the middle, and a thermal emitter (TE) at the back in direct contact with the objects to be cooled as shown in Figure 1a. On the exposed side, the SSF displays colors by wavelength-selectively reflecting parts of the incident visible light and absorbing other parts, with zero transmittance at all visible wavelengths (Figure 1d). For invisible wavelengths, the SSF functions as a selective radiative window, transmitting light in the atmospheric transparency window (typically, 8–13 $\mu$m in wavelength) and reflecting the other wavelengths. With this spectral filtering, the TE can release radiative heat toward the outer space while being radiatively insulated from other heat sources such as the sun and the atmosphere. This design approach allows the use of common broadband thermal emitters such as most polymers or water as TE materials. These materials need to have high emittance in the transparency window but their emittance at the wavelengths in the grayed-out, irrelevant region of
Figure 1d do not affect the thermodynamic state of the system. Alternatively, the design of the SSF can be simplified if the role of wavelength-selective reflection of unwanted spectral ranges of visible and infrared light is delegated to the TE or the SHTL, at the expense of increased complexity in the material selection and structural design of the TE or SHTL (Note S2, Supporting Information).

The key component in maintaining thermal non-equilibrium is the SHTL subsystem in the middle. This suppresses heat exchange between the hot SSF and cold TE regions while allowing thermal radiation to pass through. While the SSF and TE may each have locally near-uniform temperature distribution, the SHTL can exhibit a steep temperature gradient owing to the potentially large temperature difference between the SSF and the TE. Hence, the constituent materials for the SHTL should have as large a thermal resistance as possible to minimize conductive heat flux while being transparent to thermal infrared light.

To analyze this non-isothermal system, we establish coupled equations for net departing power densities of the SSF ($P_{SSF}$) and TE ($P_{TE}$) (both in units of W m$^{-2}$), which consider radiative and non-radiative interactions between subsystems and with outside environments, as

$$P_{SSF} = W_{SSF} + \phi_{SSF, atm} + \phi_{SSF, SHTL}$$  \hspace{1cm} (1)

$$P_{TE} = W_{TE} + \phi_{TE, SHTL} + \phi_{TE, inside}$$  \hspace{1cm} (2)

where $W_{SSF}$ and $W_{TE}$ are radiative contributions to the net departing power densities from the SSF and TE, respectively, and the non-radiative heat flux densities ($\phi_{SSF, atm}$, $\phi_{SSF, SHTL}$, $\phi_{TE, SHTL}$, and $\phi_{TE, inside}$) are also defined in the outgoing direction from the subsystem of interest (either the SSF or TE) to the adjacent object identified in the subscript (detailed formulations can be found in the Experimental Section). The steady-state temperatures of the SSF and TE can be determined from

**Figure 1.** Schematic of colored radiative coolers. a) Radiative and non-radiative heat exchange scheme with the sun (white arrows), atmosphere (yellow arrows), and outer space (black arrows). b–d) Spectral profiles for: b) colored selective emitter, c) colored broadband emitter, and d) RINE system. The spectra in (b) and (c) are optimized for minimum solar absorption and maximum thermal emission. The spectrum of the SSF below 4 µm in (d) is matched with that of (c). The irrelevant regions in (d) correspond to zero transmittance of the SSF where the SHTL and TE are radiatively isolated from the outside.
\( P_{SSF} = P_{TE} = 0 \) conditions. We note that this non-isothermal description reverts to the simpler descriptions in previously reported isothermal systems if the thermal resistance between the SSF and TE is negligible such that the temperatures of the TE and SSF are effectively the same (Note S3, Supporting Information). Oppositely, when vacuum is applied for perfect non-radiative insulation, the system can be simply described without \( \phi_{SSF,SHTL} \) and \( \phi_{SSF,SHTL} \) as shown in previous works.[31,32] However, in vacuum-free and thermally finite RINE systems, all the heat transfers must be considered.

2.3. Analysis for the Steady-State Temperature

We evaluated and compared the cooling performance of the three colored radiative cooling schemes, as illustrated in Figure 1. Given their spectral emittance in the mid-IR range, their steady-state temperatures can be determined by solving the above coupled equations for a given solar thermal load \( (W_{sun}) \) and non-radiative heat coefficients \( (h_{c,amb} \text{ and } h_{c,SHTL} \text{ for the SHTL}) \). We assume that the TE is in thermal equilibrium with the inside object to be cooled (i.e., \( \phi_{TE,\text{inside}} = 0 \)). Figure 2a shows the steady-state temperature of an isothermal selective emitter as a function of \( W_{sun} \) and \( h_{c,amb} \) with unity emittance in the 8–13 \( \mu \)m window and zero emittance at other mid-IR wavelengths. As \( W_{sun} \) increases from zero, the temperature of the selective emitter monotonically rises and exceeds the ambient temperature \( (T_{amb} = 300 \text{ K}) \) when \( W_{sun} \) surpasses 101 W m\(^{-2}\). Increasing \( h_{c,amb} \) to strengthen the non-radiative heat exchange with the environment lowers the absolute temperature difference between the emitter and the environment. However, the control of \( h_{c,amb} \) does not change whether the emitter’s temperature is above or below the ambient temperature for a given \( W_{sun} \); although it can change how much the emitter is cooler or hotter than the ambient temperature. The colored broadband emitter with a unity emittance at all wavelengths over 4 \( \mu \)m can be cooled more (less) than the selective emitter when \( W_{sun} \) is higher (lower) than 95 W m\(^{-2}\), as shown in Figure 2b. This confirms the intuitive understanding that broadband emitters are better at above-ambient cooling conditions and selective emitters for below-ambient cooling.[38] However, as with the selective emitter, whether the broadband emitter is cooled below or heated above the ambient temperature is not affected by \( h_{c,amb} \) and the emitter is in fact heated, not cooled, for most parts of the possible range of \( W_{sun} \) in both designs.

In Figure 2c, we illustrate the steady-state temperatures of the SSF and TE in the RINE system as a function of \( h_{c,SHTL} \) and \( W_{sun} \) with \( h_{c,amb} = 12 \text{ W m}^{-2} \text{ K}^{-1} \). In this case, we set the range of \( h_{c,SHTL} \) so as to be practically achievable with vacuum-free design where \( h_{c,SHTL} = 0.1 \text{ and } 3 \text{ W m}^{-2} \text{ K}^{-1} \), respectively, correspond to 26 and 0.87 cm air thickness in normal pressure. The results reveal two critical differences compared to previous isothermal emitters. First, \( W_{sun} \) is no longer limited to
≤100 W m\(^{-2}\) for sub-ambient cooling. Second, better insulation of the emitter from the environment or other subsystems of the cooler (lower \(h_{\text{c,amb}}\) for isothermal emitters and lower \(h_{\text{c,SHTL}}\) for the RINE system) always results in a lower temperature of the emitter for all considered \(W_{\text{sun}}\). Both of these differences are the result of the non-equilibrium nature of the cooling system. While the SSF may be heated above the ambient temperature, the TE can be cooled below the ambient temperature if \(h_{\text{c,SHTL}}\) is small. More specifically, with \(h_{\text{c,SHTL}} < 1.35\) W m\(^{-2}\) K\(^{-1}\), the TE reaches sub-ambient temperatures even if the SSF absorbs almost all the sunlight with \(W_{\text{sun}} = 1000\) W m\(^{-2}\), which is nearly ten times as high as the isothermal emitters’ solar absorption limit for sub-ambient cooling. Because the TE temperature is always lower than the ambient temperature, a better insulation further reduces the temperature of the cooled object or results in more cooling power, regardless of the sun condition. For isothermal emitters, better insulation results in lower cooling temperatures or more cooling power only for small \(W_{\text{sun}}\) values (≤100 W m\(^{-2}\)). This makes the insulation design difficult because the requirement is the opposite at nighttime (small \(h_{\text{c,amb}}\) is desirable for \(W_{\text{sun}} \leq 100\) W m\(^{-2}\)) compared to daytime (large \(h_{\text{c,amb}}\) is desirable for \(W_{\text{sun}} \geq 100\) W m\(^{-2}\)) for most colors. We also note that the broadband TE in the proposed design can reach a steady-state temperature that is lower than the lower bound of the steady-state temperature of the conventional broadband emitter in Figure 2b, even if they have the same broadband emittance in the mid-IR range. This is due to the spectral filtering properties of the SSF, which allows the use of a simple, blackbody-like broadband TE instead of an optimal selective emitter with a precisely designed spectral emittance.

As illustrative examples, we present the expected temperatures of each scheme for five representative colors assuming optimized solar absorption spectra (i.e., \(W_{\text{sun}}\) is set to its lowest possible value for each given color) (Note S1, Supporting Information). Figure 2d,e shows that chromatic exhibition of black (\(L^a = 0, a^a = 0, b^b = 0\) in the CIELAB color space where \(L^b\) is perceptual lightness, and \(a^a\) and \(b^b\) are chromatic quantities for green-red and blue-yellow intermediate colors, respectively), red (\(L^a = 55, a^a = 80, b^b = 68\)), and green (\(L^a = 87, a^a = -88, b^b = -109\)) colors overheat both selective and broadband isothermal emitters because \(W_{\text{sun}}\) is much greater than 100 W m\(^{-2}\) for these colors. The steady-state temperature of cyan color is very close to \(T_{\text{amb}}\) and, among the five color choices, only the white-colored (\(L^a = 100, a^a = 0, b^b = 0\)) isothermal emitter exhibited appreciable sub-ambient cooling performance. As can be seen from these examples, the upper bound of the solar absorption in isothermal emitters under sub-ambient cooling constraints fundamentally limits their color diversity, allowing only white or very pale colors, regardless of the level of thermal insulation. On the other hand, our RINE system can express all colors in the absorptive color space, including pure black, and achieve sub-ambient cooling at the same time if \(h_{\text{c,SHTL}}\) is below 2.36 W m\(^{-2}\) K\(^{-1}\), as shown in Figure 2f.

The advantage of the non-equilibrium configuration of the RINE system becomes more intuitively understandable if we look at the direction of the non-radiative heat transfer between the colorant and the ambient. Under sub-ambient cooling conditions, the colorants in the isothermal emitters had a lower temperature than the ambient. Therefore, the direction of non-radiative heat exchange with the ambient is toward the colorants and adds to the thermal load already present on the emitter-colorant composite system because of the solar absorption required for coloration. In contrast, in most situations, except for very pale colors or dim lighting conditions, the colorants in the SSF have a higher temperature than \(T_{\text{amb}}\) because of solar absorption. Consequently, non-radiative heat transfer helps reduce the thermal load on the system. Thus, a large \(h_{\text{c,amb}}\) is beneficial as it can lower the temperature of the SSF by dissipating heat into the ambient environment. With a high \(h_{\text{c,amb}}\), the temperature difference between the SSF and the TE is reduced, which diminishes the non-radiative heat flow from the SSF to the TE, resulting in improved cooling performance of the TE (Note S4, Supporting Information). In contrast, the previous approach to achieve good sub-ambient cooling performance was to decrease \(h_{\text{c,amb}}\) as much as possible by implementing non-radiative shields, such as air encapsulated by a thin polymeric sheet\(^\text{[2,4,5,7,8,14]}\) and aerogel\(^\text{[6,39]}\) to the isothermal emitters. Although our design requires good internal insulation between the SSF and the TE, it does not require special thermal insulators between SSF and the outer ambient, as found in previous studies\(^\text{[13]}\). This can be beneficial in practical applications that have other mechanical and chemical requirements such as scratch resistance of the exterior surface or reliability in harsh environments.

2.4. Experimental Design

Following the theoretical studies above, we designed an exemplary vacuum-free non-equilibrium radiative cooling system with dark colors. The system comprises three vertically integrated sub-systems and is uniform (the SSF and TE) or periodic (the SHTL) in horizontal directions as shown in Figure 3a. First, for the SSF design, germanium was used as a mid-IR transparent, visibly absorbing rigid substrate. To express the target color and enhance the transmission of 8–13 µm wavelength mid-IR light, we applied five stacked layers of ZnS and Ge using magnetron sputtering on the exterior surface of the substrate. The thicknesses were chosen based on needle optimization targeted at black and dark red colors (as explained further in the Experimental Section). We also deposited a single 1100 nm thick ZnS layer on the opposite side of the substrate for anti-reflection of mid-IR light in the atmospheric transparency window. As with commercially available multi-layer dielectric filters, more layers of coating on both sides of the substrate would result in improved solar reflection as well as better mid-IR transmittance characteristics. However, we limited them to five and one layers to demonstrate that the RINE principle can have a significant effect even with simple, readily realizable structural designs. A visual inspection in Figure 3b of the fabricated samples revealed that they exhibited the targeted colors, and their cross-sectional images captured by scanning electron microscopy in Figure 3c confirmed the layer configurations as designed. To check the spectral properties in the solar and mid-IR ranges quantitatively, we measured the SSFs with UV–NIR and FT-IR spectrometers, respectively; incident angles for reflectance and transmittance were set at 30° and 0° from the normal axis of the sample, respectively. We note that the measured
reflectance of SSFs shows good consistency with the calculation results, which indicates that, as expected, the optimized SSFs are well established in this work (Note S5, Supporting Information). In the solar spectral range, Figure 3d shows two SSFs presenting distinctive spectral reflectance, and both have almost zero transmittance below 1.6 \( \mu \)m wavelength. Based on the measurement results, the absorbed solar power densities can be calculated under AM1.5 conditions for SSF-black and SSF-red, which are 646 and 672 W m\(^{-2}\), respectively. This is more than six times the maximum allowed value of \( W_{\text{sun}} \) for isothermal emitters for sub-ambient cooling. In the mid-IR region, Figure 3e, which follows color scheme in Figure 3d, shows that both SSFs exhibit high transmittance in the 8–13 \( \mu \)m atmospheric transparency window and low transmittance at other wavelengths. In Note S6, Supporting Information, we also show that various colors other than black and red (such as green, blue, cyan, magenta, and yellow) are also feasible in SSF, with high transmittance in mid-IR regions, based on similar design complexity in Figure 3c.

To implement the SHTL with vacuum-free high thermal resistance in the vertical direction, we adopted an air-and-frame approach, in which the frame comprised expanded polystyrene insulation (EPS) walls in a square-grid pattern, and the remaining volume was filled with air. We covered the side surfaces of the EPS frame with thin Al foil (thickness \( \approx 18 \mu \)m) to reflect the radiative emission of the TE at high angles toward the outside. In addition, the Al foil was sectioned into a few horizontal strips to reduce the vertical heat conduction through the foil (Note S7, Supporting Information). To estimate the non-radiative heat coefficient of SHTL, \( h_{c,SHTL} \), depending on height and filling ratio of the frame. In this plot, high \( h_{c,SHTL} \) over 3 W m\(^{-2}\) K\(^{-1}\) is colored in gray for easy illustration.
Finally, we adopted a very simple design for the TE of 330 μm thick polydimethylsiloxane (PDMS) coated on an Al foil. Its emittance in the mid-IR range is close to unity over a broad range of wavelengths. Its absorptance is high in the solar spectral range with $W_{\text{sun}} = 597 \, \text{W m}^{-2}$ under AM1.5 conditions, but this does not result in actual absorption because the radiative interaction of the TE with the outside is spectrally filtered by the SSF. The calculated $W_{\text{TE}}$ reached 89 W m$^{-2}$ at $T_{\text{amb}}$ for the red SSF and 87 W m$^{-2}$ at $T_{\text{amb}}$ for the black SSF (Note S9, Supporting Information).

We included two other SSFs as reference systems to demonstrate the strong dependence of the cooling performance on the spectral selectivity of the SSF. The first reference system was a blackbody (BB) filter that does not transmit but fully absorbs any radiation from UV to mid-IR and is made of black foil (Metal Velvet, Acktar Ltd.) attached to either side of a Si wafer. The measured absorptance was 99.5% on average in the wavelength range 0.3–24 μm (Note S10, Supporting Information). The second reference system was an SSF-less case that is all-transmissive in the solar and mid-IR spectral ranges. The cooling performance of the TE without spectral filtering on top can be checked using this reference. In this case, convection between the outer ambient air and the air of the SHTL may interrupt the cooling performance of the TE, but the thermal state of the TE (whether its temperature is above or below $T_{\text{amb}}$) cannot be changed by the ambient air.

The outdoor cooling performance measurement setup is shown in Figure 4a. The samples were placed in separate chambers where the side and bottom were thermally insulated by vacuum-insulated panels, which approximately sets thermal periodic boundary conditions in horizontal direction while allowing thermal interactions in vertical direction. We emphasize that such insulation panels are not the essential components in RINE system but allows the finite-sized samples to be modeled as a large-scaled system. The outer surface of the setup was covered with barium sulfate paint (pre-mix white coating, Edmund Optics Inc.) to exclude parasitic solar heating of the samples through the setup. In addition, we measured the ambient temperature near the setup where white-coated extruded polystyrene (EPS) shields direct solar illumination. Such a solar shield on the ambient sensor can prevent the overestimation of the ambient temperature and the cooling performance of the samples under test. During the measurements, the setup and pyranometer were placed horizontally on the ground. The outdoor experiment was conducted at KAIST in Daejeon (36.4°N, 127.4°E), South Korea, and the climate conditions on the measurement day were as follows: during the daytime, the atmosphere was cloudless, the average wind speed was 3.8 ms$^{-1}$, the average humidity was 57%, and the solar irradiance reached a maximum value of 743 W m$^{-2}$ on a horizontal surface (more details are provided in Note S11, Supporting Information).

### 2.5. Experimental Results

The outdoor temperature measurement results for the RINE systems are presented in Figure 4b. In daytime, black and red SSFs were heated up to 14.0 and 12.5 K over $T_{\text{amb}}$ with 5.3 and 5.0 K over $T_{\text{amb}}$ on average, respectively. However, the TEs for both the black and red SSFs were cooled below $T_{\text{amb}}$ at all time during the day. Figure 4c shows their temperatures dropped to 6.9 and 7.4 K below $T_{\text{amb}}$ with 3.5 and 3.7 K below $T_{\text{amb}}$ on average, respectively. This showed that the RINE scheme can achieve sub-ambient cooling even with dark-colored exteriors directly exposed to the sun on a clear day. Similar results were also observed even under very different weather conditions with longer measurement time (~3 days), which ensures that the color and cooling performance of this scheme is reproducible and reliable (Note S12, Supporting Information). This also implied that the color in the SSF can be diversified significantly over what was previously possible with an isothermally colored emitter while keeping the TE cool below $T_{\text{amb}}$.

To check the possible color variety in the actual experimental conditions, we compared the $W_{\text{sun}}$ of the fabricated SSFs with that of all other colors in the absorptive color space as described in Note S1, Supporting Information. The $W_{\text{sun}}$ of SSFs can be calculated using the spectral solar irradiance in the horizontal plane and the absorptive spectrum of SSFs at the solar elevation angle (Note S5, Supporting Information). The calculated $W_{\text{sun}}$ values of the black and red SSFs reached peak values of 475 and 490 W m$^{-2}$ at noon, respectively. Interestingly, such values of $W_{\text{sun}}$ can cover over 99% of the volume fraction of the 3D absorptive color space at noon in mid-latitude summer.

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Figure 4. Outdoor temperature measurement results. a) Photographic images for measurement setup with the inset for sensing location. The right picture shows the sky conditions on the day the measurement was conducted. b) The measured temperature for SSFs, TEs, and the ambient. The colored area indicates solar irradiance (scales on the right). c) The temperature of the TEs compared to $T_{\text{amb}}$. The gray-colored area indicates nighttime.
(with optimal colorants with minimal $W_{\text{sun}}$ for each given color assumed), which is a major advance compared to the previous color expression limit of 5% volume fraction.

On the other hand, the reference system with the BB filter presented quite different results in the daytime. Contrary to the optimized SSFs, the BB filter not only blocked the radiative interaction of the TE with the outer space but also emitted significant thermal radiation to the TE. Consequently, the results show that the TE was heated up to 6.8 K above $T_{\text{amb}}$ and stayed significantly above ambient temperature during high solar altitude time from 10:17 to 15:32. In this case, the non-radiative heat flow was smaller than that of the RINE system because of the smaller temperature gap between the filter and the TE, thus revealing that the overheating of the TE mainly arises from radiative heat from the hot BB filter. Therefore, a good transmittance in the mid-IR atmospheric transparency window is a critical requirement for the SSF if sub-ambient cooling is intended. Without it, the emitter temperature rises above the ambient even when all solar energy is blocked by the SSF.

As another point of reference, we include the results for the all-transmissive SSF case. In that configuration, the solar illumination reached the TE, and the TE was heated up to 4.7 K above $T_{\text{amb}}$. It remained above-ambient temperature during most times of the day from 10:02 to 17:27. This emphasizes the importance of the ability of the SSF to block sunlight. The TEs in both reference cases cooled below $T_{\text{amb}}$ only at night or near sunrise and sunset when solar illumination is weak due to the low elevation angle of the sun.

3. Conclusions

In conclusion, we have proposed a non-equilibrium design for colored radiative cooling, which ensures that an internal emitter is able to release radiative heat to outer space but to be insulated from radiative and non-radiative heat sources outdoors. Based on the theoretical study in colorimetry, we have shown that the potential color variety in our scheme is significantly extended beyond the color expression limit in previous designs of colored emitters for sub-ambient cooling, and it is possible to use almost any color in the absorptive color space. In addition, with the help of the spectral filtering ability of the outer layer, a simple broadband emitter can be used instead of a precisely designed wavelength-selective emitter. We have experimentally demonstrated vacuum-free RINE systems for black and dark-red colors with broadband emitters that are cooled below the ambient temperature during the daytime. Our design suggests a viable way to express diverse colors without severe degradation of radiative cooling performance.

In practical view, achievements of this work are also prominent by showing that RINE systems are available with common materials and easy-to-fabricate design. We verified that ultra-high vacuum is unnecessary for non-radiative insulations but composite structure in normal pressure is enough to realize sub-ambient cooling with various color expression. These results can potentially increase the commercial feasibility of radiative cooling for wider range of practical applications as relieving the concerns in hazardously dazzling exterior and loss of color aesthetics in conventional radiative coolers.

4. Experimental Section

Calculation of the Net Cooling Power Density: To solve the coupled Equations (1) and (2), the radiative and non-radiative heat exchange terms between subsystems and between a subsystem and the environment were enumerated. First, the net radiative cooling power densities of the SSF and the TE can be arranged as

$$W_{\text{SSF}} = W_{\text{SSF,all}} - W_{\text{TE,SSF}} - W_{\text{sun,SSF}} - W_{\text{atm,SSF}} - W_{\text{space,SSF}}$$

$$W_{\text{TE}} = W_{\text{TE,all}} - W_{\text{SSF,TE}} - W_{\text{sun,TE}} - W_{\text{atm,TE}} - W_{\text{space,TE}}$$

where $W_{\text{SSF,all}}$ and $W_{\text{TE,all}}$ are the radiant exitance of the SSF and TE, respectively, excluding the amount absorbed back by themselves due to reflections from other surfaces; $W_{\text{TE,SSF}}$, and $W_{\text{SSF,TE}}$ are the absorbed irradiances on the SSF, and TE emitted from the TE, and SSF, respectively; $W_{\text{sun,SSF}}$ and $W_{\text{sun,TE}}$ are the absorbed irradiances on the SSF and TE, respectively, emitted from the sun; $W_{\text{atm,SSF}}$, and $W_{\text{atm,TE}}$ are the absorbed irradiances on the SSF and TE, respectively, emitted from the atmosphere; and $W_{\text{space,SSF}}$, and $W_{\text{space,TE}}$ are the absorbed irradiances on the SSF and TE, respectively, emitted from outer space. In this case, $W_{\text{space,SSF}}$ and $W_{\text{space,TE}}$ can be ignored owing to the large radiative temperature difference of outer space ($\approx 3K$) and other objects. Given the radiative properties of the subsystems and environment, the remaining terms in Equations (3a) and (4) can be expressed as

$$W_{\text{SSF,all}}(T_{\text{SSF}}) = \int \int \int \left( e_{\text{SSF}} \left( \lambda, \Omega, T_{\text{SSF}} \right) + e_{\text{SSF,2}} \left( \lambda, \Omega, T_{\text{SSF}} \right) - \frac{e_{\text{SSF}} \left( \lambda, \Omega, T_{\text{SSF}} \right)}{1 - e_{\text{SSF}} \left( \lambda, \Omega, T_{\text{SSF}} \right)} \right) \cos \theta \lambda d\Omega$$

$$W_{\text{TE,SSF}}(T_{\text{SSF}}, T_{\text{TE}}) = \int \int \int \left( e_{\text{TE}} \left( \lambda, \Omega, T_{\text{TE}} \right) e_{\text{SSF,2}} \left( \lambda, \Omega, T_{\text{SSF}} \right) \right) \cos \theta \lambda d\Omega$$

$$W_{\text{sun,SSF}}(T_{\text{SSF}}, T_{\text{TE}}) = \int \int \int \left( e_{\text{sun}} \left( \lambda, \Omega, T_{\text{SSF}} \right) + \frac{e_{\text{TE}} \left( \lambda, \Omega, T_{\text{TE}} \right) e_{\text{SSF,2}} \left( \lambda, \Omega, T_{\text{SSF}} \right)}{1 - e_{\text{SSF}} \left( \lambda, \Omega, T_{\text{SSF}} \right)} \right) \cos \theta \lambda d\Omega$$

$$W_{\text{atm,SSF}}(T_{\text{SSF}}, T_{\text{TE}}, T_{\text{amb}}) = \int \int \int \left( e_{\text{sun}} \left( \lambda, \Omega, T_{\text{SSF}} \right) + \frac{e_{\text{TE}} \left( \lambda, \Omega, T_{\text{TE}} \right) e_{\text{SSF,2}} \left( \lambda, \Omega, T_{\text{SSF}} \right)}{1 - e_{\text{SSF}} \left( \lambda, \Omega, T_{\text{SSF}} \right)} \right) \cos \theta \lambda d\Omega$$

$$W_{\text{space,SSF}}(T_{\text{SSF}}, T_{\text{TE}}) = \int \int \int \left( e_{\text{sun}} \left( \lambda, \Omega, T_{\text{SSF}} \right) + \frac{e_{\text{TE}} \left( \lambda, \Omega, T_{\text{TE}} \right) e_{\text{SSF,2}} \left( \lambda, \Omega, T_{\text{SSF}} \right)}{1 - e_{\text{SSF}} \left( \lambda, \Omega, T_{\text{SSF}} \right)} \right) \cos \theta \lambda d\Omega$$

$$W_{\text{space,TE}}(T_{\text{SSF}}, T_{\text{TE}}) = \int \int \int \left( e_{\text{sun}} \left( \lambda, \Omega, T_{\text{SSF}} \right) + \frac{e_{\text{TE}} \left( \lambda, \Omega, T_{\text{TE}} \right) e_{\text{SSF,2}} \left( \lambda, \Omega, T_{\text{SSF}} \right)}{1 - e_{\text{SSF}} \left( \lambda, \Omega, T_{\text{SSF}} \right)} \right) \cos \theta \lambda d\Omega$$
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because they showed good performance and were easy to fabricate.


dependence on the temperature differences:

are similarly defined and calculated for the TE instead of the SSF.

due to multiple reflections in the cooler. Equation (4a) presents the

of the SSF through the outer and inner sides, respectively. The third term

owing to multiple reflections between the SSF and the TE. The second

where $\Delta \lambda = \lambda + \Delta \lambda - \lambda - \Delta \lambda$ is the reflectance of the SSF, TE, and ambient air, respectively; $\epsilon_{SSF,1}$  and $\epsilon_{SSF,2}$ are the emittances of the outer and inner sides of the SSF, respectively; $r_{SSF,1}$  and $r_{SSF,2}$ are the reflectances for the outer and inner sides of the SSF, respectively; $T_{SSF,1}$, $T_{SSF,2}$, $T_{TE}$, and $T_{ambient}$ are the temperatures of the SSF, TE, and ambient air, respectively; $k_B$ is Planck’s constant, $h$ is the speed of light in a vacuum, and $k_b$ is the Boltzmann constant. $I_{sun}(\lambda, \Omega)$ for given temporal and spatial conditions was obtained by using a simple model of the atmospheric radiative transfer of sunshine (SMARTS 2.9.5, NREL). $I_{ambient}(\lambda, \Omega, T_{ambient})$ was calculated by multiplying $I_{SSL}(\lambda, T)$ and the atmospheric emittance $\epsilon_{ambient}(\lambda, \Omega, T_{ambient})$ which was modeled by a spherical shell model as $\epsilon_{ambient}(\lambda, \Omega, T_{ambient}) = 1 - r_{ambient}(\lambda, T_{ambient}) \times A(	heta, \phi)$ where $r_{ambient}$ is the atmospheric transmittance in the zenith direction, and $A(	heta, \phi)$ is an attenuation factor of the atmosphere at zenith angle $\theta$.

In Equation (3a), the first and second terms are the thermal emissions of the SSF through the outer and inner sides, respectively. The third term accounts for the partial absorption by the SSF itself of the second term owing to multiple reflections between the SSF and the TE. The second term in Equations (3c) and (3d) also correspond to additional absorption due to multiple reflections in the cooler. Equation (4a) presents the emitted thermal radiation from the TE. Terms in Equations (4a) to (4d) are similarly defined and calculated for the TE instead of the SSF.

Non-radiative power densities in Equations (1) and (2) were also defined to be positive in the direction from the first to the second object tagged with the subscripts and assumed to have the following linear dependence on the temperature differences:

$$\Delta E(\lambda) = \alpha_1 \Delta T_e^2 + \alpha_2 \int_4^{10} (1 - |r(\lambda)|^2) d\lambda + \alpha_3 \int_8^{14} (1 - |r(\lambda)|^2) d\lambda + \alpha_4 \int_8^{14} (1 - |r(\lambda)|^2) d\lambda$$

where $\Delta E_{iso}$ is a color distance metric defined as in CIE DE2000(43) under D65 illumination. Normalization factors $\alpha_1$, $\alpha_2$, and $\alpha_3$ were applied to balance the different objectives. While the performance can further increase with more layers, the authors chose to deposit five layers because they showed good performance and were easy to fabricate.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest

The authors declare no conflict of interest.

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Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
color diversity, non-equilibrium, radiative cooling, sub-ambient cooling, trade-off

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