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Hierarchically structured passive radiative cooling ceramic with high solar reflection

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Abstract:

Passive radiative cooling using nanophotonic structures is limited by its high cost and poor compatibility with existing end uses, while polymeric photonic alternatives lack weather resistance and effective solar reflection. We developed a cellular ceramic that can achieve highly efficient light scattering and a near-perfect solar reflection of 99.6%. Coupled with high thermal emission, the ceramic provides continuous sub-ambient cooling in an outdoor setting with a cooling power over 130 W/m^2 at noon, demonstrating energy-saving potential on a worldwide scale. The color, weather resistance, mechanical robustness, and ability to depress the Leidenfrost effect are key features ensuring the durable and versatile nature of the cooling ceramic, thereby facilitating its commercialization in various applications, particularly in building construction.

One-sentence summary:

A radiative cooling ceramic was developed with near-ideal solar reflection resulting in high energy conservation.

Energy used for cooling continues to rise. Carbon dioxide emissions resulting from space cooling have more than doubled to almost 1 Gt over the past thirty years (*1*). Unfortunately, the carbon footprint of cooling systems indirectly contributes to global warming, creating a vicious cycle further exacerbating the need for air-conditioning. To mitigate these environmental concerns, renewable energy sources, such as wind, tidal and solar power, have been harnessed to meet the ever-increasing energy demand. However, the development and implementation of these energy systems require extensive land use and costly installations. In contrast, passive radiative cooling (PRC), in which surfaces utilize the cryogenic universe as a natural heat sink for heat removal, provides an energy-neutral solution for energy transfer and space cooling (*2-4*).

In recent decades, radiative cooling systems (coolers) of various photonic architectures with subwavelength-scale dimensions have been designed for tuning the thermal spectrum (*5-17*). Although the tailored longwave infrared spectrum helps to suppress heat gain from atmospheric radiation, the sophisticated material composition for thermal selectivity sacrifices solar reflection. In addition, even though these designs can easily achieve deep night-time sub-ambient cooling, they struggle to generate cooling during periods of high cooling demand in the daytime.

Atmospheric window (AW) transmittance (τ_{AW}), which serves as the only avenue for radiative heat transfer between the cooler and the universe, is highly affected by the local climate and environment (*18-20*). On the other hand, solar radiation dominates the radiative heat exchange of a cooler during daytime considering the Sun (5,800 K) emits electromagnetic radiation at an intensity that is 11 orders of magnitude higher than that of a room temperature object (288 K). We numerically solved the steady-state heat transfer model for a sky-facing cooler, enabling us to estimate the impact of a cooler's optical properties, i.e., solar reflection (R_{solar}) and AW emission (ε_{AW}), on the cooling performance (Fig. S1). The model assumes a constant surrounding air temperature and solar intensity, so that the cooler's cooling power changes according to the cooler's optical properties. The calculation results (Fig. S1) clearly indicate that enhancing R_{solar} can yield a higher cooling capacity over enhancing ε_{AW} by the same amount regardless of τ_{AW}.

However, the development of a daytime PRC material with both high solar reflection and practicality for outdoor application is challenging. In contrast to patterned and periodic optical designs which are small scale and costly, random media, such as particles (*21-27*) and micropores (*28-35*), have recently gained attention for achieving applicable daytime PRC. Researchers have investigated disordered designs, such as those of particle-doped polymers (*21-27*), aerogels (*28*), porous membranes (*29-33*), fibers (*34, 36*) and delignified wood (*35*). An inherent advantage of these designs is their ability to obviate the need for intricate parameter control, affording simplicity and scalability. However, solar absorption by these materials is inevitable. The dielectric pigments (e.g., titanium dioxide and zinc oxide) and polymers used in these disordered designs absorb sunlight within different wavelength ranges (*37, 38*). In addition, a high content of organic material potentially leads to degradation during long-term outdoor use (*39*). For potential application scenarios, like buildings, this could lead to frequent replacement or maintenance of the building envelope and result in exorbitant cost. The trade-off between the optical properties and applicability has always posed a challenge toward practical implementation of PRC technology in the real world. Recently, the PRC designs using pure inorganic materials to achieve reliable stability throw the insight to address this challenge (*40-42*). In this work, we designed a hierarchically porous PRC material in the form of bulk ceramic, which can be easily obtained using accessible inorganic materials through facile fabrication processes. The design simultaneously achieves near-ideal solar reflection and robust applicability, showing great potential toward application in the real world.

Bio-whiteness

Cyphochilus, a beetle native to Southeast Asia, is the whitest insect on Earth. We learned from the intricate biological structure of this beetle to design a robust ceramic-format cooler. Based on the investigation of the scattering system of the beetle's scales, our cooling ceramic was engineered with a hierarchically porous structure which led to a near-ideal R_{solar}. This cooler can be obtained with easy fabrication, requiring neither the employment of precision instruments nor meticulous regulation of parameters, boasting a high daytime cooling performance to reduce energy consumption for indoor cooling. In the vast forest ecosystem, the beetle's white appearance serves as camouflage against fungus backgrounds, shielding it from predators. The Cyphochilus specimen used for morphological and optical characterization (Fig. 1A), depicts the beetle's bright white exoskeleton comprising the head, thorax and forewings. Upon closer examination using scanning electron microscope (SEM), we discovered the very small scales that densely cover the white areas, with approximately 15,000 scales per square centimeter (Fig. 1B). These scales, shaped like teardrops, are only 6 μm thick and comprise a highly connected random network of chitin with a filling fraction of approximately 60% and a typical diameter of 0.25 ± 0.05 μm (Fig. 1C and Fig. S2). Spectroscopic characterization revealed that the scale-covered skeleton exhibited an average R_{solar} higher than 60%, a stark contrast to the value of only 32% for a scale-free skeleton (Fig. 1D and Fig. S3). Notably, the scale covering contributed more than 40% to the reflection within the visible (VIS) range (i.e., 0.38-0.75 μm), responsible for the beetle's brilliant whiteness. The exceptional visual whiteness of such a thin structure exhibits potential for the development of efficient R_{solar} in daytime PRC applications.

In the plastic, ink and paint industries, products are often rendered white by incorporating pigments with high refractive index values into polymers. Similarly, the whiteness of Cyphochilus beetle scales can be attributed to a scattering system comprising a chitin filament network and a complementary interconnected structure of air pockets. To better understand the whiteness of scales, we modeled the Mie scattering behavior of chitin filament based on Maxwell's equations (Fig. S4). Considering a refractive index value of 1.56 to simulate chitin (*43*), we calculated the backscattering intensity at four incident wavelengths covering the ultraviolet (UV) to near-infrared (NIR) ranges (Fig. 1E). The results show that chitin filament with a diameter of 0.3 μm strongly scatters light with blue wavelengths, and as the size of chitin filament increases, the peak of the scattering intensity shifts toward red wavelengths (Fig. 1E). Because the Cyphochilus has most of its chitin filament sizing from 0.2 to 0.3 μm, the scale is most efficient in scattering light from 0.5 to 0.7 μm, which results in high opaqueness within the visible range. Additionally, we calculated the ratio of the backscattering intensity to the overall scattering for 500 nm incident light, and found that the beetle's chitin filament dimension is notably coupled with one of the backscattering peaks located at 0.25 μm, confirming that the size of chitin filament is optimized for maximum scattering of visible light to achieve high visual whiteness (Fig. 1F).

High-solar-reflection cooling ceramic

Based on the analysis of the biostructure, we engineered alumina particles through phase inversion and sintering to obtain the cooling ceramic (Fig. 2A and Fig. S5). In detail, a three-component homogeneous solution, composed of polysulfone (PES), n-methyl-2-pyrrolidone (NMP), and α-alumina, was cast on a flat substrate and immersed in ethanol. The phase inversion takes place when the ethanol diffuses into the casting and dissolves with NMP. This process results in a polymer-rich membrane, forming an anisotropic porous network carrying alumina particles. It should be noted that the porous alumina-polymer membrane can be flexible and imprinted with patterns or shaped into any desired form. In a high temperature sintering process, PES starts to combust above 500 °C. Both energy-dispersive spectroscopy (EDS) mapping (Fig. S6A) and thermo-gravimetric analysis (TGA) (Fig. S6B) confirmed the complete removal of PES through the sintering process. Meanwhile, alumina particles were bonded, resulting in the cooling ceramic with a well-preserved porous structure. Manipulating the alumina concentration in the phase inversion precursor solution yielded a short transport mean free path leading to high R_{solar} of the thin cooling ceramic (Fig. S7). The as-obtained cooling ceramic shows intense whiteness under natural light (Fig. 2A). The cooling ceramic shares a similar structure with that of Cyphochilus scales, with a densely packed outer layer and numerous internal voids but with a wider structural dimension distribution (Fig. 2B-C). The cooling ceramic exhibits near-perfect reflection in the UV, VIS and NIR ranges, leading to a R_{solar} value of 99.6%, versus a value of 89.5% for silver, a value of 88.6% for white pigmented polymer, and a value of 76.2% for white commercial tiles (Fig. 2D). For scattering systems containing a certain volume of pores, a multi-dispersed pore system is more favorable for scattering in a broadband way than a mono-dispersed system (Fig. 2E and Fig. S8) (*26*). This explains why hierarchical pores render the cooling ceramic not only white in the VIS range, similar to the appearance of Cyphochilus, but also white in the UV and NIR ranges.

The cooling ceramic is composed solely of porous α-alumina, which possesses ideal intrinsic electromagnetic properties for PRC applications. Among common white and transparent inorganic materials, alumina has the top ranked high bandgap with a relatively high refractive index (Fig. S9). The bandgap of α-alumina reaches 7.0 eV, which is well above the upper boundary for photon energy in the solar spectrum (4.13 eV) (*44, 45*). The high bandgap of α-alumina results in a low extinction coefficient across the solar wavelength range (Fig. S10), and a low absorption of solar photons, which makes the high R_{solar} possible. On the other hand, arising from the vibrational modes of the Al-O chemical bonds, alumina attains a high extinction peak within the AW range (Fig. S10), resulting in a high ε_{AW} of 96.5%. Therefore, the cooling ceramic can efficiently radiate heat through the AW, where peak blackbody emissions from terrestrial surfaces coincide with the high atmospheric transmittance into space. Considering the high R_{solar} and high ε_{AW}, the cooling ceramic can be regarded as a superior PRC material over state-of-the-art counterparts (Fig. S11). The whiteness of the cooling ceramic was achieved in a diffused way, with high angular solar reflection across its full solid angle (Fig. 2F). At the thermal wavelengths, the angular emissivity was also consistent, with only a slight decrease at low zenith angles. We attributed the high ε_{AW} value of the cooling ceramic within the wide angular range (Fig. 2G) to the open, porous surface and the effective medium behavior of the nanopores at high wavelengths (*33*).

The efficient scattering by the hierarchical pore system enables the cooling ceramic to achieve the desired optical performance in a material-saving manner. Cooling ceramic with a thickness of only 150 μm can achieve R_{solar}>95% , while high-performance roof cooling coatings typically require over 1 mm thickness to achieve the same level of optical performance (*46*) (Fig. S12). As the thickness of the cooling ceramic increases, its solar transmittance decreases due to increased backscattering, leading to continuous enhancement of R_{solar}. Eventually, when the thickness of the cooling ceramic reaches 600 µm, its R_{solar} reaches saturation at 99.6% (Fig. S12). On the other hand, the cooling ceramic exhibits low reflection within the AW range at any thickness. Therefore, a thick cooling ceramic can dissipate heat through its own high emissivity, and a thin cooling ceramic does not hinder the radiative dissipation of its substrate, making it favorable for application on substrates with already adequate ε_{AW} values, e.g., concrete.

Cooling performance assessment

We demonstrated the cooling performance of our cooling ceramic by employing a custom-designed thermal setup (*27*) in Hong Kong and compared it to that of commonly used white commercial tiles as a control (R_{solar}=76.2%, ε_{AW}=88.5%) (Fig. 3A, Table S1). Throughout a continuous 84-hour measurement period, the cooling ceramic consistently maintained a temperature below the ambient air temperature with an average sub-ambient temperature difference of 3.8 °C and a maximum sub-ambient temperature difference of 8.8 °C (Fig. 3B and Fig. S13). In contrast, the white commercial tiles only provided cooling during night-time. During the daytime, the cooling ceramic delivered an average sub-ambient temperature reduction of 4.3 °C. Given perfect R_{solar}, the cooling ceramic could achieve >4 °C sub-ambient cooling even around midday (between 11 a.m. and 2 p.m.), leading to a more than 8 °C lower temperature than that of the white commercial tiles. At the same time, another identical setup coupled with a controllable heating system was installed in parallel to measure the cooling power of the samples. To ensure repeatability, we conducted cooling power measurements over four short periods (Fig. 3C). During the two measurements at night, the cooling ceramic generated average cooling power of 142 and 125 W/m^2, versus values of 128 and 117.3 W/m^2 for the white commercial tiles (Fig. 3C). To examine the cooling performance of the cooling ceramic under extreme incoming heat flux conditions, the two daytime measurements were conducted around solar noon with a solar intensity up to 800 W/m^2. Despite the challenging conditions, the cooling ceramic demonstrated exceptional cooling with cooling power of 134.5 and 133.8 W/m^2. In contrast, the white commercial tiles, which strongly absorb solar radiation, failed to generate cooling power. For traditional daytime PRC materials, a higher cooling power can normally be obtained at night while the daytime cooling power is obviously lower than that at night due to solar heat absorption (*22, 35*). As a result of the ideal R_{solar}, the cooling ceramic exhibited comparable or even superior cooling performance during the daytime as compared to that at night, which is highly desired for addressing the high-demand daytime cooling energy demand. It should be noted that Hong Kong is a coastal city with a humid climate, which is very unfavorable for heat dissipation via thermal radiation. The average humidity during the field test was around 50%. Considering a 3,000 atm-cm water column (*47*), the local τ_{AW} during the field test was calculated as less than 0.6 (*48*), which is not ideal for PRC applications (Fig. S1). Although direct comparison to the cooling performance determined in other studies is virtually impossible due to the notable influence of geography and meteorological variances on the local field test results, the high cooling power exceeded 100 W/m^2 under these unfavorable test conditions, strongly indicating that the cooling performance of the engineered cooling ceramic is superior to recent results reported in the literature.

Apart from Hong Kong, we have also validated the cooling performance of the cooling ceramic in different climates. In Yellowstone National Park (U.S.), the cooling ceramic achieved a cooling effect of sub-ambient temperature reduction of 1-7 °C at noon (Fig. 3D). In urban areas, such as Philadelphia (U.S.) and Boston (U.S.), the cooling ceramic also achieved a sub-ambient temperature reduction of about 3 °C (Fig. 3D). For the field test conducted in Beijing, the cooling ceramic showed 3.3 °C sub-ambient temperature reduction around midday (13:30-14:30) with an average solar intensity value of 876 W/m^2, while the white porous polymer cooler (R_{solar}=96.2%, ε_{AW}=96.0%) and white porous alumina-polymer membrane (R_{solar}=97.6%, ε_{AW}=97.2%) only showed 2.4 °C and 2.7 °C sub-ambient temperature reduction, respectively, but the white commercial tile failed to achieve sub-ambient temperature reduction (Fig. S14). These results demonstrate the ability of the cooling ceramic to ensure stable cooling performance in various application environments.

Energy-saving evaluation

External building surfaces are the main recipients of solar radiation and contribute notable heat gains to the indoor environment. The most direct and appealing method to exploit PRC technology would be to use the coolers to cover the building envelope surfaces where the cooler can be directly exposed to the sky to reduce the building thermal load. To investigate the cooling effect in real applications, two identical model houses were constructed (Fig. 4A). One of them was roofed with white cooling ceramic with the other roofed with white commercial tiles purchased from the market as control. The model house roof was designed with 30-degree pitch angles to increase the projection areas for direct solar irradiation. First, we conducted continuous thermal measurement for the two model houses over 4 days. The roof temperature showed large difference in the daytime between the two model houses (Fig. 4B). Especially, the roof with white cooling ceramic could be almost 5 °C cooler than that with the white commercial tiles at noon time (Fig. 4B). As a result of the lower roof temperature, the heat transfer from the roof to the indoor space was reduced, resulting in a lower indoor temperature for the model house fitted with the white cooling ceramic (Fig. 4B). The largest indoor air temperature difference reached 2.5 °C. The thermal load of a building is directly related to the cooling demand for regulating the indoor environment. To intuitively quantify the energy-saving potential of the engineered cooling ceramic, we conducted additional assessments by operating an air-conditioning unit within the model house in summer days (July 2022). We continuously monitored the air-conditioning electricity usage over three periods with set temperatures of 25, 23 and 20 °C. With less heat load, the cooling ceramic-based model house consumed less electricity, with energy savings of 26.8%, 22.6% and 19.6%, respectively, during each set temperature period (Fig. 4C). Moreover, we conducted an energy consumption simulation of a full-scale building with a model of a typical 4-story mid-rise apartment building (Fig. S15, Table S2) to assess the energy saving performance on a worldwide scale by applying the cooling ceramic as the external envelope materials on the walls and roofs (Fig. 4D). Considering the energy usage of HVAC systems, application of the cooling ceramic could benefit tropical regions the most. In particular, the annual energy savings could reach more than 10% (25 GJ, approximately 7,000 kWh) per year for indoor air-conditioning in these extremely hot areas.

Applicability investigation

Beyond cooling, the cooling ceramic could also offer diverse functionalities, bringing it closer to practical applications. The interaction between water and surfaces at high temperatures is a critical yet often overlooked phenomenon in the applications involving evaporating cooling. When a building experiences a fire, the heat generated by combustion could cause extensive damage. To extinguish a fire and lower a building's temperature, it is essential to allow direct contact between the envelope surface and water using evaporative cooling. Most commercial tiles prevent water from wetting the overheated surface over 280 °C (Fig. 5A, Fig. S16, and Movie S1), resulting in poor evaporative cooling due to the Leidenfrost effect (*49, 50*). In contrast, our cooling ceramic exhibits superhydrophilicity enabling immediate droplet spreading, while facilitating rapid impregnation of droplets due to its interconnected porous structure (Fig. S17). Consequently, the cooling ceramic inhibits the Leidenfrost effect at temperatures above 800 °C (Fig. 5A, Movie S1) during the evaporative cooling process. The effective evaporative cooling performance of the cooling ceramic was demonstrated by the rapidly decreasing surface temperature, while only a negligible temperature variation was recorded for the commercial tiles by the infrared camera (Fig. 5B, Movie S2).

The cooling ceramic can also turn from superhydrophilic to hydrophobic by impregnating with organosilicon compounds, which is the most commonly used method to protect porous materials against moisture and fulfill applications requiring water repellence. Upon fluorosilane treatment, the cooling ceramic featured high superhydrophobicity with a water contact angle (CA) of ~150° (Fig. S18). The interconnected porous structure of the cooling ceramic enabled the fluorosilane solution to penetrate the material, resulting in water resistance on both the surfaces and interior (Fig. S18). Importantly, this treatment does not affect the high-temperature evaporative cooling performance of the cooling ceramic because the fluoro-silane chemical groups start to evaporate at a temperature over 250 °C (Fig. S19). For the optical performance of the fluorosilane-treated cooling ceramic, its solar reflectivity slightly dropped to around 99.0% due to the absorption of bonded fluoro-silane chemical groups (Fig. S20). A dust resistance test using standard pollutants (GB/T 97780-2013) confirmed a good anti-pollution performance of the fluorosilane-treated cooling ceramic with solar reflectivity of over 97% maintained after multiple polluting-washing test cycles (Fig. S21).

The cooling ceramic possesses a dense all-inorganic structure that inherently endows it with excellent resistance to UV radiation. The extremely low UV absorption and high bond strength of alumina makes the cooling ceramic less susceptible to photodegradation, compared with polymer-based coolers. For verification, the cooling ceramic was exposed to a UV lamp with a 5 W/m^2 UV power for 3 months. The optical properties measured before and after UV exposure showed negligible differences, confirming the high resistance of the cooling ceramic to UV degradation (Fig. S22). A durability test of the cooling ceramics under a real-world condition was also conducted by exposing them in an outdoor open space for one year, experiencing solar radiation of ~5000 MJ (*51*). The results show that the solar reflectivity of the cooling ceramic only dropped by 1.3%, still reaching 98.3% (Fig. S23). Because alumina is nonflammable, the cooling ceramic can remain intact and undamaged even under extreme fire exposure (Fig. S24). The cooling ceramic also possesses a high mechanical strength with a breaking strength over 100 MPa (bending test according to the ISO 10545-4), which meets the standards for application as building envelope materials (> 35 MPa) (Fig. S25). Furthermore, the cooling ceramic can be recycled (Fig. S26), which is highly desirable for sustainability. When damaged or polluted, the developed cooling ceramic can be ground into raw materials (alumina particles) and then reused in the fabrication of new cooling ceramic with well-preserved optical properties.

The high and broadband sunlight reflection are crucial for cooling, yet completely reflecting all visible light would yield a white cooler, which cannot fulfil the aesthetic need of contemporary urban landscapes. Based upon the white cooling ceramic, we have developed a colored cooling ceramic that attains equilibrium between chromatic presentation and reduction of thermal load. The colored cooling ceramic was simply obtained by sintering a thin layer of colored glaze on top of the white cooling ceramic. We fabricated four colored cooling ceramics: yellow, red, green and black. The color of the cooling ceramic was controlled to match that of commercial tile products purchased from the market (Fig. 5C-D). Both the colored commercial tiles and colored cooling ceramics had high absorption in VIS light for creating vivid color (Fig. 5E, Table S3). As the thin color glaze of the colored cooling ceramic enables NIR light to transmit through and be reflected by the underlying high reflection layer, the colored cooling ceramic attained substantially higher reflection in the NIR spectrum (95% / 96% / 87% / 39% for the yellow / red / green / black ceramics, respectively) than the colored commercial tiles (76% / 57% / 66% / 16% for the yellow / red / green / black tiles, respectively) (Fig. 5E, Table S3). We experimentally verified the thermal performance of the colored ceramics against the colored commercial tiles by exposing the samples under direct sunlight at midday (Fig. 5F). In detail, the red cooling ceramic maintained an average temperature of 4.7 °C lower than that of the commercial red tile, followed by 2.8 / 1.7 / 1.3 °C temperature reductions for the yellow / green / black cooling ceramics (Fig. 5F). The temperature reduction obtained for each color corresponded well to the R_{solar} contrast between the cooling ceramic and commercial tiles. The light absorption in the visible range determines the color intensity, which therefore influences the overall solar reflection. With high NIR reflection, the colored cooling ceramic is also able to achieve R_{solar} over 0.9 by tuning the concentration of color glazing (Fig. S27). These results confirmed that the colored design based on the white cooling ceramic could provide the desired color along with high NIR reflection and showcased the great potential in reducing the thermal load and even sub-ambient cooling. Last, the colored cooling ceramics can be fabricated into curved shapes using the same procedure as for the white cooling ceramics. This makes it a versatile material suitable for a wide range of applications, for example houses with curved roofing tiles (Fig. S28). The ability to shape the material into curved forms allows for more creative and unique designs, adding aesthetic value to different applications.

Conclusion

In summary, we developed an energy-free and robust daytime PRC material in the form of ceramic for reducing the cooling demand of the indoor environment. The cooler features a biomimetic porous structure, which efficiently scatters solar irradiation to achieve a solar reflection of 99.6%. In real-world application demonstrations and whole-building energy simulations, our cooling ceramic demonstrated a promising energy-saving potential. With high weather resistance, high mechanical strength, favorable recyclability, notable Leidenfrost depression and optional color features, the cooling ceramic can readily be applied to different scenarios and outdoor infrastructures on a large scale. With its unique combination of advanced features and demonstrated performance, the technology holds great potential for contributing to the development of more sustainable and energy-efficient building solutions in the future. Although we have not yet explored the cooling power modulation of the cooling ceramic, on the basis of the design of high solar reflection, the cooling ceramic may integrate with optical-adaptive materials to obtain the temperature-response regulation on optical properties, and therefore smartly suppress the cooling effect during cold weather (*52, 53*). On the other hand, to retain a high radiative cooling power with vivid color, we can combine the cooling ceramics with photoluminescent materials (*54*), such as carbon dots, to recover the solar absorption in the visible range.

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Data and materials availability: All data are available in the main text or the Supplementary Materials.

Supplementary materials

Materials and Methods

Supplementary Text
Figs. S1 to S28
Tables S1 to S3
References (*55–68*)
Movies S1 to S2

Fig. 1. Whitest beetle in the world. (**A**) Photograph of the Cyphochilus specimen demonstrating its white appearance. (**B**) SEM image of Cyphochilus scales. (**C**) Cross-sectional SEM image of a Cyphochilus scale. (**D**) Measured solar reflectivity of Cyphochilus exoskeleton surfaces with and without scale covering. (**E**) Simulated backscattered power for incident light of four wavelengths, i.e., 0.3, 0.5, 0.7 and 1.0 µm, as a function of the chitin filament diameter. (**F**) Simulated scattering-center-dimension-dependent variation in the ratio of the backscattered power and the total scattered power for 0.5 µm incident light. The orange shading indicates the size distribution of the chitin filament.

Fig. 2. Engineered hierarchically porous cooling ceramic. (**A**) Photograph of the cooling ceramics with flat and curved shapes. Patterns can also be applied on the cooling ceramic surface. (**B**) SEM images of a fabricated cooling ceramic sample showing the hierarchically porous structure. (**C**) Volume concentration of pores within the cooling ceramic. (**D**) Comparison of the optical properties of the white cooling ceramic with a 600 µm thickness and a 70% porosity to those of white pigmented polymer (Al_2O_3-doped polydimethylsiloxane), silver and white commercial tile. (**E**) Simulated scattering efficiency of porous alumina systems, including three mono-dispersed systems and one multi-dispersed system (the total pore volume concentrations are the same). The multi-dispersed case includes 0.3, 0.5, and 2 $\boldsymbol{\mu m}$ pores with a volume concentration ratio of 1:1:2. (**F**) Angular $\boldsymbol{R_{solar}(\theta)}$ value of the cooling ceramic. (**G**) Angular $\boldsymbol{\varepsilon_{AW}(\theta)}$ value of the white cooling ceramic.

Fig. 3. Cooling performance characterization. (**A**) Experimental setup for characterizing the sub-ambient cooling and cooling power. (**B**) Temperatures of the samples and ambient air, measured in Hong Kong over 84 continuous hours from November 11-14, 2021. (**C**) Cooling power measurements during the four periods, i.e., November 11 20:30-21:00, November 12 12:15-14:25, November 13 13:45-14:45, and November 13 22:15-22:50. (**D**) Temperatures of the samples and ambient air, measured in Philadelphia, Yellowstone National Park, and Boston.

Fig. 4. Application as a building envelope. (**A**) Photograph of the model houses, with the white cooling ceramic and white commercial tile applied on the roof (area: ~1.15 m^2). The model houses were installed 2 meters apart during the experiment to eliminate interference. (**B**) Differences in the roof and indoor air temperatures for the two model houses. (**C**) Electricity usage of the two model houses with air-conditioning set points of 25, 23 and 20 °C. (**D**) Energy-saving performance on a worldwide scale considering the energy consumed by cooling systems, fans and heating equipment.

Fig. 5. Applicability of the cooling ceramic. (**A**) Water droplets contacting the commercial tiles and cooling ceramic at a surface temperature of 600 °C. Regarding the commercial tiles, water cannot directly contact the surface due to the Leidenfrost effect. After spreading due to the impact force, the droplets bounce and return to a spherical shape. In contrast, water on the cooling ceramic is constantly pinned and remains flattened upon spreading, leading to rapid evaporation. Scale bar, 2 mm. (**B**) Variation in the surface temperature when the samples are impacted by water droplets at 5-s intervals. The infrared thermal images show the surface

temperature of the samples after thermal stabilization. Scale bar, 5 cm. (**C**) Photographs of the fabricated colored cooling ceramic, along with colored commercial tiles showing vivid and identical colors. (**D**) Chromaticity of the colored cooling ceramic and colored commercial tiles in the CIE 1931 color space. (**E**) Comparison of the solar reflectivity spectra of yellow, red, green and black cooling ceramics to those of commercialized colored tiles of the same colors. (**F**) Outdoor temperature measurements of the colored cooling ceramics around midday, using colored commercial tiles as a control. The line color corresponds to the sample color.