

RESEARCH ARTICLE

Polymer coating with gradient-dispersed dielectric nanoparticles for enhanced daytime radiative cooling

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Funding information

City University of Hong Kong, Grant/Award Number: 9610434

Abstract

Polymeric coatings with randomly distributed dielectric nanoparticles have attracted intensive attention in the passive daytime radiative cooling application. Here, we propose a modified Monte–Carlo method for investigating the spectral response and cooling performance of polymer coating with gradient-dispersed nanoparticles. Using this method, we carry out a quantitative analysis on the solar reflectance, infrared emittance and cooling power of four categories of gradient structures. It is shown that the gradient profile of particle distribution at the near-surface region has a significant influence on the overall performance of the coatings. Compared to a randomly distributed structure, the downward size-gradient structure exhibits superiority in both solar reflectance and cooling power. The presented gradient design, also applicable to porous structures, provides an effective and universal strategy for significantly improving the cooling performance of radiative cooling coatings.

KEYWORDS

dielectric nanoparticles, gradient structures, Mie scattering, Monte–Carlo simulation, polymeric coating, radiative cooling

1 | INTRODUCTION

Passive daytime radiative cooling as a promising energy conservation strategy has shown great potential for saving the building energy, mitigating the urban heat island effect and combatting global warming.^{1,2} Compared to conventional active refrigeration technologies, it takes advantages of the passive nature of thermal radiation and the transparent atmospheric window (8–13 μm) to dissipate heat from a terrestrial object ($\sim 300\text{ K}$) to the cold universe ($\sim 3\text{ K}$). Anti-intuitive sub-ambient radiative cooling without any energy consumption and green-house gas emission can be achieved even under direct sunlight.^{3,4} To maximize the cooling effect, the radiative cooler should be entitled with high emissivity within the atmospheric

window and high solar reflectance simultaneously. Recently, photonic structures,^{3,5–7} metamaterials,^{8–11} particle dispersed polymeric coatings,^{12–15} and porous structures^{16–21} have been investigated to simultaneously achieve high solar reflectance as well as high infrared radiation. Among these methods, polymeric coatings have shown the best potential for real-world large-scale applications for its low cost, ease in production and excellent long-term durability.²²

Generally, polymeric coatings consist of a polymer matrix and randomly distributed micro/nano dielectric particles as fillers. The high thermal radiation originates mainly from the intrinsic vibrational modes of functional groups/bonds of the polymer matrix and partially from the phonon resonances of filled particles,^{9,23} while the

high solar reflectance of the coatings benefits from the multiple interfacial Mie scattering between the polymer matrix and the filled particles.²⁴ Therefore, materials with a high refractive index and large band gap are preferred for use as fillers to enhance Mie scattering and thus the overall solar reflectance. Various numerical and experimental studies have explored different strategies for optimizing such scattering effect based on changing key parameters such as particle size, volume fraction and coating thickness, for which different fillers (e.g., TiO_2 , BaSO_4 , Al_2O_3 , CaCO_3) have been utilized to scatter the incident sunlight in a random-dispersed and multiple-sized manner.^{6,12–14,25} However, when mixing the nanoparticles and liquid polymer solution, sedimentation always occurs due to the gravity effect and results in the size and density gradients.^{26–28} In other words, a heterogeneous distribution may be formed instead of an ideal homogeneous one during the formation of the polymeric nanocomposite coating. In general, the gradient distribution caused by sedimentation was utilized to separate different species with different mass and sizes.²⁹ Inspired by natural/biological materials, artificial control of gradient structure has been also studied to facilitate functional graded materials with tunable performance, e.g., reinforcement of mechanical properties, thermal properties, electromagnetic properties and optical properties.^{30–35}

In this study, we numerically investigate the optical properties of a polymeric coating from ultra-violet to mid-far infrared regions, as well as its cooling potential, using both density- and size-gradient structures. An effective multilayer Monte-Carlo method is established to solve the radiative transfer equation for the gradient structures, of which the solar reflectance, infrared emittance and net cooling power are investigated. We have observed an obvious impact of gradient distribution on the cooling performance of the coating and the downward size-gradient structure is superior to the randomly distributed one.

2 | MATERIALS AND METHODS

2.1 | Materials and optical constants

Many kinds of polymers, including polydimethylsiloxane (PDMS), polymethyl methacrylate (PMMA), polyvinylidene fluoride (PVDF), polymethyl pentene (TPX), etc., have been used as the polymer matrix that makes the radiative cooler feature low solar absorption and strong thermal emissivity ascribing to the functional groups such as C—O, C—F, C—H, and O—H. In this study, PDMS is chosen as the polymer matrix due to its lower refractive index (~ 1.4 within the solar band) and good infrared

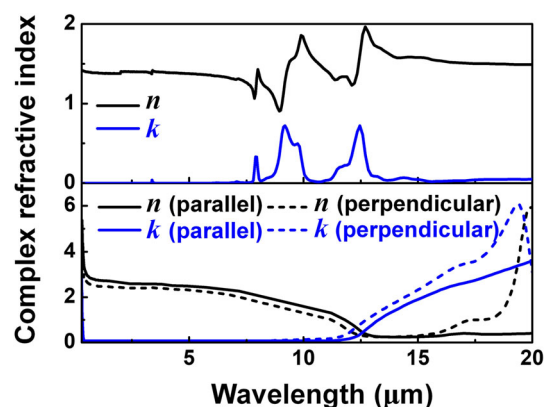


FIGURE 1 Real part (dark) and imaginary part (blue) of complex refractive indices of PDMS (top panel, Adapted with permission from: Copyright 2020, Elsevier³⁷ and Copyright 2020, Optical Society of America³⁸) and TiO_2 (bottom panel, solid line for parallel polarization and dashed line for perpendicular polarization)³⁹

emissivity within the atmospheric window.³⁶ The refractive index and extinction coefficient are shown in the top panel of Figure 1 according to the measurement by Zhang et al.^{37,38}

Nano-sized dielectric fillers can significantly boost the solar reflectivity through Mie scattering; therefore, an appropriate filler should be selected with consideration of its complex refractive index. The real part, refractive index n , should be high enough than the polymer matrix to achieve an excellent scattering efficiency according to Mie theory, while the imaginary part, extinction coefficient k , needs to be as low as possible to diminish the parasitic absorption under illumination. Therefore, dielectric materials with large bandgap (over 6 eV), such as BaSO_4 , Al_2O_3 , and CaCO_3 , are preferred in order to reduce solar absorption. Nevertheless, the refractive indices of these dielectric materials are around 1.6–1.7 over the solar spectrum, which are slightly higher than most polymer matrices. The rutile TiO_2 , however, retains the refractive index over 2.4 within the solar spectrum and are widely used as a commercial coating component, as shown in the bottom panel of Figure 1.³⁹ Hence, we chose TiO_2 as the filler to take full advantage of Mie scattering. Though TiO_2 bears intrinsic UV absorption owing to a bandgap of ~ 3 eV, it can be minimized by a recently proposed Purcell-effect-enhanced-fluorescence method, in which the fluorescent materials compete with TiO_2 in UV absorption that can be converted and re-emitted as visible light.²²

2.2 | Theories and methods

To investigate the spectral solar reflectivity and infrared emissivity, a statistical Monte-Carlo method, in which a

mass number of light paths are traced, rather than finite element method is applied to reduce the computational efforts. The required scattering and absorption properties of both medium and particles will be obtained by Mie theory, and then coupled with the radiative transfer equations (RTE) which will be solved in the Monte–Carlo model.

2.2.1 | Mie theory

For each single particle in the medium, the scattering efficiency, extinction efficiency and asymmetry parameter can be calculated by solving Maxwell equations^{40,41}:

$$Q_{\text{sca}} = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1) (|a_n|^2 + |b_n|^2) \quad (1)$$

$$Q_{\text{ext}} = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1) \text{Re}\{a_n + b_n\} \quad (2)$$

$$g = \frac{4}{Q_{\text{sca}} x^2} \left[\sum_{n=1}^{\infty} \frac{n(n+2)}{n+1} \text{Re}\{a_n a_{n+1}^* + b_n b_{n+1}^*\} + \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} \text{Re}\{a_n b_n^*\} \right] \quad (3)$$

where x is the size parameter defined by the particle size, wavelength and refractive index of polymer matrix, a_n , b_n , a_n^* , and b_n^* are the Mie coefficients and their conjugates. In the Monte–Carlo calculation for a nanoparticle–polymer composite, the uniform distribution leads to a layer of effective medium. The effective properties of the coating can be directly obtained by accumulating all the parameters of fillers.^{12,24} However, the gradient distribution of particles creates a continuous but non-homogenous phase that cannot be regarded as a single layer effective medium. Here, we treat the gradient structure as many thinner sublayers, and every sublayer could be considered as homogeneous. Then the effective scattering and absorption properties of the i th sublayer become:

$$\sigma_{i,\lambda} = \sum \frac{3f_{ij} Q_{\text{sca},j}}{4r_j} \quad (4)$$

$$\kappa_{i,\lambda} = \sum \frac{3f_{ij} Q_{\text{abs},j}}{4r_j} + \frac{4\pi k_{\text{mat}}}{\lambda} \quad (5)$$

where the subscript j represents the j th kind of particle, f_{ij} is the corresponding volume fraction in i th sublayer, r_j is corresponding radius, k_{mat} is the extinction

coefficient of polymer matrix. Since TiO_2 particles shows different complex refractive indices for parallel and perpendicular polarization, here the same amount of TiO_2 particles is assumed for both polarizations in the coating.¹²

2.2.2 | Modified Monte–Carlo method

The spectral reflectance and emittance of the coating can be estimated by solving the quasi-steady form of radiative transfer equation⁴¹:

$$\frac{dI_\lambda}{ds} = \kappa_\lambda I_{b,\lambda} - (\kappa_\lambda + \sigma_\lambda) I_\lambda + \frac{\sigma_\lambda}{4\pi} \int I_\lambda(\hat{s}_i) \Phi_\lambda(\hat{s}_i, \hat{s}) d\Omega' \quad (6)$$

where I_λ and $I_{b,\lambda}$ are the spectral radiative intensities of the coating and a blackbody, s denotes the geometric path of radiative transfer, $\Phi_\lambda(\hat{s}_i, \hat{s})$ is the scattering phase function describing the scattering probability from direction $\hat{s}_i$ to direction $\hat{s}$ of the incoming heat flux at solid angle of $d\Omega'$, κ_λ and σ_λ are the effective properties obtained by Equations (4) and (5).

As mentioned above, Monte–Carlo method was implemented to solve RTE in coatings with random particle distribution and achieved good feasibility for photon transport estimation. However, to evaluate the optical properties of gradient structures, a new calculation method should be developed to quantitatively estimate the spectral responses of the coating considering such inhomogeneity. In addition to the multi-sublayer assumption, the interfacial effect is neglected when the light propagates from one sublayer to another due to their same matrix. The flowchart of modified Monte–Carlo method used for gradient structures is shown in Figure 2. Random numbers (RN) are used in the model to statistically trace the light path. Effective properties of sublayers and scattering features of particles are marked using the layer flag i and particle type flag j , respectively.

2.2.3 | Radiative cooling performance

Two key parameters, net cooling power at ambient temperature P_{net} and sub-ambient temperature difference ΔT at the thermodynamic equilibrium state, were usually deployed to evaluate the cooling performance of the radiative cooler. While for a typical application (e.g., on building envelope), the coatings are always at near or above the ambient temperature due to thermal interaction with surrounding urban environment and indoor heat generation.²³ Hence, here we calculate the net cooling power only for estimating the cooling performance of the gradient structured coating.

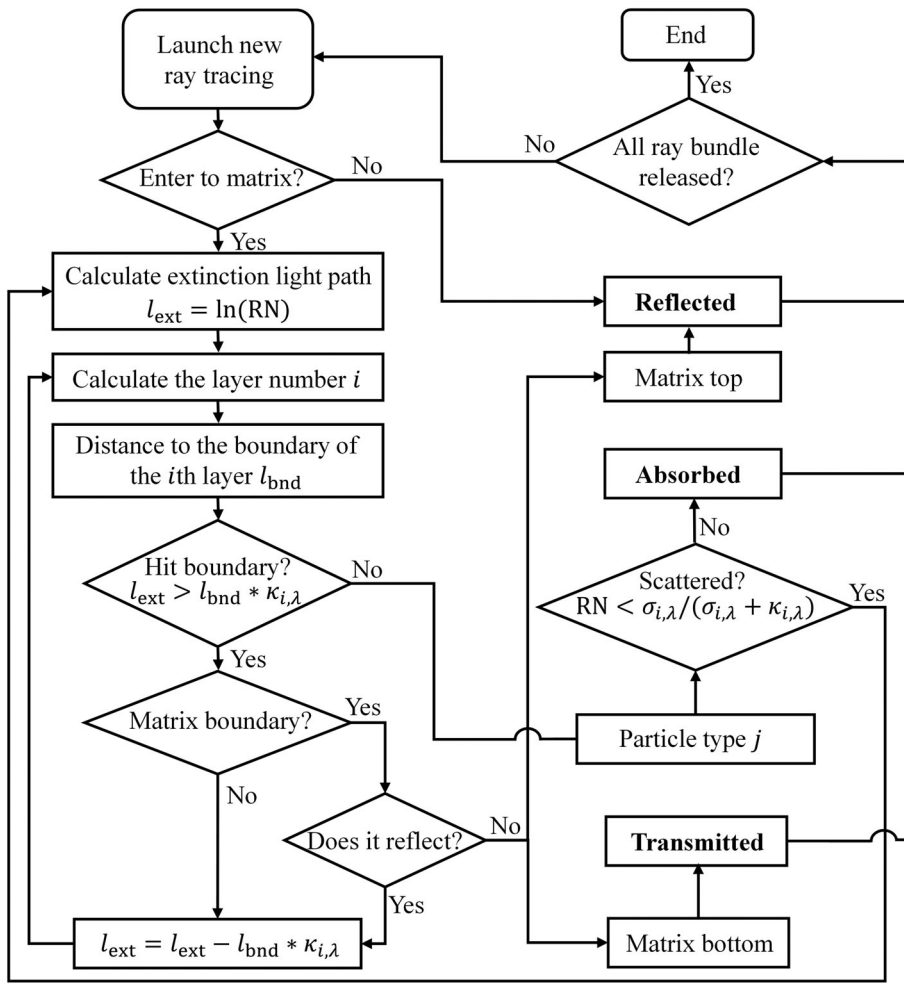


FIGURE 2 Flowchart of the modified Monte-Carlo method for analyzing the spectral response of gradient structures with multi-sublayer and multi-sized particles

Considering all the thermal exchange processes, the net cooling power P_{net} of a radiative cooler at temperature T can be expressed as³:

$$P_{\text{net}}(T) = P_{\text{rad}}(T) - P_{\text{atm}}(T_{\text{amb}}) - P_{\text{sol}} - P_{\text{non-rad}} \quad (7)$$

where P_{rad} is the radiated power by the cooler, P_{atm} , P_{sol} , and $P_{\text{non-rad}}$ are the absorbed power of atmospheric radiation, solar irradiation and non-radiative (conductive and convective) thermal energy, respectively, T_{amb} ($= 300$ K) is the typical temperature of an ambient environment. Each thermal exchange process can be described as:

$$P_{\text{rad}}(T) = 2\pi \int_0^\infty \int_0^{\pi/2} \varepsilon(\lambda, \theta, T) I_{\text{BB}}(T, \lambda) \cos\theta \sin\theta d\theta d\lambda \quad (8)$$

$$P_{\text{atm}}(T_{\text{amb}}) = 2\pi \int_0^\infty \int_0^{\pi/2} \varepsilon(\lambda, \theta, T) \varepsilon_{\text{atm}}(\lambda, \theta) I_{\text{BB}}(T_{\text{atm}}, \lambda) \cos\theta \sin\theta d\theta d\lambda \quad (9)$$

$$P_{\text{sol}} = \cos\theta_{\text{sun}} \int_0^\infty \varepsilon(\lambda, \theta, T) I_{\text{solar}}(\lambda) d\lambda \quad (10)$$

$$P_{\text{non-rad}} = h_{\text{eff}}(T_{\text{amb}} - T) \quad (11)$$

where $\varepsilon(\lambda, \theta, T)$ is the angular spectral emissivity of the cooler, $I_{\text{BB}}(T, \lambda)$ is the spectral radiance of blackbody at temperature T , $\varepsilon_{\text{atm}}(\lambda, \theta)$ is the angular dependent emissivity of the atmosphere that is related to the atmospheric transparency in the zenith direction.⁴² θ_{sun} is the angle between the sun and zenith direction. h_{eff} is the effective coefficient of non-radiative heat transfer. Here, the temperature of the cooler is assumed to be the same as the ambient, thus the non-radiative contribution will be neglected, that is, $P_{\text{non-rad}} = 0$.

3 | RESULTS AND DISCUSSIONS

3.1 | Validation of modified Monte-Carlo method

First, for validating the effectiveness of our developed Monte-Carlo method, the optical properties of random particle distribution coating are calculated under both

methods (i.e., the traditional one and the modified one) for comparison, where the coating is assumed to consist of 100 μm thick PDMS and randomly distributed TiO_2 nanoparticles with a volume fraction of $f = 0.05$ and uniform radius of $r = 200$ nm. The obtained reflectivity at solar range and emissivity at infrared band from both methods matched perfectly each other, as shown in Figure 3, which proves the feasibility of the multi-sublayer assumption and neglecting the interfacial effect. Here, the 100 μm thick coating is divided into 5, 10, and 20 sublayers with the sublayer thickness of 20, 10, and 5 μm for the modified Monte–Carlo method, respectively.

3.2 | Density-gradient and size-gradient structures

In practice, the sedimentation effect may lead to the formation of four gradient distributions of particles, incorporating two types of gradients (i.e., density-gradient and size-gradient) and two directions of gradients (i.e., downward and upward). As shown in Figure 4, downward gradient manifests that the size or volume fraction gradually increases from the top boundary to the bottom boundary of the coating while the upward gradient features the opposite trend. To explore the optical properties and cooling performance of the density-gradient coating, the overall solar reflectance and infrared emittance are calculated using the modified Monte–Carlo method and are shown in Figure 5A,B, where the 300 μm thick PDMS coating is filled with TiO_2 nanoparticles at a uniform radius of $r = 200$ nm. By increasing the volume fractions at the boundaries (f_{top} , at the top boundary and f_{bot} , at the bottom boundary) from 0.01 to 0.3, we can clearly see that both the reflectance and emittance are significantly boosted. Therefore, the best cooling performance can be obtained at the highest volume fraction (i.e., $f_{\text{top}} = f_{\text{bot}} = 0.3$), as shown in Figure 5C. Moreover, it should be noticed that the upward gradient coating outperforms the downward gradient one in the solar reflectance since a higher volume fraction of TiO_2 at the top boundary can scatter the sunlight more efficiently.

Further, the optical and cooling characteristics of size-gradient coating is investigated in Figure 5D–F, where the particle radii at the boundaries (r_{top} at top boundary and r_{bot} at bottom boundary) vary from 100 to 1000 nm. It can be observed that the downward size-gradient coating exhibits a superior solar reflectance compared to its upward size-gradient counterpart. Since the scattering efficiency of TiO_2 nanoparticles approaches the maximum at the radius around 100–200 nm and gradually falls down at larger sizes,²⁵ downward size-gradient coating that has smaller particles at the top always

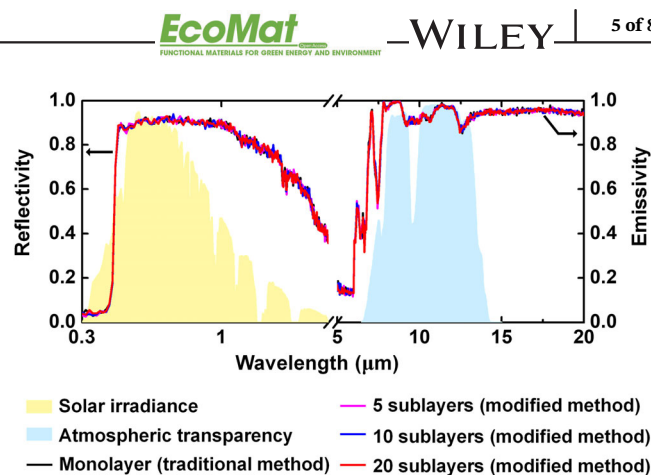


FIGURE 3 Reflectivity (left y axis) and emissivity (right y axis) of 100 μm thick PDMS- TiO_2 coating calculated by both traditional Monte–Carlo method (black line) and the modified one (magenta, blue and red lines for 5, 10, and 20 sublayers, respectively)

scatters the sunlight more efficiently than the upward size-gradient coating except for the case denoted by a red triangle in Figure 5D, in which the particles at the top ($r_{\text{top}} = 100$ nm) has a slightly lower scattering efficiency than the bottom ($r_{\text{bot}} = 200$ nm). Finally, the spectral properties and cooling performance of the coating with random particle distribution are calculated in Figure 5G–I through the traditional Monte–Carlo method for comparison. It can be seen that the solar reflectance manifests a similar reduction with increasing the size of particles. However, we can see obvious differences between the random distribution and upward/downward size-gradient structures. For example, comparing to the downward size-gradient structure, the randomly distributed structure exhibits a larger reduction of solar reflectance and a marginal improvement of infrared emissivity when the size distribution is broadened. An opposite trend is observed between the randomly distributed and upward size-gradient structures.

Detailed comparisons of the spectral properties and cooling performance are demonstrated in Figure 6. It can be observed that at a broad size distribution ($r = 100 - 1000$ nm), the downward size-gradient structure leads to a superior solar reflectivity and considerable infrared emissivity as shown in Figure 6A. The randomly distributed structure exhibits a better infrared emissivity at the wavelength below 6 μm , while the downward size-gradient structure leads to a higher infrared emissivity at the range of 6–9 μm and 13–20 μm . Thus, although the downward size-gradient structure does not perform the best infrared emissivity, its superior solar reflectivity enables an extra cooling power up to $\sim 36 \text{ W/m}^2$ than the randomly distributed structure, as shown in Figure 6B. On the contrary, the upward gradient distribution shows poorer performance for both solar reflectivity and

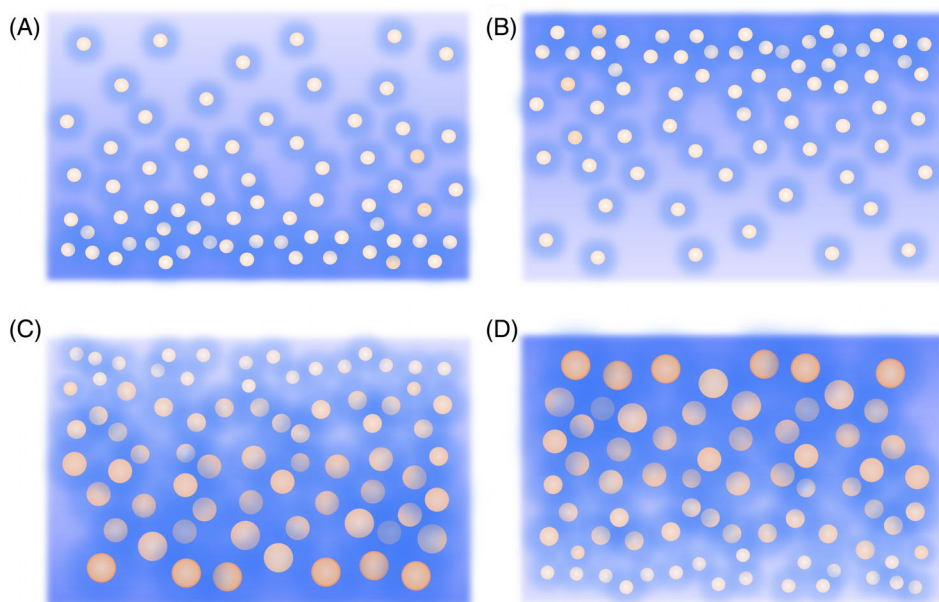


FIGURE 4 Schematics of (A) downward, (B) upward density-gradient structures, and (C) downward, (D) upward size-gradient structures

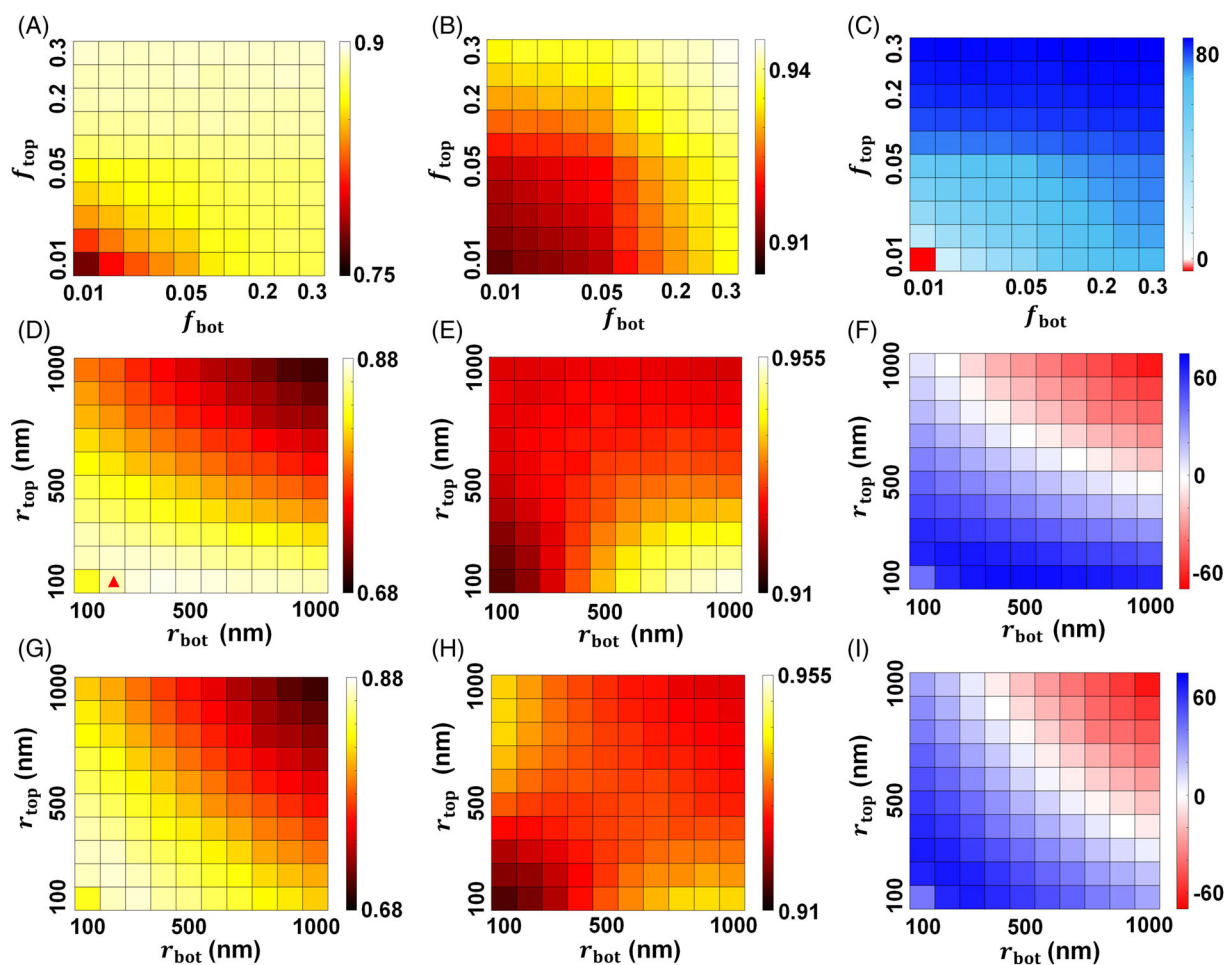


FIGURE 5 (A–C) Calculated solar reflectance (A), infrared emittance (B) and net cooling power (C) of density-gradient structures at ambient temperature. The size of TiO_2 is fixed as $r = 200$ nm. (D–F) Solar reflectance (D), infrared emittance (E) and net cooling power (F) of size-gradient structures at ambient temperature. The volume fraction is fixed as $f = 0.05$. (G–I) Solar reflectance (G), infrared emittance (H) and net cooling power (I) of randomly distributed structures at ambient temperature. The volume fraction is also fixed as $f = 0.05$. The thickness of all the coatings is $300 \mu\text{m}$

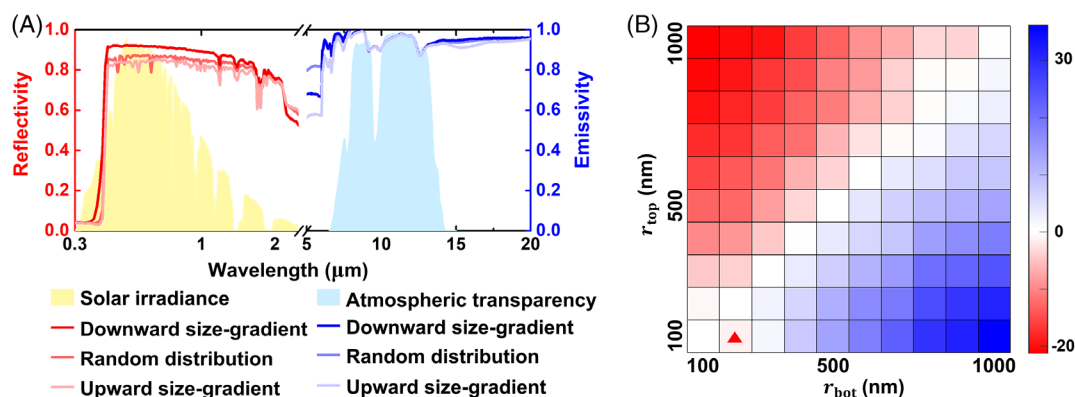


FIGURE 6 (A) Comparison of solar reflectivity (red) and infrared emissivity (blue) among a randomly distributed structure, a downward size-gradient structure and an upward size-gradient structure with the size distribution from 100 to 1000 nm. (B) Difference of net cooling power between size-gradient structures and randomly distributed structures at ambient temperature. The volume fraction of TiO₂ particles in PDMS and the coating thickness are $f = 0.05$ and 300 μm, respectively. The red triangle denotes the exceptional superiority of downward size-gradient structures

infrared emissivity, and thus the cooling power. It should be noticed that there is an exception for cooling power difference in Figure 6B, which corresponds to the reflectance exception in Figure 5D. Based on our calculation results, the downward size gradient, which could be naturally formed during the production of an actual coating, may enable further enhancement of the cooling performance than the random size distribution. Such structure can also be intentionally utilized to configure the coating for better cooling performance in future.

4 | CONCLUSION

Considering the sedimentation effect during curing of polymer coating, we have explored the spectral properties and cooling potentials for gradient structures under two types and two directions of gradients. Traditional Monte-Carlo method is modified through multiple sublayers simplification while ignoring the interfacial effect. A significant impact of gradient distribution on the coating performance is observed. The upward density-gradient and downward size-gradient perform better in all four studied gradient structures because the light interacts with particles at the top of the coating first. Compared to the randomly distributed structure, the downward size-gradient structure leads to an improvement of the cooling power up to ~36 W/m² at a broad size distribution, while upward size-gradient structure behaves the opposite. Therefore, though the sedimentation effect was not considered in previous studies, the construction procedure may produce the size gradient to an extent, resulting in a better cooling performance than the prediction based on the random distribution assumption. The findings arisen from the present theoretical study has

shed light on how to optimize the performance of a radiative cooling coating through introducing gradient-distributed nanoparticles into the polymer matrix.

ACKNOWLEDGMENTS

This work was funded by The City University of Hong Kong (Project No. 9610434).

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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How to cite this article: Fu Y, An Y, Xu Y, Dai J-G, Lei D. Polymer coating with gradient-dispersed dielectric nanoparticles for enhanced daytime radiative cooling. *EcoMat*. 2022;4(2):e12169. doi:10.1002/eom2.12169