Investigation of double-layer coating pigmented with CuO particles of different concentrations on aesthetic and thermal aspects

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Abstract

The pigmented coating with high near-infrared reflectance against solar irradiation is drawing more and more attention in recent years considering both aesthetic and thermal aspects. In this study, a new approach of using double-layer pigmented coating with different volume fractions of CuO submicron particles is proposed to achieve better performance. Comparison of the calculated spectral reflectance of the double-layer coating with the uniformly pigmented coating (single layer) shows that the double-layer coating with a higher volume fraction in the upper layer can significantly reflect the solar irradiation especially in the near-infrared region while maintaining the same color appearance. Furthermore, coatings with different volume fraction distributions, thicknesses, particle diameters, as well as substrate conditions are investigated. The performance may be optimized using a set of carefully designed volume fraction distribution of the double-layer coating, thickness of the coating, particle sizes, over the standard white substrate.

Keywords: double-layer coating; spectral reflectance; optimization parameter

NOMENCLATURE

c_0	propagation speed within vacuum, m/s
d	particle diameter, μm
f_v	volume fraction distribution
g	asymmetry factor
i	imaginary part
I	radiative intensity, $\text{W}/(\text{m}^2 \cdot \text{sr})$
k	extinction coefficient
K	normalization factor
L	thickness of the coating, μm
m	complex refractive index
M	discrete number of the polar angle in $[0, \pi]$
n	refractive index
N	discrete number of elements within the medium
N_T	number density of particles
$Q_{abs,\lambda}$	absorption efficiency factor
$Q_{ext,\lambda}$	extinction efficiency factor
$Q_{sca,\lambda}$	scattering efficiency factor
R_d^s	DRESOR value, $1/\text{m}^3$, or $1/\text{m}^2$
R_{opt}	optimization parameter
$\hat{s}$	directional vector

S	radiative source function, $\text{W}/(\text{m}^2 \cdot \text{sr})$
x, y, z	normalized color coordinate
$\bar{x}, \bar{y}, \bar{z}$	color-matching function
Y	brightness of the coating

Greek letters

β_λ	spectral extinction coefficient, $1/\text{m}$
θ	scattering angle
κ_λ	spectral absorption coefficient, $1/\text{m}$
ρ	spectral reflectivity
σ_λ	spectral scattering coefficient, $1/\text{m}$
Φ_λ	scattering phase function
ω	scattering albedo

Subscripts

0	left surface
i_1, i_2	element i_1, i_2
$N+1$	right surface
w	surface or wall

1. Introduction

The solar energy that reaches the surface of the earth is in the wavelength range from 300 nm to 2500 nm, which is divided into three regions: the ultraviolet region, visible region and near infrared region, accounting for 5%, 43% and 52% of the solar irradiance spectrum (air mass = 1.5), respectively [1-5]. The buildings, vehicles and other man-made objects on the earth are exposed to the sunlight in the daytime. Due to the massive decrease in urban green area and the excessive absorption of solar radiation by buildings and roads, the urban heat island effect drives the temperature of city center 3 to 5 °C higher than surrounding areas [6, 7]. This absorption increases the interior temperature and necessitates a large cooling load for air conditioning.

One of the most effective approaches to deal with these problems is to develop the cool pigmented coatings. Baneshi et al. [8-11] investigated the performance of titanium dioxide (TiO_2) used as the pigment to maximize the reflectivity of the near-infrared (NIR) region to reduce thermal heating and minimize the visible (VIS) reflected energy received by human eyes for aesthetic appeal. George et al. [12] found that $\text{La}_2\text{Mo}_2\text{O}_9$ was thermally and chemically stable when used as a white inorganic pigment. Johnson et al. [13] optimized the grain size distribution of zinc oxide (ZnO) pigment in a thermal control coating (TCC) to maximize diffuse solar reflectance at a thin coating thickness and reduce the pigment volume concentration. However, white solar reflective coatings are not always popular because they make people's eyes uncomfortable for their high reflected glare [14, 15] and also lack the aesthetics compared with darker colored coatings [16-19]. In addition, white coatings are prone to contamination that attenuates their solar reflectance [20].

Therefore, non-white pigmented coating is one of the most promising preferred

choices for roofs and exterior walls of buildings. Several relevant studies recently have been carried out by some investigators. The Fe^{3+} doped $\text{La}_2\text{Mo}_2\text{O}_7$ pigments with cubic fluorite structure were synthesized by acrylamide gel technique, which displayed yellow in color with high NIR reflectance [21]. The method to create colorful cool gray coatings with exceptional solar reflectance was studied by mixing pigments of complementary colors and white [22]. A series of NIR reflective inorganic pigments with the general formula $\text{LaFe}_{1-x}\text{Al}_x\text{O}_3$ [23] and $\text{Zn}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ [24] having an orthorhombic crystal structure and displaying a wide range of colors had been synthesized by a Sol-Gel method. The cooling effect and the energy savings potential of black coatings with different black pigments were estimated. Furthermore, the cost and practicality of the black coatings separately pigmented with chromite iron nickel black, manganese ferrite black spinel, perylene black and dioxazine purple were analyzed [25]. The performance of copper-dioxide (CuO)-pigmented coating with dark appearance was studied both numerically and experimentally [26, 27]. In all these studies, however, the particles are assumed to be uniformly distributed in the resin medium. The effect of volume fraction distributions of submicron particles on the spectral reflectance and the use of different layers with different volume fractions have not been extensive studied.

In this study, double-layer pigmented coating with different volume fraction distributions of CuO submicron particles is proposed and numerically analyzed. Performance improvement is demonstrated by maximizing the NIR reflectance and minimizing the VIS reflectance. The DRESOR (Distribution of Ratios of Energy Scattered by the medium Or Reflected by the boundary surface) method [28-32] which is based on the ray-tracing technology is extended to numerically calculate the radiative properties of the double-layer coating systems. The radiative properties of

single CuO particles in a wide range of wavelength and particle size in a non-absorbing resin are calculated based on the Mie theory [33]. The use of the DRESOR method to solve the Radiative Transfer Equation (RTE) for pigmented coatings is validated by comparison to the previously published results. The influences of different volume fraction distribution of particles, thickness of the coating, particle diameters and substrate conditions on the spectral reflectance are investigated.

2. Methodology

2.1. Radiative properties of single particle

The scattering and absorption of radiation by a single homogeneous spherical particle in a non-absorbing matrix can be obtained by solving the Maxwell's equations, which depend on the incident wavelength λ , particle diameter d , and the complex refractive index of the particle $m = n - ik$.

The spectral distribution of complex refractive index of CuO particle in the range of 0.3 - 2.5 μm [34] is shown in Fig. 1. The extinction coefficient k , decreases rapidly from 0.3 μm to 0.8 μm , and then almost keeps unchanged until 2.5 μm . Using the spectral complex refractive index, the radiative properties of the particle, such as the extinction efficiency factor $Q_{ext,\lambda}$, the scattering efficient factor $Q_{sca,\lambda}$, and the absorption efficient factor $Q_{abs,\lambda}$, can be calculated [33]. The host medium is assumed to be non-absorbing with a refractive index equal to 1.5. The ray will be scattered from its original direction when it travels in the coating. In order to deal with the anisotropic scattering problems, the anisotropic phase function obtained by the Mie theory is also considered.

As discussed in Refs. [8, 33], independent scattering is a good assumption for nearly all heat transfer applications including paints and pigments. Several researches

[26, 27, 35] have shown that independent scattering assumption gives reasonable results for volume fractions less than 5%. Besides, when the volume fraction exceeds 5%, particles will coagulate, as discussed in Ref. [26]. So we consider independent scattering assumption in all our cases. For a group of monodispersed particles, the scattering and absorption coefficients can be calculated using the following equations [26]:

$$\sigma_{\lambda} = N_T \frac{\pi d^2}{4} Q_{sca, \lambda}, \quad (1)$$

$$\kappa_{\lambda} = N_T \frac{\pi d^2}{4} Q_{abs, \lambda}, \quad (2)$$

$$f_{v, cal} = N_T \left(\frac{\pi d^3}{6} \right), \quad (3)$$

where $Q_{sca, \lambda}$ and $Q_{abs, \lambda}$ are the scattering and absorption efficiencies, respectively, d is the particle diameter, $f_{v, cal}$ is the particle volume fraction and N_T is the number density of particles.

2.2. Solving the RTE by the DRESOR method

The schematic of solar radiation incident on a one-dimensional double-layer pigmented coating with different volume fraction distribution of submicron particles is shown in Fig. 2. In this study, the participating particles are assumed to be monodispersed. The elements 0 and $N+1$ act as the boundary elements and collimated solar irradiation [36] incident onto the coating from element 0 is assumed. The refractive index of element 0 is unity. Between elements 0 and 1, the specular reflection is calculated with Fresnel's equation at interfaces [37, 38]. The substrate represented by element $N+1$ is black or white.

In order to analyze the radiative transfer in the pigmented coating, we treat the

coating as a participating medium in a one-dimensional plane parallel system. The radiative transfer equation describing the intensity at position z , direction $\hat{s}$ and wavelength λ within a fixed refractive index can be written as [33]:

$$\frac{dI(z, \hat{s}, \lambda)}{ds} = -\beta_\lambda I(z, \hat{s}, \lambda) + \frac{\sigma_\lambda}{4\pi} \int_{4\pi} I(z, \hat{s}_i, \lambda) \Phi_\lambda(\hat{s}_i, \hat{s}) d\Omega_i, \quad (4)$$

where I is the radiative intensity, $\beta_\lambda = \kappa_\lambda + \sigma_\lambda$ is the extinction coefficient and Φ_λ is the phase function. Integration of Eq. (4) leads to,

$$\frac{I(z, \hat{s}, \lambda)}{n^2} = \frac{1}{n_{z_w}^2} I(z_w, \hat{s}_w, \lambda) \exp\left(-\int_0^s \beta_\lambda ds'\right) + \int_0^s S(z', \hat{s}', \lambda) \exp\left(-\int_{s'}^s \beta_\lambda ds''\right) \beta_\lambda ds'. \quad (5)$$

The first term of the right hand side indicates the contribution of the boundary intensity, the second term denotes the indirect scattering contribution of the medium. S is the source term and can be given as:

$$\begin{aligned} S(z', \hat{s}', \lambda) &= \frac{\omega}{4\pi} \left[\int_{4\pi} I(z', \hat{s}_i, \lambda) \Phi_\lambda(\hat{s}_i, \hat{s}') d\Omega_i \right. \\ &= \frac{1}{4\pi\beta_\lambda} \int_w \frac{1}{n_{z'}^2} \pi I(z_w, \hat{s}_w, \lambda) R_d^s(z_w, z', \hat{s}', \lambda) dA. \end{aligned} \quad (6)$$

Submitting Eq. (6) into Eq. (5), the formula for the radiative intensity at the wavelength λ can be obtained by the DRESOR method [30-32]:

$$\begin{aligned} \frac{I(z, \hat{s}, \lambda)}{n^2} &= \left[\frac{1}{n_{z_w}^2} I(z'_w, \hat{s}_w, \lambda) + \frac{1}{\pi} \int_w \frac{1}{n_{z_w}^2} \pi I(z'_w, \hat{s}_w, \lambda) R_d^s(z'_w, z_w, \hat{s}, \lambda) dA \right] \exp\left(-\int_0^s \beta_\lambda ds'\right) \\ &+ \int_0^s \frac{1}{4\pi\beta_\lambda} \left[\int_w \frac{1}{n_{z'}^2} \times \pi I(z'_w, \hat{s}_w, \lambda) R_d^s(z_w, z', \hat{s}', \lambda) dA \right] \exp\left(-\int_0^s \beta_\lambda ds''\right) \beta_\lambda ds', \end{aligned} \quad (7)$$

where the DRESOR values $R_d^s(z'_w, z_w, \hat{s}, \lambda)$ denote the ratios of energy emitted by the surface element z'_w and reflected by surface element z_w towards direction $\hat{s}$ at wavelength λ . The DRESOR values $R_d^s(z_w, z', \hat{s}', \lambda)$ represent similar meanings except that z' denotes element in the medium. It should be noted that the DRESOR values

$R_d^s(z'_w, z_w, \hat{s}, \lambda)$ have unit of $1/\text{m}^2$ while those of $R_d^s(z_w, z', \hat{s}', \lambda)$ have unit of $1/\text{m}^3$.

The calculation of these values will be discussed in the following section.

As for the schematic presented in Fig. 2, solar irradiation emits from the top surface into the coating and the volume fraction of submicron particles keeps stable in the whole coating during the calculation. The detailed process to discretize grids and directions can be found in previous work by Wang et al. [39]. After the discretization, the volume fraction of the particles in an arbitrary position z is $f_v(z)$ (for instance, $f_{v1}(z) = 3\%$ ($0 \leq z < 0.5L$), $f_{v2}(z) = 1\%$ ($0.5L \leq z \leq L$))

The intensity at an element i_1 , direction θ_{i_1} and wavelength λ , $I(i_1, \theta_{i_1}, \lambda)$, can be obtained by discretizing Eq. (7):

$$\begin{aligned} \frac{I(i_1, \theta_{i_1}, \lambda)}{n^2} = & \left[\frac{1}{n_0^2} I(0, \theta_0, \lambda) + \frac{1}{\pi} \left(\frac{1}{n_{N+1}^2} \pi I(0, \theta'_0, \lambda) \times R_d^s(0, N+1, \theta', \lambda) \right) \right] \exp(-\tau_{0 \rightarrow i_1}) + \\ & \frac{1}{4\pi\beta_\lambda} \sum_{i_2}^{\text{along the path}} \left[\frac{1}{n^2} \pi I(0, \theta''_0, \lambda) \times R_d^s(0, i_2, \theta_{i_2}, \lambda) \right] \left| \exp(-\tau_{i_2-1 \rightarrow i_1}) - \exp(-\tau_{i_2 \rightarrow i_1}) \right|. \end{aligned} \quad (8)$$

In applying the DRESOR method for solving the RTE, the DRESOR values, such as $R_d^s(z'_w, z_w, \hat{s}, \lambda)$ and $R_d^s(z_w, z', \hat{s}', \lambda)$, are very crucial. The DRESOR values are obtained by ray tracing based on the Monte Carlo method (MCM). All the initial DRESOR values are set as zero in the beginning. We trace the energy rays incident on the boundary surface. Once the ray passes through one element, the ratios of energy scattered by this element to all directions can be calculated and recorded as the DRESOR values. The transmitting direction and propagating distance will be reconfirmed based on the principle of the DRESOR method [40]. The propagation process will continue until the residual energy of this calculated ray decreases to a minimum value or it leaves the medium from the boundaries. After all the energy rays

are traced, all the DRESOR values will be obtained. A DRESOR value R_d^s can be renewed when an updating value ΔR_d^s is obtained, which can be described as

$$R_{d,new}^s = R_{d,old}^s + \Delta R_d^s. \quad (9)$$

As for a unit area z_w , the updating for $R_d^s(z'_w, z_w, \hat{s}, \lambda)$, reflected by the boundary surface, can be calculated as

$$\Delta R_d^s(z'_w, z_w, \hat{s}, \lambda) = C_0 \frac{E_0}{N_0} \rho(z_w, \hat{s}', \hat{s}), \quad (10)$$

where C_0 is the compensating factor, E_0 is the original energy of each ray, N_0 is the total number of rays traced and ρ is the surface reflectivity.

As for a unit volume z' , the updating for $R_d^s(z_w, z', \hat{s}', \lambda)$, scattered by the medium, can be calculated as

$$\Delta R_d^s(z'_w, z', \hat{s}, \lambda) = C_0 \frac{E_0}{N_0} \left\{ 1 - \omega(z') \exp(-|\Delta \tau(z')|) \right\} \Phi_\lambda(\hat{s}', \hat{s}), \quad (11)$$

where $\omega(z')$ is the scattering albedo at position z' and $\Delta \tau(z')$ is the optical distance around position z' . Details of calculating $\Delta \tau(z')$ can be found in our previous work [39].

2.3 Definition of the optimization parameter and color evaluation

Two parameters ρ_{TSR} and ρ_{VIS} [26] are proposed to evaluate the reflectivity of pigmented coating for solar reflectance in the solar spectrum region and the esthetic performance of a pigmented coating by considering spectral eye sensitivity, respectively. The optimization parameter R_{opt} can be calculated as follows:

$$R_{\text{opt}} = \frac{\rho_{\text{TSR}}}{\rho_{\text{VIS}}} = \frac{\int_{0.30}^{2.50} \rho(\lambda) I(\lambda) d\lambda}{\int_{0.38}^{0.78} \rho(\lambda) \bar{y}(\lambda) I(\lambda) d\lambda} \bigg/ \frac{\int_{0.30}^{2.50} I(\lambda) d\lambda}{\int_{0.38}^{0.78} I(\lambda) d\lambda}, \quad (12)$$

where $I(\lambda)$ is the solar irradiation and $\rho(\lambda)$ is the spectral reflectance of the pigmented coating. To achieve an optimized coating, the parameter R_{opt} should be maximized.

For color characterization, we conducted a color analysis according to the International Commission on Illumination (CIE) system, which consists of a luminance parameter Y and two color coordinates x and y . The coordinates specify a point on the chromaticity diagram. Denoting the color-matching function for the three CIE 1964 primaries (X , Y and Z) by $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, and $\bar{z}(\lambda)$, respectively, we can compute the CIE tristimulus values for any given spectral distribution of reflectivity $\rho(\lambda)$. The detailed calculations of parameter Y and the coordinates can be found in the work [8-11].

3. Results and discussion

3.1. Validation of the DRESOR method

The validation is carried out first for the DRESOR method to deal with radiation transfer problem in the coating. In this case, two different diameters of particles, d , are chosen to be $0.093 \mu\text{m}$ and $0.778 \mu\text{m}$, respectively. The volume fraction is $f_v(z) = 1\%$, the thickness of the coating is $L = 100 \mu\text{m}$ and the substrate is black. The results of the spectral reflectance obtained by the DRESOR method are compared with those of Baneshi et al [8, 9] using the radiation element method by ray emission model (REM²) as shown in Fig. 3, which verifies that the effectiveness and accuracy of the DRESOR method in dealing with the coating problem.

3.2. Non-uniform and uniform volume fraction distributions

In this section, the spectral reflectance of double-layer pigmented coating with non-uniform volume fraction distribution of CuO particles is investigated and the results are compared with those of uniform volume fraction distribution, as well as graded volume fraction distribution, as depicted in Fig. 4. The cases with graded volume fraction distributions of $f_v(z) = 4\% - 3\% \times (z/L)$ and $f_v(z) = 1\% + 3\% \times (z/L)$, and double-layer volume fraction distributions of $f_{v1}(z) = 4\%$ ($0 \leq z < 0.5L$), $f_{v2}(z) = 1\%$ ($0.5L \leq z \leq L$) and $f_{v1}(z) = 1\%$ ($0 \leq z < 0.5L$), $f_{v2}(z) = 4\%$ ($0.5L \leq z \leq L$), and uniform volume fraction distribution of $f_v(z) = 2.5\%$ are taken as case 1.1, case 1.2 case 1.3, case 1.4 and case 1.5, respectively. The particle diameter is $d = 0.50 \mu\text{m}$, the thickness of the coating is $L = 50 \mu\text{m}$, and the substrate is black. The spectral reflectance of coating is calculated by the DRESOR method. It should be stated that although the volume fraction of CuO particles in the five cases distributes very differently in the resin, however, the total number density of particles are equivalent, which can be analyzed by Eq. (3).

As can be seen from Fig. 4, the five cases have almost the same reflectance in the VIS region. However, the NIR reflectance of the graded volume fraction distribution for case 1.1 as well as the double-layer one for case 1.3 is much higher than that of the uniform one for case 1.5. It demonstrates that the volume fraction distribution of the particles in the host medium have a great influence on the spectral reflectance. The optimized parameter R_{opt} is 17.11, 14.43, 17.24, 13.30 and 16.44 for case 1.1, case 1.2 case 1.3, case 1.4 and case 1.5, respectively, as shown in Table 1. In detail, the NIR reflectance of the double-layer volume fraction distribution of case 1.3 with 4% in the upper layer and 1% in the lower layer is higher than that of case 1.4 with the inversed

volume fraction distribution. Similarly, case 1.1 with the graded volume fraction linearly varying from 4% in the upper layer to 1% in the bottom layer also has a higher NIR reflectance than that of case 1.2 with the volume fraction inversely linearly varying from 1% in the upper layer to 4% in the bottom layer. The reason lies in that when the sunlight incidents onto the media, coating with higher volume fraction of particles in the upper layer shown in Fig. 2 will scatter more energy rays in all directions and less rays will travel forward and arrive at the black substrate being absorbed, resulting in making a greater contribution to the spectral reflectance. A similar explanation is also valid for the phenomena that appear in cases 1.1 and 1.2. Since the graded cases are difficult to put into practice and the double-layer one performs better than the graded one, the double-layer cases will be investigated in the following sections. And the brightness Y is 4.48% and 4.46% for double-layer cases 1.3 and 1.4 respectively, which means that the coating will keep black-color appearance with double-layer coating of CuO particles. In order to maximize the optimization parameter R_{opt} , the double-layer coating with a higher volume fraction distribution in the upper layer of CuO particles is studied.

3.3. The effect of double-layer coating with different volume fraction distributions

The volume fraction distributions of $f_{v1}(z) = 4\%$ ($0 \leq z < 0.5L$), $f_{v2}(z) = 1\%$ ($0.5L \leq z \leq L$), $f_{v1}(z) = 4.5\%$ ($0 \leq z < 0.5L$), $f_{v2}(z) = 0.5\%$ ($0.5L \leq z \leq L$) and $f_{v1}(z) = 3.5\%$ ($0 \leq z < 0.5L$), $f_{v2}(z) = 1.5\%$ ($0.5L \leq z \leq L$) are taken as case 2.1, case 2.2 and case 2.3, respectively. The particle diameter is $d = 0.50 \mu\text{m}$, the thickness of the coating is $L = 50 \mu\text{m}$ and the substrate is black. As shown in Fig. 5, the three cases also have a similar VIS reflectance. However, in the NIR region the spectral reflectance varies. The larger discrepancy of the volume fraction distribution of particles between the

upper and lower coatings is, the higher NIR reflectance will be. The double-layer coating with a higher volume fraction of particles in the upper space will reflect more rays and less energy will arrive at the substrate being absorbed compared with other cases. The optimization parameter R_{opt} , brightness Y , and a chromaticity coordinate (x, y) of the three cases are also tabulated in Table 1. It can be seen from the table that the optimization parameter R increases as the gradient of the volume fraction gets larger. However, the brightness Y and the chromaticity coordinate (x, y) of these cases show little difference. The coordinate (x, y) of these points are shown on the chromaticity diagrams of Fig. 6. The color coordinates for these CuO pigmented coatings are in white area and the similar phenomenon can be found in the following cases. The brightness Y for these cases is around 4.48% while the brightness of optimized CuO pigmented coating is about 5.67% [26]. It means that the proposed pigmented coating shows a darker gray color and may be more pleasant to the human eyes. In the following discussions, the volume fraction distribution $f_{v1}(z) = 4.5\%$ ($0 \leq z < 0.5L$), $f_{v2}(z) = 0.5\%$ ($0.5L \leq z \leq L$) is taken into account.

3.4. The effect of different coating thicknesses

In this section, the effect of thickness of the coating is studied. The thickness of coating $L = 10 \mu\text{m}$, $20 \mu\text{m}$, $50 \mu\text{m}$, $80 \mu\text{m}$ and $100 \mu\text{m}$ are chosen as case 3.1, case 3.2, case 3.3, case 3.4 and case 3.5, respectively. The particle diameter is $d = 0.50 \mu\text{m}$, the double-layer volume fraction distribution of CuO particles is $f_{v1}(z) = 4.5\%$ ($0 \leq z < 0.5L$), $f_{v2}(z) = 0.5\%$ ($0.5L \leq z \leq L$), and the substrate is black. In the VIS region, the spectral reflectance of the five cases experiences a similar trend. Nevertheless, the spectral reflectance in the NIR region is very different from each other. When a significant amount of light is transmitted within the coating, much more energy will be

scattered by the particles within the media with the increase of the thickness of the coating, resulting in a larger spectral reflectance. When the thickness of the coating further increases, the energy forward scattered by the medium also increases, which eventually arrives at the black substrate, bringing about the decrease of spectral reflectance at some wavelengths. The optimization parameter R_{opt} , brightness Y , and a chromaticity coordinate (x, y) of the five cases are also shown in Table 1. It can be seen that case 3.3 has the largest R_{opt} among these cases, so the thickness of the coating which is around $50 \mu\text{m}$ may be a better choice.

3.5. The effect of different particle diameters

The particle diameter of CuO with $d = 0.30 \mu\text{m}$, $0.50 \mu\text{m}$, $0.65 \mu\text{m}$, $0.89 \mu\text{m}$ and $2.0 \mu\text{m}$ is taken as case 4.1, case 4.2, case 4.3, case 4.4 and case 4.5, respectively. The thickness of the coating is $L = 50 \mu\text{m}$, the double-layer volume fraction distribution is $f_{v1}(z) = 4.5\%$ ($0 \leq z < 0.5L$), $f_{v2}(z) = 0.5\%$ ($0.5L \leq z \leq L$), and the substrate is black. The spectral reflectance of the five cases shows different variations over the whole wavelength range. The values of optimization parameter R_{opt} , two color coordinates x and y and luminance parameter Y of CuO pigmented coatings with different diameter particles are also listed in Table 1. The particle diameter does have a great effect on the radiative properties of the particles as discussed in Refs [8, 9]. As a result, the radiative transfer in the coating will be greatly affected. When the particle diameter becomes larger, the optimization parameter R_{opt} does not always monotonically increase. There exists an optimizing value of particle diameter for the spectral reflectance under the double-layer coatings. And among the calculated cases, the particle diameter $d = 0.50 \mu\text{m}$ is the best choice. In addition, with the increase of the particle diameter, the brightness Y decreases. Figure 9 presents the absorption efficiency, the scattering

efficiency and the asymmetry parameter of different particle diameters, which are obtained using a program [33] based on the Mie theory. As seen in Fig. 9(c), the asymmetry parameter g is positive in the wavelength range of 0.3 - 2.5 μm , which means that the CuO coating is a forward-scattering medium against solar irradiation for all cases. As shown in Fig. 9(a), the absorption efficiencies of the five cases within the range of 0.3 - 1.0 μm are obviously larger than those within the range of 1.0 - 2.5 μm , so the energy will be greatly absorbed in the range of 0.3 - 1.0 μm , which makes the spectral reflectance much lower than that in the wavelength range of 1.0 - 2.5 μm as shown in Fig. 8. Besides, the scattering efficiencies of these cases show great discrepancies so that the spectral reflectance varies from each other. It should be noted that the radiative properties of the case $d=2.0 \mu\text{m}$ fluctuate seriously along the solar spectrum among the listed cases. For large sphere, there is diffraction of radiation passing near the particles. The diffracted intensity fluctuates along the particle surface [41], thus, making the scattering efficiency fluctuates as shown in Fig. 9(b). The phase function for diffraction from large particles varies along with the surface [41], making the asymmetry factor g which is related to the phase function fluctuates as shown in Fig. 9(c). The extinction efficiency converges to its asymptotic value of 2 by obeying Babinet's principle [42]. As can be seen in Figs. 9(a) and (b), the radiative properties of the case $d=2\mu\text{m}$, especially the scattering efficiency, fluctuate seriously around 2.0 among the solar spectrum. Thus, the spectral reflectance of case 4.5 also fluctuates owing to the radiative properties as discussed in the Methodology part.

3.6. The effect of substrate conditions

The substrate plays a very important role in radiative heat transfer analysis. In this section, the bottom surface conditions of black substrate, diffuse reflection with

reflectivity $\rho = 0.5, 0.7$ and 1.0 are taken as case 5.1, case 5.2, case 5.3 and case 5.4, respectively. The particle diameter d is $0.50 \mu\text{m}$, the double-layer volume fraction distribution of CuO particle is $f_{v1}(z) = 4.5\%$ ($0 \leq z < 0.5L$), $f_{v2}(z) = 0.5\%$ ($0.5L \leq z \leq L$) and the thickness of the coating is $L = 50 \mu\text{m}$. The effect of different substrate conditions on the spectral reflectance is shown in Fig. 10. The spectral reflectance of the four cases is independent of the reflectance of substrate in the spectrum range of $0.3 - 1.0 \mu\text{m}$ due to high absorptivity of the coating in these regions. Similar phenomena can be found in Figs. 4, 5 and 7. However, when the wavelength is beyond $1.12 \mu\text{m}$, the spectral reflectance differs from each other. The higher reflectivity of the substrate is, the larger spectral reflectance will be within the concerned wavelengths. With a larger reflectivity of the substrate, the ratios of energy reflected by the substrate will increase and thus make more contributions to the spectral reflectance. Particularly, the NIR reflectance of the coating on the standard white substrate is higher than those of the others. The results of R_{opt} with different substrates are listed in Table 1. There is no doubt that case 5.4 shows the biggest R_{opt} . In order to maximize the optimization parameter R_{opt} , the standard white substrate is recommended, but this requirement is not always met in the practical application.

4. Conclusions

Double-layer pigmented coating with different volume fractions of CuO submicron particles is proposed to increase the spectral reflectance while maintaining the aesthetic appearance. The spectral reflectance of the coatings among the uniform, graded and double-layer particle distributions is numerically investigated and compared. Meanwhile, the effects of double-layer coating with different volume fraction distributions, coating thicknesses, particle diameters as well as substrate

properties are examined. The main conclusions drawn from this study are given in the following.

- (1) The pigmented coating with double-layer volume fraction distribution of CuO submicron particles is introduced and it presents both good thermal and aesthetic performance. Furthermore, the double-layer coating which can be easily put into practice with a higher volume fraction distribution of submicron particles in the upper layer can obtain a better performance compared with the graded and uniform ones.
- (2) The double-layer volume fraction distribution of $f_{v1}(z) = 4.5\%$ ($0 \leq z < 0.5L$), $f_{v2}(z) = 0.5\%$ ($0.5L \leq z \leq L$) is recommended, since a better optimization parameter R_{opt} of the coating can be obtained compared with the cases of $f_{v1}(z) = 4\%$ ($0 \leq z < 0.5L$), $f_{v2}(z) = 1\%$ ($0.5L \leq z \leq L$) and $f_{v1}(z) = 3.5\%$ ($0 \leq z < 0.5L$), $f_{v2}(z) = 1.5\%$ ($0.5L \leq z \leq L$).
- (3) The radiative properties of CuO particles, such as absorption efficiency and scattering efficiency, have a significant influence on the spectral reflectance under different particle diameters. The particle diameter $0.50 \mu\text{m}$ is recommended among the calculated cases. In addition, the thickness of the coating around $50 \mu\text{m}$ and the standard white substrate are better options to maximize the optimization parameter though white substrate is not always met in the practical application.

Compared with the single layer coating, the proposed CuO double-layer one presents a higher spectral reflectance against solar irradiation especially in the near infrared region.

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References

- [1] R. Levinson, P. Berdahl, H. Akbari, Solar spectral optical properties of pigments—Part I: model for deriving scattering and absorption coefficients from transmittance and reflectance measurements, *Sol. Energy Mater. Sol. Cells* 89 (2005) 319-349.
- [2] G. Xie, J.Y. Xiong, H.T. Liu, B.P. Xu, H.F. Zheng, Y.J. Yang, Experimental and numerical investigation on a novel solar still with vertical ripple surface, *Energy Convers. Manage.* 98 (2015) 151-160.
- [3] O. Behar, A. Khellaf, K. Mohammedi, Comparison of solar radiation models and their validation under Algerian climate—The case of direct irradiance, *Energy Convers. Manage.* 98 (2015) 236-251.
- [4] Z. Zhou, Q. Cheng, P.P. Li, H.C. Zhou, Non-imaging concentrating reflectors designed for solar concentration systems, *Sol. Energy* 103 (2014) 494-501.
- [5] Q. Cheng, J.L. Chai, Z. Zhou, J.L. Song, Y. Su, Tailored non-imaging secondary reflectors designed for solar concentration systems, *Sol. Energy* 110 (2014) 160-167.
- [6] M. Zinzi, S. Agnoli, Cool and green roofs - An energy and comfort comparison between passive cooling and mitigation urban heat island techniques for residential buildings in the Mediterranean region, *Energy Build.* 55 (2012) 66-76.

- [7] B. Kaur, N. Quazi, I. Ivanov, S. Bhattacharya, Near-infrared reflective properties of perylene derivatives, *Dyes Pigments* 92 (2012) 1108-1113.
- [8] M. Baneshi, S. Maruyama, H. Nakai, A. Komiya, A new approach to optimizing pigmented coatings considering both thermal and aesthetic effects, *J. Quant. Spectrosc. Radiant. Transfer* 110 (2009) 192-204.
- [9] M. Baneshi, S. Maruyama, A. Komiya, The effects of using some common white pigments on thermal and aesthetic performances of pigmented coatings, *J Therm Sci Tech-jpn* 4 (2009) 131-145.
- [10] M. Baneshi, S. Maruyama, A. Komiya, Infrared radiative properties of thin polyethylene coating pigmented with titanium dioxide particles, *J Heat Tranfer* 132 (2010) 023306.
- [11] M. Baneshi, H. Gonome, A. Komiya, S. Maruyama, The effect of particles size distribution on aesthetic and thermal performances of polydisperse TiO_2 pigmented coatings: Comparison between numerical and experimental results, *J. Quant. Spectrosc. Radiant. Transfer* 113 (2012) 594-606.
- [12] G. George, G. George, P.P. Rao, M.L. Reddy, Synthesis and characterization of environmentally benign nontoxic pigments: $\text{RE}_2\text{Mo}_2\text{O}_9$, *Chem Lett* 34 (2005) 1702-1703.
- [13] J.A. Johnson, J.J. Heidenreich, R.A. Mantz, P.M. Baker, M.S. Donley, A multiple-scattering model analysis of zinc oxide pigment for spacecraft thermal control coatings, *Prog Org Coat* 47 (2003) 432-442.
- [14] M. Santamouris, A. Synnefa, T. Karlessi, Using advanced cool materials in the urban built environment to mitigate heat islands and improve thermal comfort conditions, *Sol. Energy* 85 (2011) 3085-3102.
- [15] K.L. Uemoto, N.M. Sato, V.M. John, Estimating thermal performance of cool

- colored paints, *Energy Build.* 42 (2010) 17-22.
- [16] R.F. Brady, L.V. Wake, Principles and formulations for organic coatings with tailored infrared properties *Prog Org Coat*, 20 (1992) 1-25.
- [17] A. Synnefa, M. Santamouris, K. Apostolakis, On the development, optical properties and thermal performance of cool colored coatings for the urban environment, *Sol. Energy* 81 (2007) 488-497.
- [18] R. Levinson, P. Berdahl, H. Akbari, W. Miller, I. Joedicke, J. Reilly, Y. Suzuki, M. Vondran, Methods of creating solar-reflective nonwhite surfaces and their application to residential roofing materials, *Sol. Energy Mater. Sol. Cells* 91 (2007) 304-314.
- [19] H. Akbari, M. Pomerantz, H. Taha, Cool surfaces and shade trees to reduce energy use and improve air quality in urban areas, *Sol. Energy* 70(3) (2001) 295-310.
- [20] X. Xue, J. Qin, J.R. Song, J. Qu, Y.X. Shi, W.D. Zhang, Z.N. Song, L.H. Jiang, J.-F. Li, H.S. Guo, T. Zhang, The methods for creating energy efficient cool gray building coatings—Part I: Preparation from white and black pigments, *Sol. Energy Mater. Sol. Cells* 130 (2014) 587-598.
- [21] A.J. Han, M.Q. Ye, L.L. Liu, W. Feng, M.C. Zhao, Estimating thermal performance of cool coatings colored with high near-infrared reflective inorganic pigments: Iron doped $\text{La}_2\text{Mo}_2\text{O}_7$ compounds, *Energy Build.* 84 (2014) 698-703.
- [22] L.H. Jiang, X. Xue, J. Qu, J. Qin, J.R. Song, Y.X. Shi, W.D. Zhang, Z.N. Song, J.F. Li, H.S. Guo, T. Zhang, The methods for creating energy efficient cool gray building coatings—Part II: Preparation from pigments of complementary colors and titanium dioxide rutile, *Sol. Energy Mater. Sol. Cells* 130 (2014) 410-419.
- [23] L.L. Liu, A.J. Han, M.Q. Ye, M.C. Zhao, Synthesis and characterization of Al^{3+}

- doped LaFeO_3 compounds: A novel inorganic pigments with high near-infrared reflectance, *Sol. Energy Mater. Sol. Cells* 132 (2015) 377-384.
- [24] L.L. Liu, A.J. Han, M.Q. Ye, W. Feng, The evaluation of thermal performance of cool coatings colored with high near-infrared reflective nano-brown inorganic pigments: Magnesium doped ZnFe_2O_4 compounds, *Sol. Energy* 113 (2015) 48-56.
- [25] J. Qin, J.R. Song, J. Qu, X. Xue, W.D. Zhang, Z.N. Song, Y.X. Shi, L.H. Jiang, J.F. Li, T. Zhang, The methods for creating building energy efficient cool black coatings, *Energy Build.* 84 (2014) 308-315.
- [26] H. Gonome, M. Baneshi, J. Okajima, A. Komiya, S. Maruyama, Controlling the radiative properties of cool black-color coatings pigmented with CuO submicron particles, *J. Quant. Spectrosc. Radiant. Transfer* 132 (2014) 90-98.
- [27] M. Baneshi, S. Maruyama, A. Komiya, Comparison between aesthetic and thermal performances of copper oxide and titanium dioxide nano-particulate coatings, *J. Quant. Spectrosc. Radiant. Transfer* 112 (2011) 1197-1204.
- [28] Q. Cheng, H.C. Zhou, The DRESOR method for a collimated irradiation on an isotropically scattering layer, *J Heat Transfer* 129 (2007) 634-645.
- [29] Q. Cheng, H.C. Zhou, Z.F. Huang, Y.L. Yu, D.X. Huang, The Solution of transient radiative transfer with collimated incident serial Pulse in a plane-parallel medium by the DRESOR method, *J Heat Transfer* 130 (10) (2008) 102701.
- [30] Z.C. Wang, J.L. Song, J.L. Chai, Q. Cheng, H.C. Zhou, The effect of BRDF surface on radiative heat transfer within a one-dimensional graded index medium, *Int J Therm Sci* 77 (2014) 116-125.
- [31] Q. Cheng, X. Zhang, Z.F. Huang, Z.C. Wang, H.C. Zhou, The DRESOR method for radiative heat transfer in semitransparent graded index cylindrical Medium, *J. Quant. Spectrosc. Radiant. Transfer* 143 (2014) 16-24.

- [32] J.L. Chai, Q. Cheng, J.L. Song, Z.C. Wang, H.C. Zhou, The DRESOR method for one-dimensional transient radiative transfer in graded index medium coupled with BRDF surface, *Int J Therm Sci* 91 (2015) 96-104.
- [33] M.F. Modest, *Radiative Heat Transfer*, Academic Press, 2003. (2nd edn)
- [34] E.D. Palik, *Handbook of Optical Constants of Solids*, Academic Press, 1998.
- [35] W.E. Vargas, A. Amador, G.A. Niklasson, Diffuse reflectance of TiO₂ pigmented paints: Spectral dependence of the average pathlength parameter and the forward scattering ratio, *Opt Commun* 261 (2006) 71-78.
- [36] Standard tables for reference solar spectral irradiances: direct normal and hemispherical on 37° tilted surface, available at: (<http://compass.astm.org/Standards/HISTORICAL/G173-03E1.htm>).
- [37] Y. Zhang, H.L. Yi, H.P. Tan, Short-pulsed laser propagation in a participating slab with Fresnel surfaces by Lattice Boltzmann method, *Int J Heat Mass Transfer* 80 (2015) 717-726.
- [38] Y. Zhang, H.L. Yi, H.P. Tan, Lattice Boltzmann method for one-dimensional transient radiative transfer in graded index medium, *J. Quant. Spectrosc. Radiant. Transfer* 137 (2014) 1-12.
- [39] Z.C. Wang, Q. Cheng, G.H. Wang, H.C. Zhou, The DRESOR method for radiative heat transfer in a one-dimensional medium with variable refractive index, *J. Quant. Spectrosc. Radiant. Transfer* 112 (2011) 2835-2845.
- [40] H.C. Zhou, D.L. Chen, Q. Cheng, A new way to calculate radiative intensity and solve radiative transfer equation through using the Monte Carlo method, *J. Quant. Spectrosc. Radiant. Transfer* 83 (2004) 459-481.
- [41] J.R. Howell, R. Siegel, M. P. Menguc, *Thermal radiation heat transfer*, CRC press, 2010. (5th edn)

- [42] C.F. Bohren, D.R. Huffman, Absorption and scattering of light by small particles, New York: Wiley, 1983.

Tables:

Table 1 Results of optimization parameter R_{opt} , two color coordinates x and y and luminance parameter Y of CuO pigmented coating

case	R_{opt}	x	y	Y (%)
case 1.1	17.11	0.3226	0.3508	4.48
case 1.2	14.43	0.3223	0.3511	4.43
case 1.3	17.24	0.3228	0.3511	4.48
case 1.4	13.30	0.3226	0.3510	4.46
case 1.5	16.44	0.3228	0.3509	4.47
case 2.1	17.24	0.3228	0.3511	4.48
case 2.2	17.34	0.3227	0.3510	4.48
case 2.3	17.07	0.3227	0.3509	4.48
case 3.1	12.17	0.3229	0.3512	4.46
case 3.2	15.29	0.3227	0.3511	4.48
case 3.3	17.34	0.3227	0.3510	4.48
case 3.4	17.28	0.3228	0.3512	4.48
case 3.5	17.05	0.3229	0.3511	4.48
case 4.1	15.75	0.3331	0.3569	5.05
case 4.2	17.34	0.3227	0.3510	4.48
case 4.3	16.76	0.3194	0.3500	4.36
case 4.4	15.94	0.3182	0.3495	4.31
case 4.5	10.10	0.3182	0.3497	4.27
case 5.1	17.34	0.3227	0.3510	4.48
case 5.2	18.22	0.3230	0.3512	4.48
case 5.3	18.72	0.3228	0.3511	4.48
case 5.4	19.80	0.3228	0.3512	4.48

Figure Captions

- Fig. 1: Complex refractive index of CuO.
- Fig. 2: Schematic of solar radiation incident on the one-dimensional double-layer pigmented coating with different volume fraction distributions of submicron particles.
- Fig. 3: The validation of the DRESOR method.
- Fig. 4: The comparison of spectral reflectance of a CuO coating among uniform, graded and double-layer volume fraction distributions.
- Fig. 5: The effect of double-layer coating with different volume fraction distributions of CuO particles on spectral reflectance.
- Fig. 6: CIE chromaticity diagram.
- Fig. 7: The effect of thickness of the CuO coating on spectral reflectance.
- Fig. 8: The effect of different particle diameters on spectral reflectance.
- Fig. 9: Absorption efficiency, scattering efficiency and asymmetry parameter of different particle diameters.
- Fig. 10: The effect of substrate conditions of the CuO coating on spectral reflectance.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10