Nanothermochromics with VO_2-based core-shell structures: Calculated luminous and solar optical properties

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Composites including VO_2-based thermochromic nanoparticles are able to combine high luminous transmittance T_{lum} with a significant modulation of the solar energy transmittance ΔT_{sol} at a "critical" temperature in the vicinity of room temperature. Thus nanothermochromics is of much interest for energy efficient fenestration and offers advantages over thermochromic VO_2-based thin films. This paper presents calculations based on effective medium theory applied to dilute suspensions of core-shell nanoparticles and demonstrates that, in particular, moderately thin-walled hollow spherical VO_2 nanoshells can give significantly higher values of ΔT_{sol} than solid nanoparticles at the expense of a somewhat lowered T_{lum}. This paper is a sequel to a recent publication [S.-Y. Li, G. A. Niklasson, and C. G. Granqvist, J. Appl. Phys. **108**, 063525 (2010)].
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I. INTRODUCTION

Nanothermochromic composites comprising VO_2 nanoparticles in a dielectric host are of considerable interest for energy efficient buildings, as discussed in a recent paper of ours.[1] The transmittance of solar energy can be significantly higher at a temperature τ below a "critical" value—i.e., at $\tau < \tau_{cr}$—than for $\tau > \tau_{cr}$ and hence the composites can modulate the throughput of solar energy in a desirable way provided that τ_{cr} lies at a comfort temperature in the vicinity of ~20 °C. The solar energy transmittance modulation, denoted ΔT_{sol}, in dilute composites can be larger, and can also be combined with a higher luminous transmittance T_{lum}, than for the more commonly studied VO_2-based thin films.[1] Nanoparticles of VO_2 can be produced by a large number of chemical and physical techniques, as reviewed before.[1] VO_2 has $\tau_{cr} \approx 68$°C,[2] which is too high for buildings-related applications, but τ_{cr} can be brought to room temperature by doping with, for example, a few percent of tungsten to form VO_2:W.[3–5] The purpose of the present paper is to demonstrate by computation that dilute composites incorporating VO_2-based core-shell nanostructures, particularly VO_2 hollow nanospheres, offer some advantages and can yield higher ΔT_{sol} than comparable materials with solid VO_2 nanoparticles.

Core-shell particles are of much current interest, and a judicious choice of core and shell can lead to novel properties. VO_2-based core-shell nanoparticles have attracted considerable attention and have been prepared both via self-assembly and templating. Hollow nanospheres and microspheres of VO_2,[6] VO_x,[7] and $VO_2 \cdot H_2O$ (Ref. 8) have been prepared by chemical synthesis, and hollow rodlike VO_2 microcrystals have been made by gas-phase synthesis.[9,10] SiO_2 nanospheres have been coated with VO_2 shells by chemical solution deposition and have subsequently been embedded in transparent polymers,[11,12] and similar nanoparticle composites have been made also via reduction of V_2O_5 shells;[13] recently such SiO_2 nanospheres have been coated with VO_2:W.[14] VO_2 shells on SiO_2 microspheres have been fabricated by pulsed laser deposition,[15] and such coatings on carbon have been prepared chemically.[16] We also note that VO_2 nanoparticle infiltration into ordered polystyrene sphere arrangements have yielded inverse opal nanostructures,[17] that VO_2 "nanoscrolls" have been made from chemically prepared $V_2O_{5-\delta}$,[18] and that sea-urchinlike nanostructures of $VO_x \cdot yH_2O$ have been deposited chemically[19] as well as electrochemically.[20]

The mentioned research on VO_2-based core-shell nanostructures represents examples of a huge endeavor to develop analogous structures of a vast range of materials, and representative recent work on hollow nanospheres—which will be shown below to have the most interesting properties for the case of VO_2—has been presented for a multitude of other oxides including MgO,[21] SiO_2,[22] γ-MnO_2,[23] NiO,[24] ZnO,[25] In_2O_3,[26,27] and SnO_2.[28,29] Other recent investigations embrace hollow nanospheres of sulfides,[30–32] selenides,[33] phosphates,[34] carbides,[35] and metals in elemental[36,37] and composite[38,39] form.

II. THEORY AND INPUT PARAMETERS

We are interested in the transmission of light through a dispersion of core-shell nanoparticles embedded in a dielectric matrix as described in Fig. 1. The host medium is characterized by a dielectric constant ε_m and contains nanospheres having cores with diameter x and dielectric constant ε_c surrounded by concentric shells of thickness t and dielectric function ε_s.

The optical properties of the structure in Fig. 1 can be described by effective medium theory, provided that the nanoparticles are much smaller than the wavelength of the incident radiation so that they are nonscattering. Following earlier work[40–43] we derive an effective dielectric function ε^{MG} by

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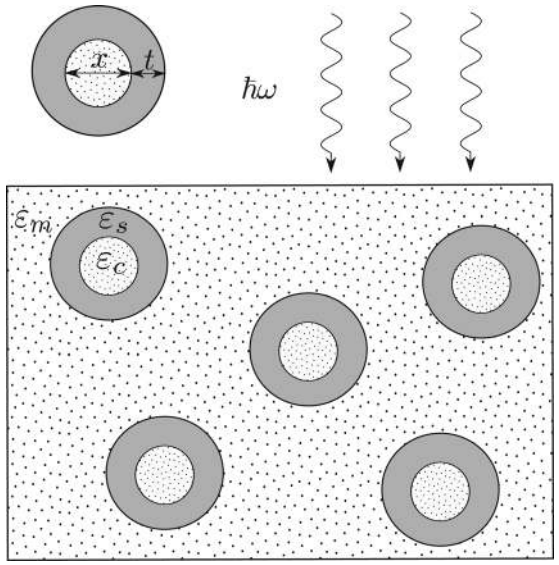

FIG. 1. Structural model representing core-shell nanoshells in a surrounding medium under irradiation of photons with energy $\hbar\omega$.

$$\varepsilon^{\mathrm{MG}} = \varepsilon_m \frac{1+\frac{2}{3}f\alpha}{1-\frac{1}{3}f\alpha}, \tag{1}$$

where f is the filling factor, i.e., the volume fraction occupied by the nanoparticles, and the polarizability α is given by

$$\alpha = 3\frac{(\varepsilon_s-\varepsilon_m)(\varepsilon_c+2\varepsilon_s)+\Omega(2\varepsilon_s+\varepsilon_m)(\varepsilon_c-\varepsilon_s)}{(\varepsilon_s+2\varepsilon_m)(\varepsilon_c+2\varepsilon_s)+\Omega(2\varepsilon_s-2\varepsilon_m)(\varepsilon_c-\varepsilon_s)}. \tag{2}$$

Here Ω is the ratio between the volumes of the inner and outer spheres according to

$$\Omega = \left(\frac{x}{2t+x}\right)^3. \tag{3}$$

In the calculations to follow it is of interest to keep the relative amount of VO_2 constant, in general at 0.01, while x/t is varied and to that end we set

$$f = 0.01/(1-\Omega). \tag{4}$$

Thus f ranges from 0.01 to 0.04 as x/t goes from zero to 20.

The specific effective medium equation in Eq. (1) applies to the Maxwell–Garnett (MG) theory[44] which describes nanoparticles embedded in a continuous medium, and alternative formulations apply to different nanotopologies.[45] Our calculations, to be presented below, were confined to small filling factors, and all effective medium equations converge in the dilute limit which means that Eq. (1) can be used without significant loss of generality.

Spectral and temperature dependent transmittance $T(\lambda,\tau)$ was calculated from $\varepsilon^{\mathrm{MG}}(\lambda,\tau)$ for $300<\lambda<2500$ nm by use of standard formulas for thin film optics for a single layer,[46] and $T_{\mathrm{lum}}(\tau)$ and $T_{\mathrm{sol}}(\tau)$ were then obtained from

$$T_{\mathrm{lum,sol}}(\tau) = \int d\lambda\, \varphi_{\mathrm{lum,sol}}(\lambda)\, T(\lambda,\tau) / \int d\lambda\, \varphi_{\mathrm{lum,sol}}(\lambda), \tag{5}$$

where φ_{lum} is the spectral sensitivity of the light-adapted human eye[47] and φ_{sol} is the solar irradiance spectrum for air mass 1.5 (the sun standing 37° above the horizon).[48]

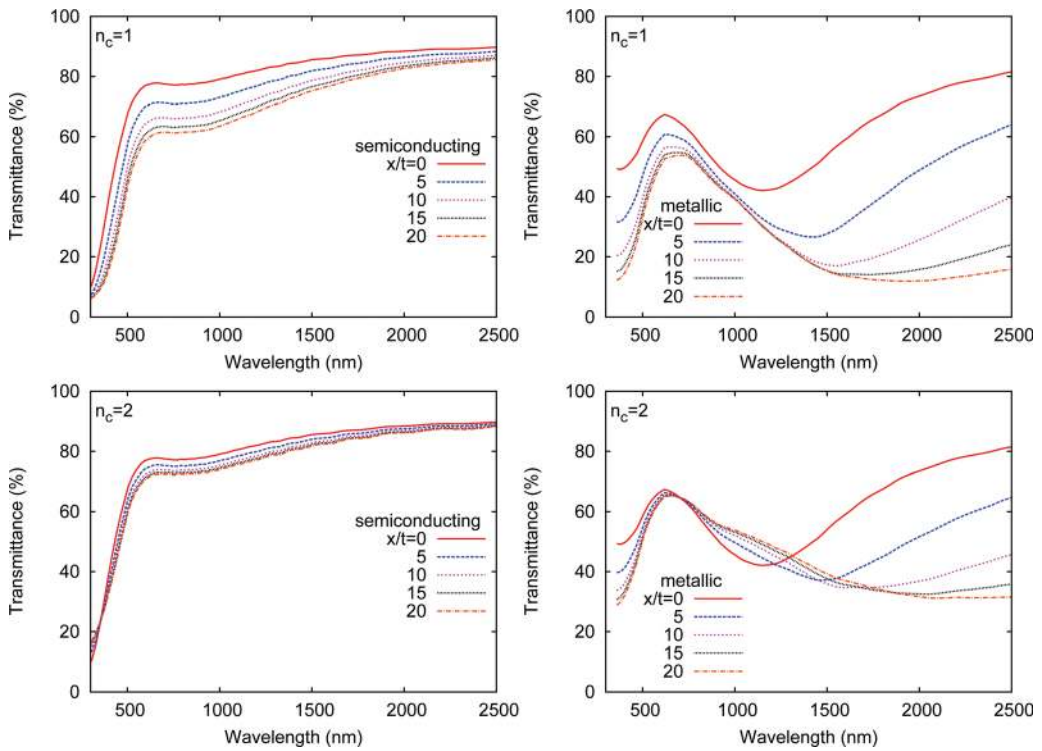

FIG. 2. (Color online) Spectral transmittance calculated for spherical shells (thickness t) of VO_2 surrounding cores (diameter x) with the shown values of the dielectric constant n_c and embedded in a dielectric medium represented by $n_m = 1.5$, as depicted in Fig. 1. Data are shown for $\tau < \tau_{\mathrm{cr}}$ (semiconducting VO_2; left-hand panels) and for $\tau > \tau_{\mathrm{cr}}$ (metallic VO_2; right-hand panels). The material was 5 μm thick and contained 1 vol. % of VO_2.

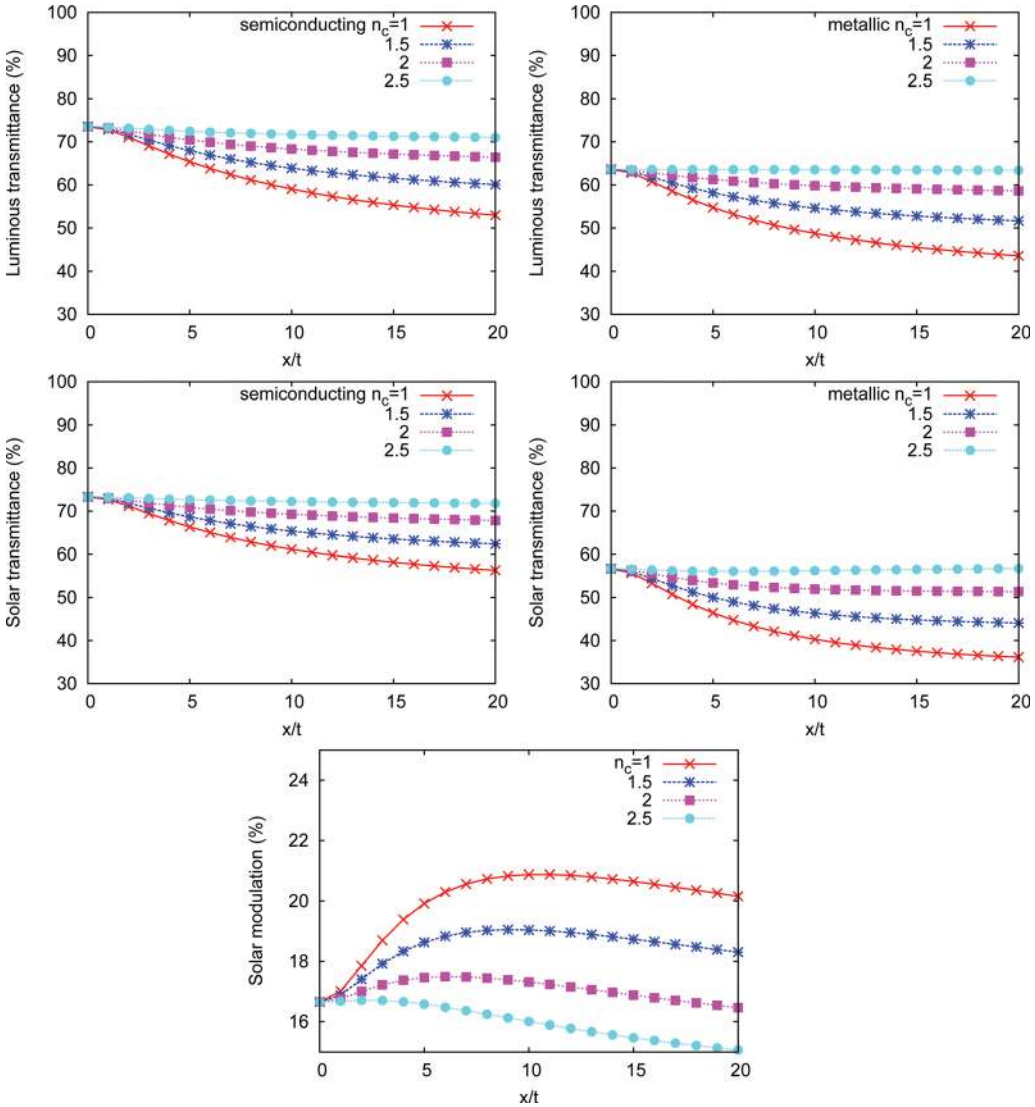

FIG. 3. (Color online) Luminous transmittance (upper two panels), solar transmittance (middle two panels), and solar modulation (lower panel) for spherical shells (thickness t) of VO_2 surrounding cores (diameter x) with the shown values of the dielectric constant n_c and embedded in a dielectric medium represented by $n_m = 1.5$, as depicted in Fig. 1. Data are shown for $\tau < \tau_{cr}$ (semiconducting VO_2; upper and middle left-hand panels) and for $\tau > \tau_{cr}$ (metallic VO_2; upper and middle right-hand panels). The material was 5 μm thick and contained 1 vol. % of VO_2.

All of the calculations used the refractive index $n_m = (\varepsilon_m)^{[1/2]} = 1.5$ for the embedding medium, which is appropriate to typical glass or polymer. For the cores we set the refractive index $n_c = (\varepsilon_c)^{[1/2]}$ equal to 1 (vacuum), 1.5 (glass or polymer), 2, and 2.5. The shells were comprised of VO_2 whose wavelength and temperature dependent dielectric function $\varepsilon_s(\lambda,\tau) = \varepsilon_{s1}(\lambda,\tau) + i\varepsilon_{s2}(\lambda,\tau)$ was obtained from earlier determinations for 50-nm-thick VO_2 films.[49] It should be noted that neither t nor x enter into the description of this dielectric function, not even for $\tau > \tau_{cr}$. This is so because the mean free paths of the electrons in the metallic state of VO_2 are of the order of or smaller than the interatomic distances[50,51] which means that VO_2 can be characterized as a "bad metal"[52] and may not even qualify as a conventional Fermi liquid;[53] this situation is very different from the one for coinage metals in which case the dielectric function must be modified to account for grain boundary scattering of the free electrons.[40,42,54]

III. CALCULATED RESULTS

Figure 2 reports $T(\lambda)$ with five values of x/t ranging from zero (solid VO_2 nanospheres) to 20 (thin-walled hollow VO_2 nanoshells) and n_c equal to 1 (vacuum) and 2 [representative of amorphous titania at $\lambda > 500$ nm (Ref. 55)]. Data are given at $300 < \lambda < 2500$ nm for $\tau < \tau_{cr}$ and $\tau > \tau_{cr}$. The investigated material has a constant VO_2 volume fraction of 0.01 and its thickness is 5 μm, implying that the VO_2 mass thickness is 50 nm. Looking at the results for $\tau < \tau_{cr}$, it is found that $T(\lambda)$ drops monotonically when x/t is increased; the effect is most pronounced for $n_c = 1$. The data for $\tau > \tau_{cr}$ display a striking valley, indicating a heavily damped plasmon resonance due to the conduction electrons in the metallic phase of VO_2,[1,56] whose minimum is shifted monotonically from ~1100 nm for $x/t = 0$ to ~2000 nm for $x/t = 20$; the minimum gets more shallow for the larger values of n_c.

Spectral transmittance data, of the kind just shown, were used to compute T_{lum} for $\tau < \tau_{cr}$ and $\tau > \tau_{cr}$, T_{sol} for $\tau < \tau_{cr}$

and $\tau > \tau_{cr}$, and ΔT_{sol} for $0 \leq n_c \leq 2.5$, with x/t being 0, 1, 2,…, 20. Data in Fig. 3 show that T_{lum} and T_{sol} decrease monotonically when x/t is increased, and that this effect gets progressively weaker when n_c is increased. An interesting result is that ΔT_{sol} has a maximum which is largest for $n_c = 1$ and decreases monotonically as n_c is increased. The largest solar modulation is $\Delta T_{sol} \approx 20.9\%$, which occurs for hollow nanospheres ($n_c = 1$) with $x/t \approx 10$ and is significantly higher than the value ~16.7% that pertains to solid VO_2 nanoparticles. This improvement of ΔT_{sol} comes at a cost, though, and T_{lum} for $\tau < \tau_{cr}$ shows a concomitant decrease from ~73.5 to ~59.0%.

The simultaneous gain in solar modulation and loss in luminous transmittance require some further analysis since high values of both of these parameters are desirable for most practical applications. Requiring that T_{lum} at $\tau < \tau_{cr}$ remains at ~73.5%, one can achieve $\Delta T_{sol} \approx 14.5\%$ for hollow nanospheres with $x/t = 10$ at a volume fraction that is only 50% of the one used for the calculations in Fig. 3, and at 60% of such nanospheres one can obtain $T_{lum} \approx 70.5\%$ and $\Delta T_{sol} \approx 16.2\%$. The latter results point at possibilities to significantly decrease the amount of VO_2 provided it is in moderately thin-walled hollow nanospheres and yet achieve properties that are only marginally inferior to those of solid VO_2 nanospheres.

IV. DISCUSSION AND CONCLUSION

In this work we used calculations based on effective medium theory applied to spherical core-shell structures with VO_2 surrounding a dielectric to demonstrate how the luminous and solar transmittance as well as the thermochromic modulation of the solar energy transmittance depend on the relative diameters of the core and shell. In particular, we found that moderately thin-walled VO_2 nanoshells could yield a significant improvement of the solar energy modulation although at the expense of a lowered luminous transmittance. Almost the same properties as for solid nanospheres could be accomplished with substantially reduced amounts of VO_2 if it was in the form of hollow nanoshells. In a practical situation, the luminous and solar properties below and above the thermochromic "critical" temperature, as well as the cost of different kinds of VO_2-based nanoparticles, all play a role and a trade-off must be reached. The present analysis, and the documented possibilities to make VO_2-based nanoparticles both by self-assembly and templating, shows that moderately thin-walled nanoshells offer advantages. We note in passing that VO_2-containing core-shell nanostructures have been studied also in some other work[57,58] though with a different scope than ours. VO_2:Mg can have enhanced values of T_{lum} (Ref. 59) and may be of interest for nanothermochromics in the future.

It is straightforward to extend the present analysis to concentric spheroids with or without specific orientation[40,41] but our previous analysis[1] does not give reasons to expect properties that are superior to those for spheres, and hence we limited the study to the latter shape.

The inverted nanostructure, with spherical shells of a dielectric with a refractive index ranging from zero to 2.5 surrounding cores of VO_2, were investigated as well. Dielectric shells may be of interest for protecting the VO_2 cores from oxidation or other types of degradation. The computed results, expectedly, did not lead to any significant improvement over the data for solid nanospheres and are not presented here.

A general result from the present study as well as from the previous one[1] is to point at the potential of nanothermochromics. In particular, polymer foils incorporating VO_2-based nanoparticles may offer interesting possibilities to merge chromogenic technology with membrane architecture[60,61] in order to accomplish radically new technologies for energy efficient buildings with high user comfort.

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