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Nanothermochromics: Calculations for VO_2 nanoparticles in dielectric hosts show much improved luminous transmittance and solar energy transmittance modulation

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VO_2-based films are thermochromic and show infrared reflectance above a "critical" temperature in the vicinity of room temperature. Implementations on energy efficient windows have been discussed for decades but have been severely curtailed since the luminous absorptance is undesirably large and the solar energy transmittance modulation is too small. Here we show by calculations based on effective medium theory that dilute composites with VO_2 nanoparticles embedded in hosts with properties mimicking glass or polymer can yield significantly decreased luminous absorption jointly with much enhanced transmittance modulation of solar energy. These results demonstrate that VO_2-based nanothermochromics opens new avenues toward energy efficient fenestration. © *2010 American Institute of Physics*. [doi:10.1063/1.3487980]

I. INTRODUCTION

This paper shows that thermochromic VO_2 nanoparticles in a dielectric host can have higher luminous transmittance and larger solar energy modulation than VO_2 films. Thus nanothermochromics—which seems to be a new concept—stands out as an interesting possibility for energy efficient fenestration.

As much as 30% to 40% of the primary energy in the world is used in buildings: for heating, cooling, ventilation, and appliances.[1] The most industrialized countries lie at the upper end of the range, specifically with 39% of the primary energy going into buildings in the USA.[2] Nanotechnology offers a multitude of possibilities for energy conservation in the built environment and, importantly, these possibilities can be combined with preserved or improved indoor comfort.[3] The latter issue is highly relevant as—again in the most industrialized countries—people spend 80% to 90% of their time indoors, in buildings, and vehicles.[4] The present work is related to chromogenic fenestration, i.e., windows whose transmittance can be altered in response to an external stimulus.[5,6] Specifically we consider thermochromic materials which enable the solar energy inflow to be decreased as the temperature τ goes above a comfort level, thereby lowering the demand for space cooling (which accounts for ~14% of the energy used in buildings in the USA[2]).

Vanadium dioxide is a well known thermochromic material[7] and has been widely discussed for temperature-dependent modulation of the solar energy throughput in windows.[8] VO_2 has a reversible structural transformation at a "critical" temperature τ_c; for temperatures $\tau < \tau_c$ the material is monoclinic, semiconducting, and rather infrared transparent, while at $\tau > \tau_c$ it is tetragonal, metallic, and infrared reflecting. The reversibility of the physical properties is excellent.[9] The transition appears to be of the Mott–Hubbard type as inferred from recent work based on infrared spectroscopy,[10,11] resistivity,[12] photoemission,[13] and x-ray diffraction.[14]

VO_2 is not immediately applicable to windows for three reasons. *First*, bulk VO_2 has $\tau_c \approx 68\ ^\circ C$,[7] which obviously is too high for buildings-related applications, but doping with transition metal ions having a valency 6+ and 5+ can decrease τ_c.[15] The most extensively studied dopant is W^{6+}, which can bring τ_c to room temperature without deteriorating the thermochromism;[16–18] the amount of tungsten for doing this seems to depend on the degree of crystalline order in the VO_2 but the relationship is not well understood. The addition of some W^{6+} does not have any large effect on the optical properties.[19] The *second* problem for using VO_2 in windows is the fact that films that display significant thermochromism have to be so thick that the luminous transmittance T_{lum} is only of the order of 50% or less and this is too low for most applications in architecture.[8] Antireflection with high-dielectric coatings can improve the situation somewhat, and three-layer coatings of $TiO_2/VO_2/TiO_2$ (Ref. 20) and $SiO_x/VO_2/SiO_x$ (Ref. 21) have been discussed. Even better properties can be obtained with five-layer coatings of $TiO_2/VO_2/TiO_2/VO_2/TiO_2$.[22,23] Deposition of VO_2 onto ordered arrays of silica microspheres offers other possibilities to increase the transmittance[24] (although, apparently, the effect was not reproduced in some other work[25]). Nevertheless the problem with too low transmittance has remained. It is related to the fact that band-to-band transitions in VO_2 yield unwanted optical absorption in the short-wavelength part of the luminous spectrum, and, therefore, it was a significant discovery that addition of Mg^{2+} led to band gap widening in proportion to the degree of doping.[26] This doping also decreases τ_c and hence gives dual benefits with regard to windows-related applications. The *third* problem has to do with the fact that the thermochromic reflectance modulation in VO_2 films is strong only in the near-infrared and at wavelengths for which the solar radiation is weak, which means

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that the modulation of the solar energy throughput between a low-temperature and a high-temperature state is modest; typically it is ~5% for a VO_2 film though, exceptionally, it can run up to 10%–15% in a well designed $TiO_2/VO_2/TiO_2/VO_2/TiO_2$ structure.[22,23]

VO_2-based nanoparticles of various types have received much interest in recent work, as discussed at length below, and there are a number of demonstrations that clear-cut thermochromic effects can be observed; data have been obtained for nanostructures made by ion implantation followed by annealing,[27–29] ion beam lithography and pulsed laser deposition,[30,31] ultrasonic spray and laser pyrolysis,[32] molten salt synthesis,[33] and aqueous chemistry.[34] Our present study demonstrates that nanoparticles dispersed in a dielectric host have advantages over what a thin solid film can offer. Specifically, calculations have shown that the thermochromic nanoparticles can give superior luminous transmittance and solar energy transmittance modulation. These data lead us to conclude that VO_2-based nanothermochromics opens new vistas for energy efficient fenestration as discussed below.

II. COMPUTATIONAL MODEL FOR DISPERSED NANOPARTICLES

A. Structural models and effective medium theory

We consider a dilute suspension of VO_2 nanoparticles in a dielectric matrix and backed by a dielectric substrate. The sizes of the nanoparticles are much smaller than the wavelengths of interest. Figure 1 illustrates the pertinent structures: Part (a) refers to spherical nanoparticles, parts (b) and (c) shows prolate spheroids(PSs)/oblate spheroids (OSs) oriented with their long/short axis perpendicular to the substrate, and part (d) deals with randomly oriented prolate nanoparticles all having the same ratio between major and minor axes. The figure also defines an aspect ratio m for the spheroids.

The optical properties of the "effective" medium comprising nanoparticles and embedding matrix are governed by an effective dielectric function ε^{MG} according to

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

where ε_m is the dielectric permeability for the matrix and f is the "filling factor," i.e., the volume fraction occupied by the particles. In the calculations below we will use $f=0.01$. The terminology follows the one in earlier papers (for example in Refs. 35 and 36). Specifically, Eq. (1) pertains to the Maxwell-Garnett theory,[37] which is appropriate for a topology with nanoparticles dispersed in a continuous matrix.[38] There are numerous other effective medium formulations as well, applicable to alternative nanotopologies, but they all coincide in the dilute limit so Eq. (1) can be applied here without any loss of generality.

The parameter α in Eq. (1) is written

$$\alpha = \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_m + L(\varepsilon_p - \varepsilon_m)}, \tag{2}$$

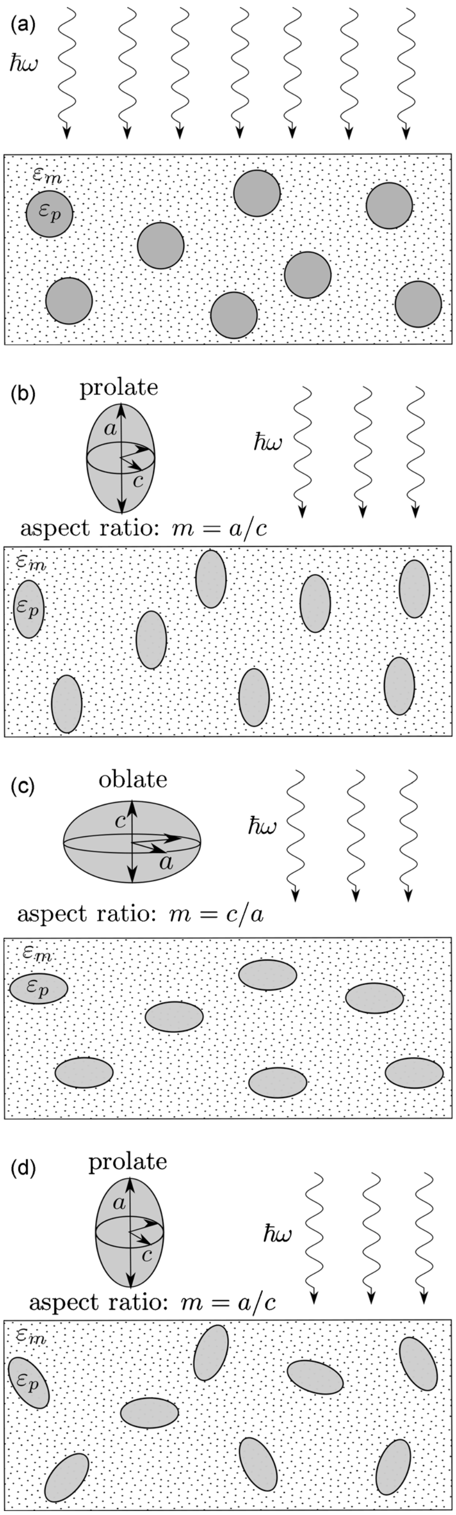

FIG. 1. Structural models for composites of nanoparticles with a dielectric function ε_p embedded in a medium with dielectric function ε_m. The nanoparticles are taken to be spherical (a), oriented prolate (b), oriented oblate (c), and random prolate (d) with major and minor axes a and c, respectively. An aspect ratio m is defined for the oblate and PSs. Electromagnetic radiation with photon energy $\hbar\omega$ is shown.

where ε_p is the dielectric function of the particles and the L is the appropriate depolarization factor. Spheres are characterized by $L=1/3$. A random distribution of ellipsoidal particles can be described via

$$\alpha = \frac{1}{3}\sum_{i=1}^{3} \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_m + L_i(\varepsilon_p - \varepsilon_m)}, \tag{3}$$

where the L_is are the triplet of depolarization factors.

Our modeling considers PSs with

$$L_1 < L_2 = L_3$$

and OSs with

$$L_1 = L_2 < L_3.$$

The depolarization factors fulfill $\Sigma L_i = 1$ and are related to the major (a) and minor (c) axes of the depolarization factors by[39]

$$L_1 = \frac{1 - e_{\mathrm{PS}}^2}{2e_{\mathrm{PS}}^3}\left(\ln\frac{1 + e_{\mathrm{PS}}}{1 - e_{\mathrm{PS}}} - 2e_{\mathrm{PS}}\right) \tag{4}$$

and $L_2 = L_3 = (1 - L_1)/2$, where

$$e_{\mathrm{PS}} = [1 - (c/a)^2]^{1/2}, \tag{5}$$

for PSs. For OSs we have instead

$$L_3 = (e_{\mathrm{OS}}^{-3} + e_{\mathrm{OS}}^{-1})(e_{\mathrm{OS}} - \arctan e_{\mathrm{OS}}) \tag{6}$$

and $L_1 = L_2 = (1 - L_3)/2$, with

$$e_{\mathrm{OS}} = [(a/c)^2 - 1]^{1/2}. \tag{7}$$

The depolarization factors for light that is incident normally toward the oriented nanostructures in Figs. 1(b) and 1(c) are L_3 and L_1 for the PSs and OSs, respectively, since the electric field direction is orthogonal to the symmetry axes. Hence, these depolarization factors were used in Eq. (2) for the computations.

B. Input data

Spectral optical constants, $n(\lambda)$ and $k(\lambda)$, for VO_2 films have been determined several times.[19,23,40–46] The values of n and k are in fair agreement and Fig. 2 shows results based on our own work[23] for a 0.05 μm thick film; these data were used in the calculations. The optical constants are related to the dielectric function $\varepsilon_f \equiv \varepsilon_{f1} + i\varepsilon_{f2}$ by $\varepsilon_{f1} = n^2 - k^2$ and $\varepsilon_{f2} = 2nk$.

The magnitude of ε_p for the metallic state is not necessary equal to the experimentally determined value ε_f appropriate to films but may need correction for the fact that the conduction electrons experience surface scattering in the particle. This can be accounted for by writing[36]

$$\varepsilon_p = \varepsilon_f - \varepsilon_f^D + \varepsilon_p^D, \tag{8}$$

where the two Drude (D) type terms are given by

$$\varepsilon_f^D = 1 - \omega_{Pf}^2/\omega(\omega + i/t_f) \tag{9}$$

and

$$\varepsilon_p^D = 1 - \omega_{Pp}^2/\omega(\omega + i/t_p). \tag{10}$$

Here ω_P denotes plasma frequency and t is mean scattering time for the conduction electrons. We put $\omega_{Pf} = \omega_{Pp}$ and

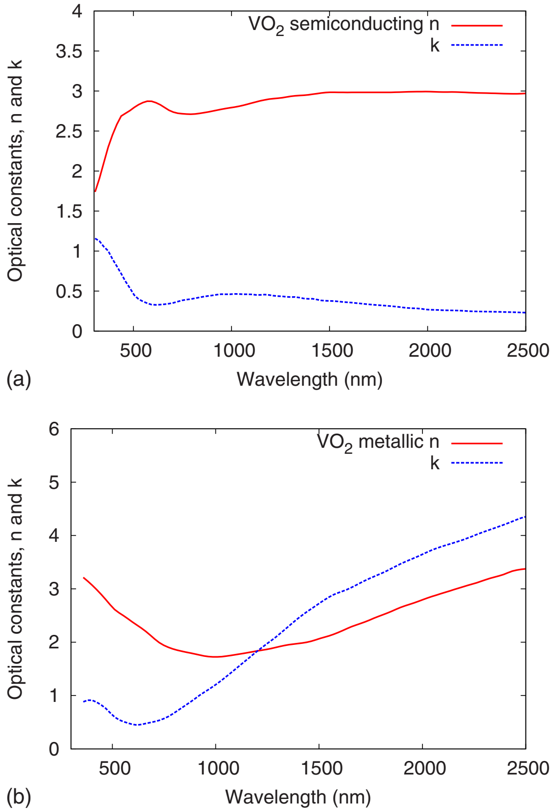

FIG. 2. (Color online) Spectral optical constants, n and k, for a VO_2 film in semiconducting (a) and metallic (b) states; from Ref. 23.

$$t_p^{-1} = t_f^{-1} + 2v_{Ff}/D_p, \tag{11}$$

where v_{Ff} is the Fermi velocity in the film and D_p is the particle diameter. This expression assumes diffuse scattering of the electrons.

It has been shown that VO_2 has an exceptionally small scattering time with $\hbar/t_f \approx 0.7$ eV according to recent results.[47,48] Since the Fermi velocity is also small, about 2.4×10^5 m/s,[49] the mean free path is about the order of the lattice constants or smaller and the material may not even be a conventional Fermi liquid.[49] Hence is appropriate to put $\varepsilon_p = \varepsilon_f$, and this approximation is used below.

III. COMPUTED OPTICAL DATA

A. Thin solid film

Calculations of spectral transmittance were done from Fresnel's equations[50] and using n and k for VO_2 according to Fig. 2 and a refractive index equal to 1.5 (or dielectric function of 2.25) to characterize a substrate. Figure 3 shows spectral transmittance $T(\lambda,\tau)$ for the semiconducting state at $\tau < \tau_c$ and for the metallic state at $\tau > \tau_c$ for a number of film thicknesses Some effects of optical interference can be seen in the thick semiconducting films.

Integrated values of luminous and solar transmittance are of interest to assess the visual and energy-related performance of thermochromic devices such as windows. These data were obtained from

$$T_{\mathrm{lum,sol}}(\tau) = \int d\lambda\, \varphi_{\mathrm{lum,sol}}(\lambda) T(\lambda,\tau) \Big/ \int d\lambda\, \varphi_{\mathrm{lum,sol}}(\lambda), \tag{12}$$

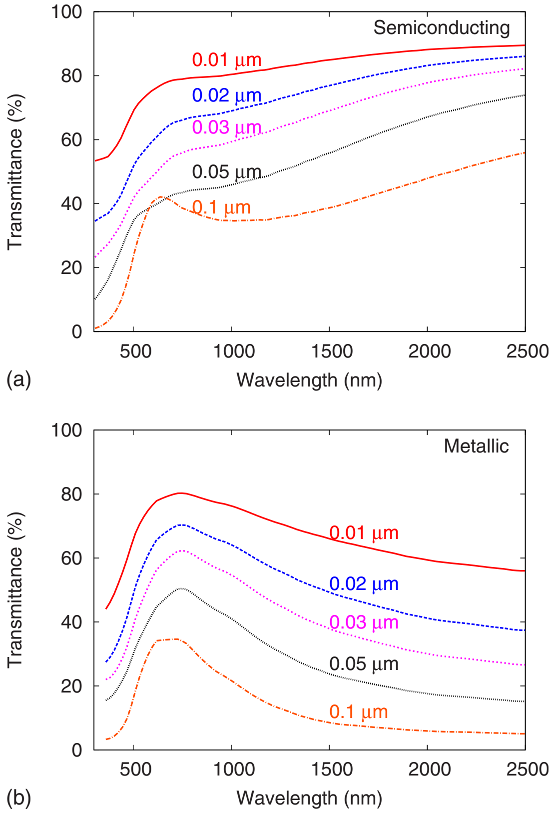

FIG. 3. (Color online) Computed spectral transmittance for VO_2 films in semiconducting (a) and metallic (b) states.

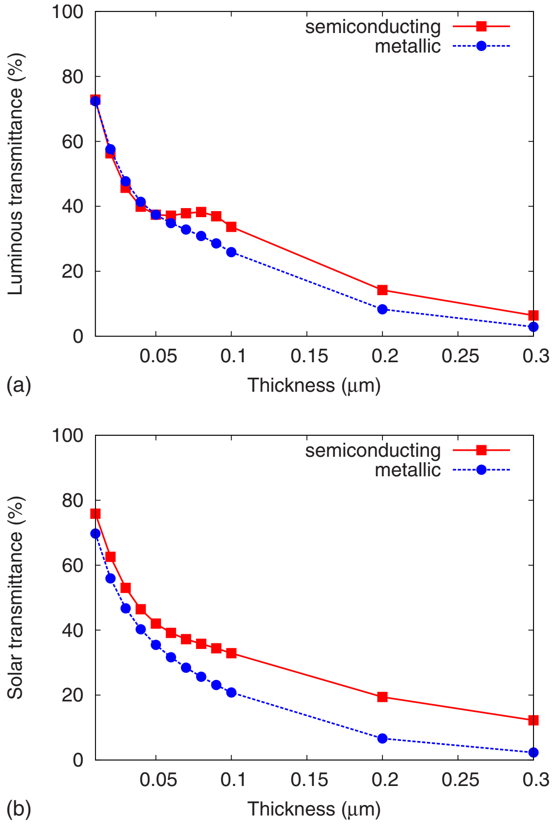

FIG. 4. (Color online) Computed luminous (a) and solar (b) transmittance as a function of thickness of VO_2 films in semiconducting and metallic states.

where φ_{lum} is the spectral sensitivity of the light-adapted eye[51] and φ_{sol} is the solar irradiance spectrum for air mass 1.5 (corresponding to the sun standing 37° above the horizon).[52]

Figure 4 shows integrated data derived from $T(\lambda,\tau)$ in Fig. 3. As expected, requiring a noticeable solar energy modulation limits T_{lum} to $\sim$40%, and the modulation of T_{sol} does not exceed $\sim$10%.

B. Composites with spheroidal particles

The optical constants in Fig. 2 were used to calculate spectral optical properties for spheroidal VO_2 particles dispersed in a dielectric matrix characterized by $\varepsilon_m=2.25$ and backed by a substrate having the same dielectric constant. This value is typical for a matrix of glass or polymer. We considered a dilute suspension with $f=0.01$ and a thickness of 5 μm. This implies that the VO_2 mass thickness was 0.05 μm and that the data for nanocomposites shown below could be compared with those for a film having the latter thickness.

We first considered spheroids oriented with their symmetry axes perpendicular to the substrate. Figure 5 illustrates data for $0.1<m<10$ and shows that $T(\lambda)$ increases monotonically as m goes from a low to a high value. The strong absorption at short wavelengths, due to band-to-band transitions in VO_2, is clearly seen. The most salient feature in Fig. 5 is the pronounced absorption band in the near-infrared that is centered at a wavelength of $\sim$1.2 μm for spheres and lies at a shorter wavelength for PSs and at a longer wavelength for OSs.

Figure 6 shows integrated data on luminous and solar transmittance as obtained from the spectra in Fig. 5. The values of T_{lum} for nanoparticle dispersions are much larger than those for corresponding films. Thus T_{lum} for spheres is 72% and 62% for the semiconducting and metallic states for particles and only $\sim$38% for the film irrespectively of its temperature. The difference in T_{sol} between the semiconducting and metallic phases is 20% for dispersions of spheres while the corresponding number for the film is $\sim$7%. Expectedly, the particle shape dependencies of T_{lum} and T_{sol} are consistent with the spectral variations in Fig. 5.

Random distributions of nanoparticles are of interest too, and Fig. 7 shows $T(\lambda)$ analogously with the data in Fig. 5. Integrated values of T_{lum} and T_{sol} are then given in Fig. 8. Large values of T_{lum}, and a significant thermochromic modulation of T_{sol}, are found again. An interesting feature is that the highest transmittance levels are found for the spherical particles.

IV. DISCUSSION

The calculations demonstrate that dilute VO_2-based nanoparticle composites can have very interesting properties for energy efficient fenestration. The question from a practical point of view is then whether such materials can be produced and to give a positive answer to this question we now review the literature and show that there are many possible

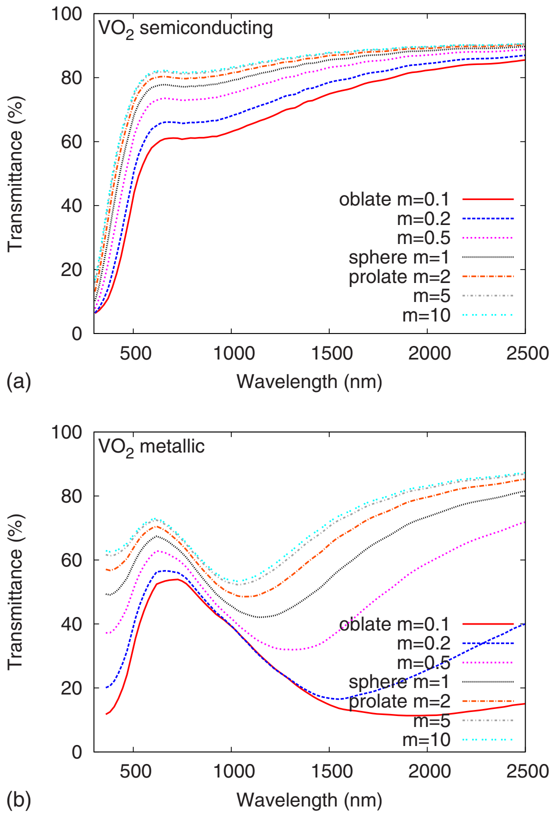

FIG. 5. (Color online) Spectral transmittance for spheroidal VO$_2$ particles, with shown aspect ratio m and a filling factor of 0.01, dispersed in a dielectric medium. The spheroids have their symmetry axes perpendicular to the substrate. Parts (a) and (b) refer to VO$_2$ in semiconducting and metallic states, respectively.

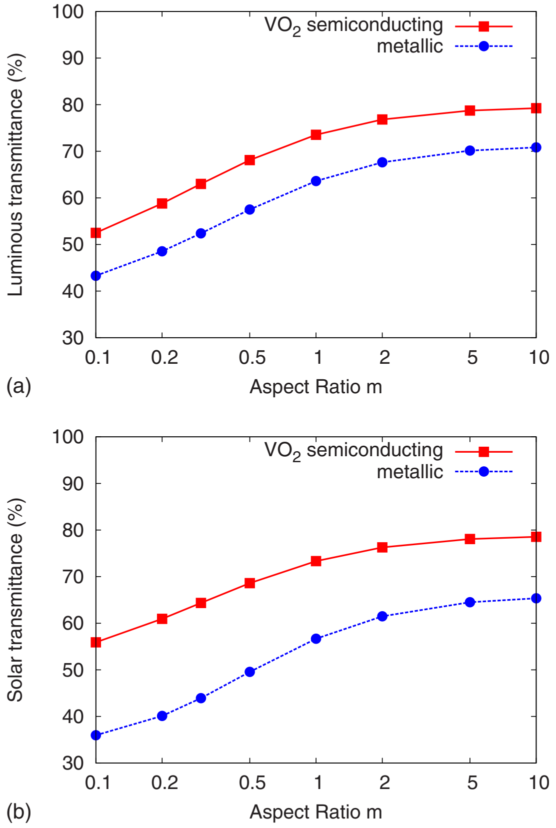

FIG. 6. (Color online) Integrated luminous (a) and solar (b) transmittance for spheroidal VO$_2$ particles, with shown aspect ratio m and a filling factor of 0.01, dispersed in a dielectric medium. The spheroids have their symmetry axes perpendicular to the substrate.

experimental routes for making VO$_2$-based nanoparticles having different shapes. In fact, experimental work on such nanoparticles has soared during recent years.

We first note that VO$_2$ nanoparticles occluded in a silica matrix have been fabricated via reduction in a glass containing V$_2$O$_5$ by use of hydrogen,[53,54] ion implantation of vanadium and oxygen ions in a silica host,[27,28] and sol-gel deposition.[55] Very well controlled nanostructures have been made by introduction of VO$_2$ into the voids of synthetic opal comprised of SiO$_2$ nanospheres.[56] The incorporation of VO$_2$ in polymer matrices[57,58] has been demonstrated too.

Nanoparticles of VO$_2$ with more or less symmetrical shapes have been made by wet chemistry,[59–66] molten salt synthesis,[67] pyrolysis,[68] confined-space combustion,[69] ion beam lithography together with pulsed laser deposition,[30,31,70] and directly by pulsed laser deposition.[71] Doped particles of this type, specifically of VO$_2$:W, have been made by wet chemistry;[59,62–64,72,73] furthermore, VO$_2$:W has been deposited onto SiO$_2$ nanoparticles by wet chemistry.[74]

There are also numerous works on nanorods (nanowires) of VO$_2$ prepared by wet chemistry,[75–82] gas phase synthesis,[32,83–89] ion implantation of vanadium and oxygen ions followed by annealing,[27–29,90] and by thermal oxidation of V;[33,91] these particles can be represented as high-eccentricity prolate particles. VO$_2$:W nanorods have been deposited by wet chemistry[92] and VO$_2$:Mo nanorods have been made by a sol-gel based technique.[93] Furthermore nanosheets (nanoplates, nanoflakes) of VO$_2$ have been made by wet chemistry,[94,95] gas phase synthesis,[84] and thermal reduction;[96] such particles can be approximated as high-eccentricity oblate particles.

A metastable form of vanadium dioxide—conventionally called VO$_2$(B)—is a well known host for lithium intercalation and hence an interesting battery material.[97] Nanorods (nanoribbons, nanobelts) of this material have been prepared by wet chemical techniques in numerous studies[95,98–115] and the capability for electrochemical lithium insertion has been investigated. VO$_2$(B) is not in itself a good thermochromic material but it can be transformed to thermochromic VO$_2$ via heat treatment, as has been demonstrated for powders[116,117] and nanorods,[103,118] which means that a large body of work made with battery applications in mind is also of relevance for thermochromics.

Core-shell particles attract much interest today, and we note that particles with VO$_2$ cores and Ag or Au shells have been studied by computation.[119] Combinations of Ag and VO$_2$ have also been explored for invoking tunable thermochromism of the near-infrared optical properties by use of metamaterials employing Ag/VO$_2$ hybrid split-ring resonators.[120]

From a practical point of view, VO$_2$ may be awkward to prepare since the vanadium ions are in states with intermediate oxidation and it may be more facile to fabricate materials under nonoxidizing (metallic V) or fully oxidizing (insulating V$_2$O$_5$) conditions. The limitations are not as

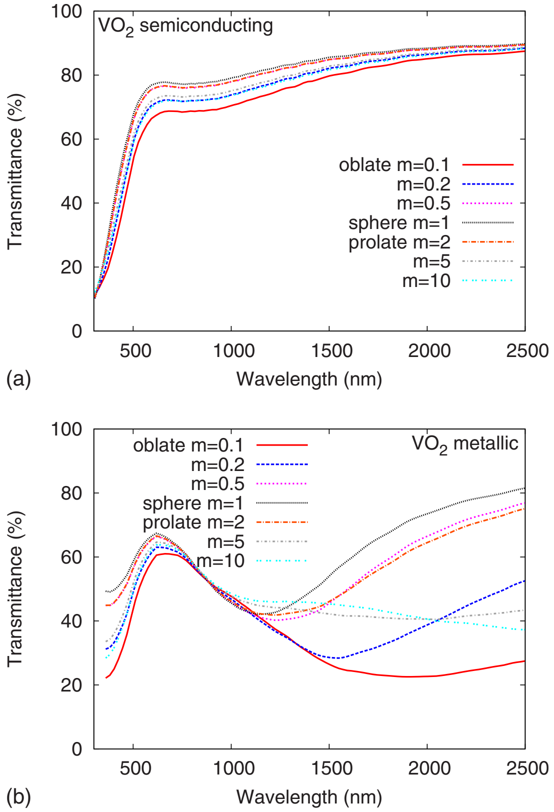

FIG. 7. (Color online) Spectral transmittance for spheroidal VO_2 particles, with shown aspect ratio m and a filling factor of 0.01, dispersed in a dielectric medium. The spheroids are randomly oriented. Parts (a) and (b) refer to VO_2 in semiconducting and metallic states, respectively.

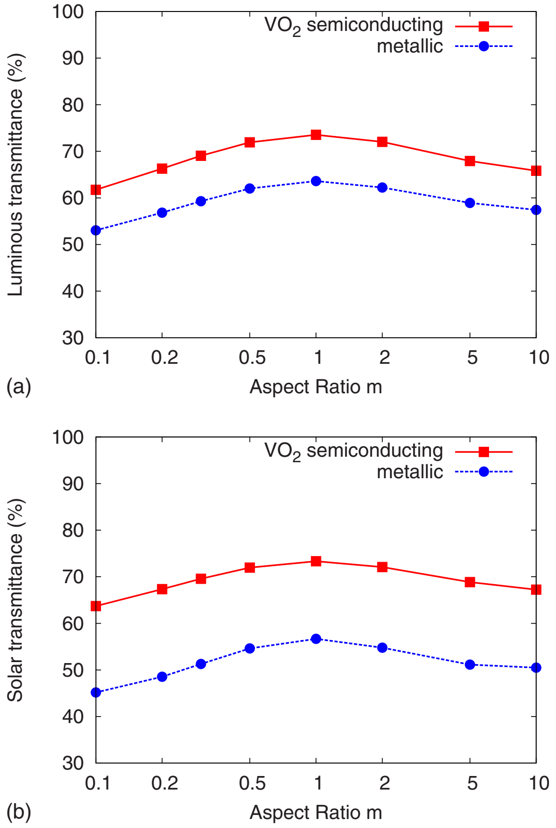

FIG. 8. (Color online) Integrated luminous (a) and solar (b) transmittance for spheroidal VO_2 particles, with shown aspect ratio m and a filling factor of 0.01, dispersed in a dielectric medium. The spheroids are randomly oriented.

stringent as they may seem, though, and it should be observed that metallic vanadium can be transformed to VO_2 by controlled oxidation[121–124] and that insulating V_2O_5 van be transformed to VO_2 by controlled reduction in films.[125–127]

There is a tendency that limited dimensions decreases τ_c and widens the hysteresis in nanocrystalline films[46,48,128–135] and nanorods.[27,28,81,90,118] This may be associated with internal stress in the particles. However, the empirical data are not entirely consistent and we prefer not to discuss the differences between particles and thin films in detail.

V. CONCLUSIONS

The main conclusion of this paper is that nanocomposites with VO_2-type particles offer a number of specific advantages over VO_2-based continuous films in that the composites can show much higher luminous transmittance combined with significantly enhanced solar energy transmittance modulation. These properties make it of interest to reopen the case of energy efficient thermochromic fenestration capable of introducing solar energy below a comfort temperature and rejecting solar energy above a comfort temperature in order diminish the need for space heating and cooling. The present work dealt with VO_2, for which the thermochromic switching temperature is undesirably high but, as we also discussed, decreasing this temperature to a comfort temperature can be done readily by replacing some of the vanadium with tungsten. Furthermore, recent work of ours[26] showed that the inherent luminous absorptance can be diminished by adding a magnesium dopant. The optical properties of VO_2:Mg nanoparticles in dielectric hosts will be investigated in future work.

The thermochromic function can be combined with electrochromics,[136] which is of particular interest for multiple glazing: Here the thermochromic material should be on the inner pane so that it follows the room temperature, while the electrochromic device should be on the outer pane in order to allow for most of the heat due to the electrically adjustable absorption to be dissipated outdoors.[137] The thermochromic and electrochromic components should be thermally decoupled by use of a spacing with minimized radiative heat transfer by implementing a coating with low thermal emittance[8] and, ideally, minimized conductive and convective heat transfer by use of vacuum insulation.[3,138]

Foil materials with desired functionalities are attracting much interest today for energy efficient and comfort enhancing fenestration, and such foils can be integrated in lamination materials suitable for windows in high-rise buildings. Thus high luminous transmittance and minimized solar transmittance can be accomplished in foils incorporating nanoparticles of, in particular, LaB_6;[3,139–141] these foils have static properties. Electrochromic foil, combining nanoporous tungsten oxide and nickel oxide, can achieve large modulation of luminous and solar transmittance along with neutral color and is being investigated for large area applications.[142] The present work shows that thermochromic foil with VO_2-based nanoparticles represents still another option of much interest.

ACKNOWLEDGMENTS

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