Thermochromic vanadium-dioxide-based thin films and nanoparticles: Survey of some buildings-related advances

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Abstract. Today's architecture uses large glazings (windows and glass facades) to obtain good indoors–outdoors contact and day-lighting. However glazings offer challenges and often lead to excessive solar energy inflow and thereby a need for energy-demanding space cooling. This paper summarizes recent work on thermochromic (TC) materials intended for energy-efficient buildings and outlines how vanadium-dioxide-based thin films and nanoparticle composites can be used in TC glazings which admit more solar energy below a comfort temperature than above this temperature, so that the cooling need is diminished, while the transmittance of visible light remains high. We also report on some very recent work on TC light scattering.

1. Introduction

The carbon dioxide content in the earth's atmosphere keeps rising dramatically and has gone from ~315 ppm at the end of the 1950s to ~400 ppm in 2016; furthermore, the rate of increase has almost tripled during this period of time [1]. The growing amount of CO_2 is caused by unrestrained burning of coal, oil and gas, and is widely believed to be of great importance to life on Earth and cause global warming and rising sea levels [2]. The CO_2 level is amplified by increased plant respiration at elevated temperature [3,4]. There may also be many adverse secondary effects of climate change, *e.g.*, reduction of average global incomes [5] and climate-induced proneness to human conflict [6]. Aggravating factors are that the world's population continues to grow and is expected to be 50% larger in 2100 than today [7] and that the population is increasingly accumulated in mega-cities which act as urban heat islands with temperatures significantly above those of the surrounding countryside [8]. The human influence is so pervasive that the present geological era (Antropocene) is distinctly different from the era before the Industrial Revolution (Holocene) [9]. Given this background, it is evident that radical measures should be taken to decarbonize the energy sector, and this highlights the importance of buildings which currently are responsible for 30–40% of the world-wide use of primary energy [10].

Energy efficiency in the built environment is too often disregarded as an opportunity for CO_2 abatement [11] but, in fact, there are numerous emerging "green" technologies that can be harnessed [12-17], and energy efficient glazings (windows and glass facades) are particularly interesting. Glazings often allow too large energy flows to enter or exit a building so that energy-demanding cooling or heating become necessary, but small glazings are not a viable solution to the problem since precious indoors–outdoors contact and day-lighting are then sacrificed. However, energy efficiency can be reached with glazings that allow adjustable throughput of solar energy and visible light, and such glazings are often called "smart" or "intelligent". These glazings make use of chromogenic

materials [18,19], and thermochromic (TC) ones are considered in this paper. TC materials have temperature-dependent properties, and thin films of them can transmit more solar energy at low temperatures than at high temperatures so that energy-efficient glazings can be accomplished and let in solar energy primarily when there is a need for such. TC-based fenestration was proposed almost 30 years ago [20,21] but has not yet made it to the marketplace—for reasons that are explained below—but there have been a number of recent advances that now seem to make practical implications much more likely [22-26]. The present paper is an update of some recent survey papers by one of the authors [27,28].

At this point it is appropriate to introduce some essentials of visible light (luminous radiation), solar irradiance and thermal radiation, which is done in figure 1. Thermal radiation, in panel (a), is governed by blackbody curves—which are shown for four values of the temperature τ—multiplied by a materials-dependent emittance which is less than unity; this radiation occurs at $\lambda > 2 \ \mu$m for ambient temperatures, where λ denotes wavelength. Solar radiation falling onto the earth's atmospheric envelope can be approximated by blackbody-like radiation corresponding to the sun's surface temperature (5505 °C) and lies at $0.2 < \lambda < 3 \ \mu$m. At ground level and under typical clear weather, this radiation is typically the one illustrated in figure 1(b). Finally, visible light is given by the bell-shaped curve in figure 1(b) which covers the $0.4 < \lambda < 0.7 \ \mu$m range and is peaked at 0.55 μm. Quantitative data on luminous (lum) and solar (sol) transmittance, denoted T_{lum} and T_{sol}, respectively, are derived by

$$T_{\mathrm{lum,sol}} = \int d\lambda \ \varphi_{\mathrm{lum,sol}}(\lambda) \ T(\lambda) \ / \int d\lambda \ \varphi_{\mathrm{lum,sol}}(\lambda) \ , \tag{1}$$

where $T(\lambda)$ is spectral transmittance, φ_{lum} is the eye's sensitivity [29] and φ_{sol} is the "air mass 1.5" solar irradiance spectrum (for the sun standing 37° above the horizon) [30]. Analogous formulas pertain to reflectance R.
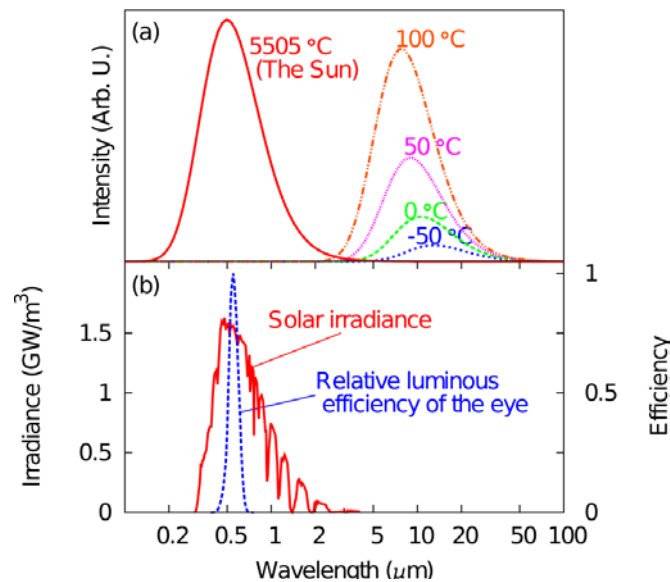

Figure 1. (a) Blackbody spectra for the shown temperatures, which include the surface temperature of the sun (the vertical scales differ for the various spectra). (b) Typical solar irradiance spectrum for clear weather (power per unit area and wavelength increment), and relative spectral sensitivity of the light-adapted human eye.

2. Vanadium dioxide thin films

It is convenient to introduce inorganic TC materials via their temperature-dependent electrical properties [20]. The conductivity changes reversibly and abruptly, sometimes by several orders of

magnitude, at a well-defined "critical" temperature τ_c, the effect being due to a modification of the crystal structure. Vanadium dioxide (VO_2) is particularly interesting since τ_c lies at ~68 °C [31], which is not vastly different from ambient temperature meaning that this material may serve as a starting point for developing TC glazings of interest for buildings. VO_2 changes between a low-temperature ($\tau < \tau_c$) phase with semiconducting properties and high infrared ($\lambda > 0.7\ \mu m$) transmittance as a thin film and a high-temperature ($\tau > \tau_c$) phase with metallic like properties and infrared reflectance. In fact, VO_2-based materials are the *only* inorganic materials considered to be likely candidates for implementation in TC glazings. The mechanism behind the reversible phase change at τ_c has been debated for decades [32] and is still not fully understood.

Figure 2 shows the most important optical properties of VO_2 thin films and nanoparticle deposits. The left-hand panels illustrate $T(\lambda)$ (upper) and $R(\lambda)$ (lower) for 50-nm-thick films in the spectral range of interest for solar radiation and demonstrate that $T(\lambda)$ is much larger in the semiconducting state at $\tau < \tau_c$ than in the metallic-like state at $\tau > \tau_c$ provided that $\lambda > 1\ \mu m$; the difference in $T(\lambda)$ between low and high temperature is increased at longer wavelengths. Clearly VO_2 films have desired properties, in principle, and a TC glazing with such a film lets through more solar energy at a low temperature than at a high temperature [22-26,33-36]. Figure 2 also indicates that $R(\lambda)$ grows monotonically towards longer wavelengths for $\tau > \tau_c$, as expected for a metallic film. The right-hand panels in figure 2 will be discussed later.
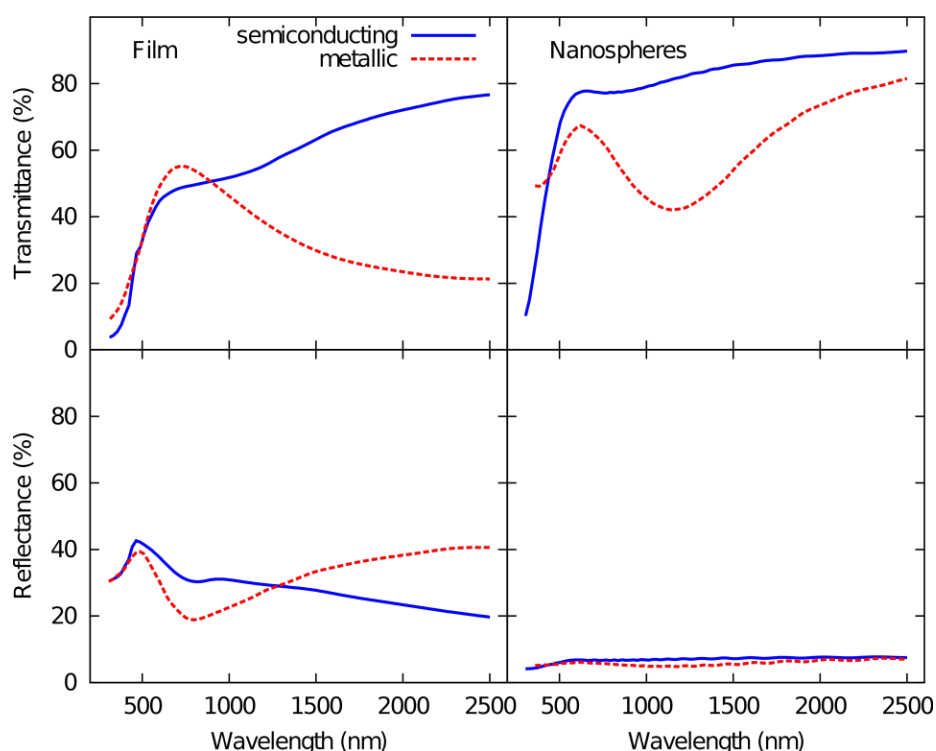

Figure 2. Spectral transmittance (upper panels) and reflectance (lower panels) for a 50-nm-thick VO_2 film (left-hand panels) and for a layer consisting of a dilute dispersion of VO_2 nanospheres, with an equivalent VO_2 thickness of 50 nm, in a medium mimicking transparent glass or polymer.

3. Towards practical VO₂-based thin films for glazings

The VO_2 films need to be modified in order to be of interest for practical glazings. Specifically, we consider three challenges [37]: (*i*) the change between semiconducting and metallic-like states occurs at ~68 °C which clearly is too high for buildings, (*ii*) according to figure 2, T_{lum} is as small as ~40%, which is too low for most practical glazings (a thinner film would yield a larger value of T_{lum} but the

modulation of T_{sol} at τ_c would be very small), and (*iii*) transmittance modulation is pronounced only at wavelengths for which the solar irradiation is weak (see figure 1) so that the solar energy modulation is only ~10% and hence rather insignificant. These three challenges can be met, however.

Challenge (*i*) is easiest, and substituting some percent of the vanadium atoms by tungsten, to make $W_xV_{1-x}O_2$ films, allows τ_c to drop to ~25 °C or lower. Such films have been extensively studied [37], and data are consistent for well-crystallized materials. Several other additives can decrease τ_c, but W appears to be most efficient.

Challenge (*ii*) is connected with short-wavelength optical absorption, which is readily seen in figure 2. This absorption is caused by the undesirably narrow optical band gap in VO_2. Significant improvements can be achieved by adding a band-gap-widening element such as Mg [38,39], certain other alkaline earth metals [39], Zn [40] or Tb [41]. Fluorination, to make films of $VO_{2-z}F_z$, is another option for enhancing T_{lum} [42-44]. The effect of Mg addition is unambiguously caused by band gap widening, as evidenced by both experiments [45] and computations [46,47]. Additions of Mg or Tb lead to decreased values of τ_c, but the effect is not as strong as for W. It was found that T_{lum} could go from 39 to 51% when the Mg content was increased from zero to 7.2% [38].

The VO_2-based thin films must be prepared by a technology that permits large-area coatings, and several techniques involving physical (evaporation, sputter deposition) or chemical vapour deposition can be used, as reported in many publications. Sputter deposition may be of particular interest and is a standard technology for glass coating [48,49]. The substrate temperature typically should be ~450 °C [50] which is not a problem for thin films on glass whereas it offers difficulties for coating of plastic foil (which is an interesting technique since roll-to-roll coating can be particularly inexpensive [51]). Recent work on high-power impulse sputtering (HiPIMS) has demonstrated that the substrate temperature can be lower than for standard magnetron sputtering [52,53] but challenges remain. In general, the deposition of VO_2-based coatings must be judiciously controlled since the vanadium–oxygen phase diagram is exceedingly complex with the most oxygen-rich component being V_2O_5 [54,55]. Deposition in a reactive atmosphere of SO_2, rather than in a more common oxygen atmosphere, may be advantageous and permit a wider range of deposition parameters [26,56].

The fact that VO_2 is not the thermodynamically stable oxide is of interest also with regard to long term durability, which is an obvious requirement for thin films to be used in TC glazings. It has been observed that VO_2 films that are exposed to ambient air tend to gradually convert to V_2O_5, but over-coatings of Al_2O_3 or AlN can effectively prevent this process and impart long-term durability at elevated temperature and humidity [57,58].

4. Nanotermochromism in VO_2-based composites

The small modulation of the solar energy transmittance around τ_c - *i.e.*, item (*iii*) above - has been the most persistent problem for developing TC glazings. However it was recently discovered via calculations that a layer consisting of spheroidal nanoparticles of VO_2 - instead of a continuous VO_2 film—can improve the situation radically [59,60]. This kind of "nanothermochromism" was demonstrated in the right-hand panels in figure 2 above with regard to $T(\lambda)$ and $R(\lambda)$ for a 5-μm-thick layer of a material representative of typical glass or polymer with 1 vol.% of well distributed VO_2 nanospheres. This choice of parameters gives an equivalent VO_2 thickness of 50 nm so that it is possible to compare with the thin-film data also shown in figure 2.

It is now evident that several important features differ among thin films and nanoparticle composites of VO_2: (*i*) the nanoparticles composite is much more transparent than the corresponding thin film, (*ii*) metallic-like nanoparticles at $\tau > \tau_c$ display a deep transmittance minimum in the $0.7 < \lambda < 1.5$ μm range, and (*iii*) the nanoparticles absorb rather than reflect. Item (*ii*) implies that the nanoparticle composite is efficient for lowering the transmittance of solar energy whereas the luminous properties are not strongly influenced. The transmittance minimum corresponds to a peak in optical absorption and is caused by plasmon absorption [61], which occurs for a wavelength interval that is almost ideally located for controlling the solar energy inflow through a transparent TC glazing. The VO_2 nanoparticles must have sizes that are much smaller than the relevant wavelengths in order

not to scatter light [62]. At larger sizes there can be pronounced TC light scattering, which is a newly observed phenomenon to which we return below.

Nanoparticle composites can be made by a variety of routes. Figure 3 reports some recent results on the nanostructure of a VO$_2$–SiO$_2$ composite prepared by reactive magnetron co-sputtering [63]. Scanning electron microscopy (SEM) displayed rounded nanoparticles with sizes of 100–300 nm and energy-dispersive x-ray (EDX) studies indicated that these particles were vanadium-rich. The films showed pronounced nanothermochromism in overall agreement with the results in figure 2(b).
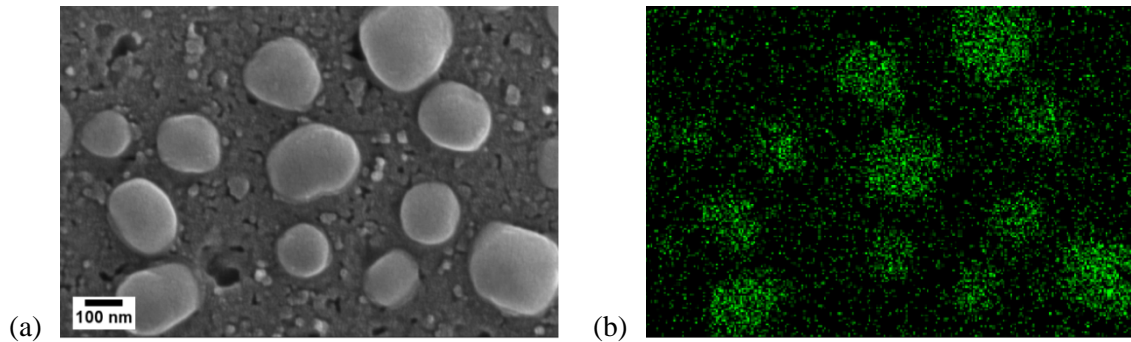

Figure 3. (a) SEM and (b) EDX data for a 220-nm-thick VO$_2$–SiO$_2$ film prepared by sputter deposition; green dots signify vanadium. From Reference 63.

5. Performance limits for thermochromic glazings

The work on VO$_2$-based thin films and nanoparticle composites that has been done during recent years makes it possible to state approximate performance limits for the luminous and solar properties of TC glazings [24]. These limits are reported in figure 4, specifically for T_{lum} at $\tau < \tau_c$ (see Equation 1) and for ΔT_{sol} defined by

$$\Delta T_{\text{sol}} = T_{\text{sol}}(\tau < \tau_c) - T_{\text{sol}}(\tau > \tau_c) . \tag{2}$$

The values of T_{lum} are similar for $\tau < \tau_c$ and for $\tau > \tau_c$. It is desirable to have large magnitudes of both T_{lum} and ΔT_{sol}.
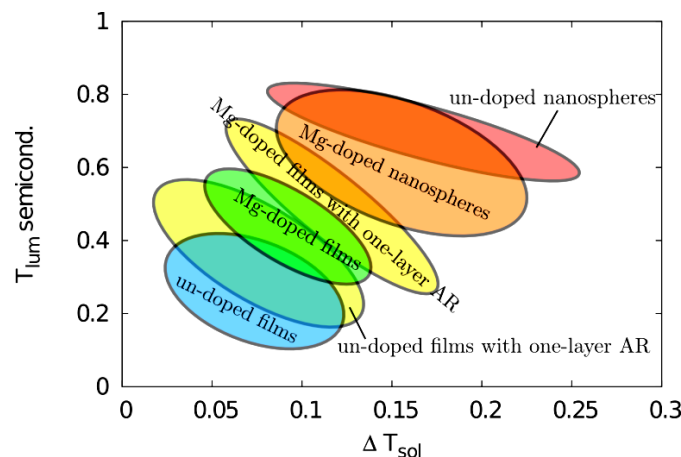

Figure 4. Approximate performance limits for thermochromic glazings incorporating VO$_2$-based materials. Data are shown for luminous transmittance at a low-enough temperature (semiconducting state) and for solar transmittance modulation. AR indicates antireflection. From Reference 24 (reproduced with permission from AIP Publishing LLC).

It is found that thin films of pure VO_2 have low values of T_{lum} and ΔT_{sol}, which highlights that these films are not of much interest for practical TC glazings. Antireflection layers can improve the performance, and particularly good data have been obtained with multilayers of TiO_2 and VO_2 [64,65]. Another possibility is to use "bio-inspired" cone-shaped surface structures to enhance the properties [66]. Mg-containing VO_2 thin films show even better properties, which can be boosted by antireflection treatment. However the best performance is obtained with VO_2 nanoparticles which are able to give $T_{lum} \approx 80\%$ together with $\Delta T_{sol} > 20\%$, and these properties are good enough to point at TC glazings as a viable option for practical implementation in buildings. Perhaps surprisingly, Mg-containing VO_2 nanoparticles do not give better results than pure VO_2 nanoparticles. The reason is that the Mg addition diminishes ΔT_{sol}, and this effect is larger than that of the band gap widening. Some small improvements can be achieved by optimized particle shapes and orientations [59] and by using core–shell structures [60].

6. Thermochromic light scattering

Temperature dependent light scattering is well known in Christiansen filters which combine materials with refractive indices that have strongly different temperature dependencies; these filters are clear when the refractive indices are matched whereas pronounced light scattering occurs when the indices are markedly different and the modulation of light scattering takes place gradually as the temperature is changed [67-69]. Light scattering from VO_2 particles has not attracted much attention in earlier work, but we recently performed an explorative investigation of a TC film with particles as large as ~1 μm [70]. This size is of the same order-of-magnitude as the wavelengths for visible light and solar radiation. The results of this study are summarized below. The applications of strongly scattering materials are not as straight-forward as for thin films and nanoparticle composites in TC glazings, but functional fibre mats [71,72] or other composites [73] may be areas where TC light scattering can be put to use.

Figure 5 shows the microstructure of a VO_2 layer made by sputter deposition onto a substrate that was pre-coated with In_2O_3:Sn (known as ITO) which promotes crystallinity and under certain conditions leads to the growth of particulate thin films [74]. The maximum peak height of the deposit was found to be ~190 nm. The structure seen in the atomic force microscopy (AFM) image was quantified with regard to particle volumes V_p and surface areas S_p using available computer code [75]. In order to enable a theoretical description of light scattering data, we modelled the individual particles by use of two different sets of equivalent sphere radii: either equal-volume spheres characterized by $r_{eq} = (3V_p/4\pi)^{1/3}$ or equal-volume-to-area spheres characterized by $r'_{eq} = 3V_p/S_p$. Prior work has shown that the latter measure can work well for representing light scattering from irregular objects [76]; the particle number is not conserved and there are more equivalent spheres than real particles. Figure 6 illustrates the corresponding radial distributions for r_{eq} and r'_{eq}.

Specular and diffuse transmittance were measured at $\tau < \tau_c$ and $\tau > \tau_c$ by spectrophotometry and there results were used to extract approximate absorption and scattering coefficients, denoted α_{abs} and α_{sca}, respectively; these data are shown in figure 7. Corresponding computed quantities, denoted K^*_{abs} and K^*_{sca}, respectively, were then derived by applying the Lorenz–Mie theory [77,78] to the particle size distributions in figure 6. It is now apparent from figure 7 that the calculations based on the equal-volume-to-area approximation can be reconciled with the experimental data at $\lambda < 0.7$ μm for absorption as well as scattering and at both low and high temperature. The equal-volume approximation clearly is less successful. Hence a semi-quantitative description of TC light scattering seems to be feasible even from highly irregular particles.
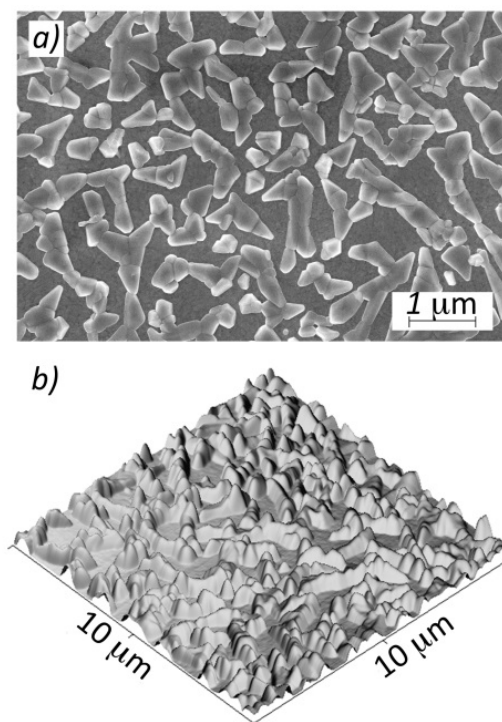
Figure 5. SEM (a) and AFM images (b) of a particulate VO_2 layer. From Reference 70 (reproduced with permission from AIP Publishing LLC).
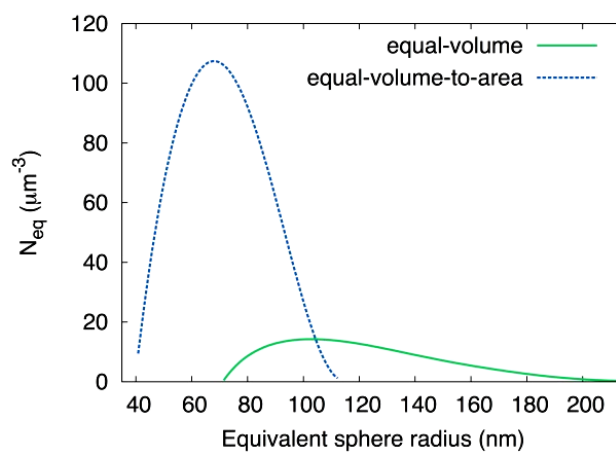

Figure 6. Distributions of the number N_{eq} of equivalent sphere radii for the data shown in figure 4(b). From Reference 70 (reproduced with permission from AIP Publishing LLC).
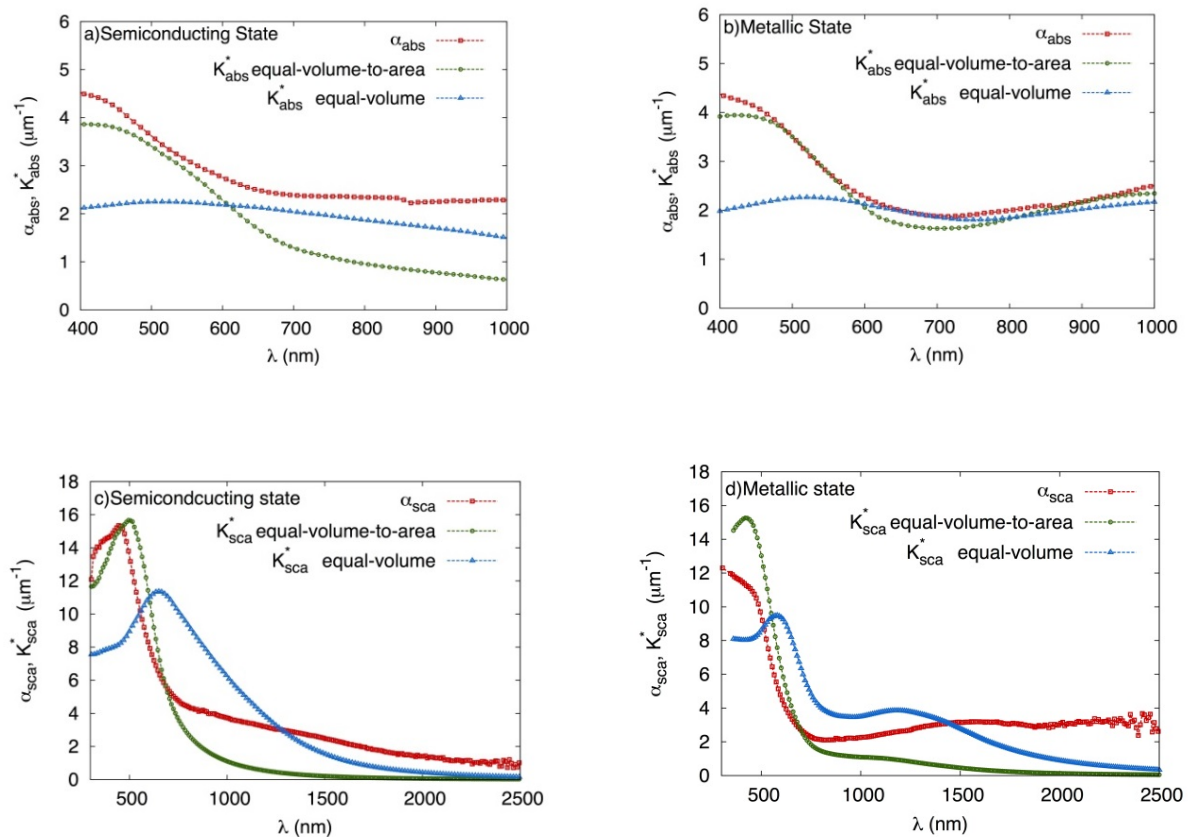
Figure 7. Experimental (α_{abs}) and theoretical (K^*_{abs}) spectral absorption data, and corresponding results for experimental (α_{sca}) and theoretical (K^*_{sca}) spectral scattering data, for the VO$_2$ sample depicted in Figure 5. The calculations used the equal-volume and equal volume-to area approximations in figure 6. Data are given for the semiconducting state at $\tau < \tau_c$ [panels (a) and (c)] and the metallic state at $\tau > \tau_c$ [panels (b) and (d)]. From Reference 70 (reproduced with permission from AIP Publishing LLC).

7. Summary and conclusions

This article summarized a large body of recent computational and experimental results for thermochromic VO$_2$-based thin films and nanoparticle composites and discussed their potential for applications in glazings in energy-efficient buildings. It is our contention that such glazings can be made with properties that make them interesting for practical applications. In particular, nanothermochromism seems to offer new possibilities and VO$_2$ nanoparticles may be incorporated in functionalized glass laminates—perhaps even in the electrolyte layer in a combined electrochromic–thermochromic glazing. We also summarized recent work that indicates that thermochromic light scattering can be achieved and theoretically understood.

Acknowledgement

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