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

Claes G Granqvist, Yu-Xia Ji, José Montero and Gunnar A Niklasson

Department of Engineering Sciences, The Ångström Laboratory, Uppsala University, P.O. Box 534, SE-75121 Uppsala, Sweden

E-mail: claes-goran.granqvist@angstrom.uu.se

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 (Anthropocene) 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 \( \lambda \) 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 \( \mu m \). Quantitative data on luminous (lum) and solar (sol) transmittance, denoted \( T_{lum} \) and \( T_{sol} \), respectively, are derived by

\[
T_{lum,sol} = \int d\lambda. \phi_{lum,sol}(\lambda) \cdot T(\lambda) / \int d\lambda. \phi_{lum,sol}(\lambda),
\]

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

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 \( \tau_c \), the effect being due to a modification of the crystal structure. Vanadium dioxide (VO\(_2\)) is particularly interesting since \( \tau_c \) lies at \( \sim 68 \) °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 (\( \lambda > 0.7 \) μm) 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 \( \tau_c \) 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 \( \lambda > 1 \) μm; 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 VO\(_2\)-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 \( \sim 68 \) °C which clearly is too high for buildings, (ii) according to figure 2, \( T_{\text{lim}} \) is as small as \( \sim 40\% \), which is too low for most practical glazings (a thinner film would yield a larger value of \( T_{\text{lim}} \) but the
modulation of $T_{soc}$ at $\tau_c$ 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,V$_{1-x}$O$_2$ films, allows $\tau_c$ 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 $\tau_c$, 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$_{2-x}$F$_x$, is another option for enhancing $T_{soc}$ [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 $\tau_c$, but the effect is not as strong as for W. It was found that $T_{soc}$ 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$_2$O$_5$ [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$_2$O$_5$, but over-coatings of Al$_2$O$_3$ or AlN can effectively prevent this process and impart long-term durability at elevated temperature and humidity [57,58].

4. Nanothermochromism in VO$_2$-based composites

The small modulation of the solar energy transmittance around $\tau_c$ - 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](image)

**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 $T_{\text{lum}}$ at $\tau < \tau_c$ (see Equation 1) and for $\Delta T_{\text{sol}}$ defined by

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

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

![Figure 4](image)

**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 $T_{\text{lum}}$ and $\Delta T_{\text{sol}}$, 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 $T_{\text{lum}} \approx 80\%$ together with $\Delta T_{\text{sol}} > 20\%$, 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 $\Delta T_{\text{sol}}$, 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 $\mu$m [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$_2$O$_3$: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 $\alpha_{abs}$ and $\alpha_{sca}$, 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 $\lambda < 0.7$ $\mu$m 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 ($\alpha_{abs}$) and theoretical ($K_{abs}^*$) spectral absorption data, and corresponding results for experimental ($\alpha_{sca}$) 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
This paper was presented at the INERA Conference on “Vapor Phase Technologies for Metal Oxide and Carbon Nanostructures”, July 5–9, 2016, in Velingrad, Bulgaria. The conference is part of the INERA REPGOT project of the Institute of Solid State Physics, Bulgarian Academy of Sciences. The work was financially supported by the European Research Council under the European Community’s Seventh Framework Program (FP7/2007–2013)/ERC Grant Agreement No. 267234 (“GRINDOOR”).
References

[1] U.S. Department of Commerce, National Oceanic and Atmospheric Administration, Earthscan System Research Laboratory, Global Monitoring Division http://www.esrl.noaa.gov/gmd/ccgg/trends/index.html

[2] Stocker T F, Qin D, Plattner G-K, Tignor M M B, Allen S K, Boschung J, Nauels A, Xia Y, Bex V and Midgley P M, editors (2013). Climate Change 2013: The Physical Science Basis. Working Group I Contribution to the Fifth Assessment Report on the Intergovermental Panel on Climate Change (Cambridge University Press, New York, NY, USA)

[3] Heimann M and Reichstein M 2008 Nature 451 289

[4] Reich P B, Sendall K M, Stefanski A, Wei X, Rich R L and Montgomery R A 2016 Nature 531 633

[5] Burke M, Hsiang S M and Miguel E 2015 Nature 527 235

[6] Kelley C P, Mohtadi S, Cane M A, Seager R and Kushnir Y 2015, Proc. US Natl. Acad. Sci. 112, 3241

[7] United Nations Department of Economic and Social Affairs 2015 World Population Prospects: The 2015 Revision (United Nations, New York, USA)

[8] Akbari H, Cartalis C, Kolokotsa D, Muscio A, Pisello A L, Rossi F, Santamouris M, Synnefa A, Wong N H and Zinzi M 2016 J Civil Engr Management 22 DOI: 10.3846/13923730.2015.1119194

[9] Waters C N et al. 2016 Science 351 137

[10] United Nations Environmental Programme 2009 Buildings and Climate Change: Summary for Decision-Makers (UNDP Sustainable Buildings & Climate Initiative, Paris, France)

[11] Richter B, Goldston D, Crabtree G, Glicksman L, Goldstein D, Greene D, Kammen D, Levine M, Lubell M, Savitz M, Sperling D, Schlachter F, Scolfield J and Dawson J. 2008 Rev. Mod. Phys. 80 S1

[12] Smith G B and Granqvist C G 2010 Green Nanotechnology: Solutions for Sustainability and Energy in the Built Environment (CRC Press, Boca Raton, FL, USA)

[13] Ginley D S and Cahen D, editors 2012 Fundamentals of Materials for Energy and Environmental Sustainability (Cambridge University Press, Cambridge, UK)

[14] Pacheco-Torgal F, Diamanti M V, Nazari A and Granqvist C G, editors 2013 Nanotechnology in Eco-Efficient Construction (Woodhead, Cambridge, UK)

[15] Pacheco-Torgal F, Mistretta M, Kauklauskas A, Granqvist C G and Cabeza L F, editors 2013 Nearly Zero Energy Building Refurbishment (Springer, London, UK)

[16] Pacheco-Torgal F, Labrincha J A, Cabeza L F and Granqvist C G, editors 2015 Eco-Efficient Materials for Mitigating Building Cooling Needs: Design, Properties and Applications (Woodhead, Cambridge, UK)

[17] Pacheco-Torgal F, Buratti C, Kalaiselvam S, Granqvist C G and Ivanov V editors 2016 Nano and Biotech Based Materials for Energy Building Efficiency (Springer International Publishers, Cham, Switzerland)

[18] Granqvist C G 1990 Crit Rev Solid State Phys Mater Sci 16 291

[19] Lipert C M and Granqvist C G, editors 1990 Large-Area Chromogenics: Materials and Devices for Transmittance Control, SPIE Institutes for Advanced Optical Technologies, Vol. 4 (SPIE Opt Engr Press, Bellingham, WA, USA)

[20] Jorgenson G V and Lee J C 1986 Sol Energy Mater 14 205

[21] Babulananam S M, Eriksson T S, Niklasson G A and Granqvist C G 1987 Sol Energy Mater 16 347

[22] Gao Y, Luo H, Zhang Z, Kang L, Chen Z, Du J, Kanehira M and Cao C 2012 Nano Energy 1 221

[23] Hoffmann S, Lee E S and Clavero C 2014 Sol Energy Mater Sol Cells 123 66

[24] Li S-Y, Niklasson G A and Granqvist C G 2014 J Appl Phys 115, 053513

[25] Warwick M E A and Binions R 2014 2014 J Mater Chem A 2 3275
[60] Li S-Y, Niklasson G A and Granqvist C G 2011 J Appl Phys 109 113515
[61] Lopez R, Haynes T E, Boatner L A, Feldman L C and Haglund Jr R F 2002 Opt Lett 27 1327
[62] Laaksonen K, Li S-Y, Puisto S R, Rostedt N K J, Ala-Nissila T, Granqvist C G, Nieminen R M and Niklasson G A 2014 Sol Energy Mater Sol Cells 130 132
[63] Ji Y-X, Niklasson G A and Granqvist C G 2016 To be published
[64] Mlyuka N R, Niklasson G A and Granqvist C G 2009 Phys Status Solidi A 206 2155
[65] Chen Z, Gao Y, Kang L, Du J, Zhang Z, Luo H, Miao H and Tan G 2011 Sol Energy Mater Sol Cells 95 2677
[66] Taylor A, Parkin I, Noor N, Tummelshammer C, Brown M S and Papakonstantinou I 2013 Opt Expr 21 A750
[67] Christiansen C 1884 Ann Phys Chem 23 298
[68] Clarke R H 1968 Appl Opt 7 861
[69] Andersson A M, Niklasson G A and Granqvist C G 1987 Appl Opt 26 2164
[70] Montero J, Ji Y-X, Granqvist C G and Niklasson G A 2016 J Appl Phys 119 085302
[71] Li S, Li Y, Qian K, Ji S, Luo H, Gao Y and Jin P 2014 ACS Appl Mater Interfaces 6 9
[72] Qian K, Li S, Ji S, Li W, Li Y, Chen R and Jin P 2014 Ceram Int 40 14517
[73] Moot T, Palin C, Mitran S, Cahoon J F and Lopez R 2016 Adv Opt Mater to be published
[74] Montero J, Ji Y-X, Li S-Y, Niklasson G A and Granqvist C G 2015 J Vac Sci Technol B 33 031805
[75] Néčas D and Klapetek P 2012 Centr Eur J Phys 10 181
[76] Grenfell T C and Warren S G 1999 J Geophys Res Atm 104 31697
[77] Mie G 1908 Ann Phys 330 377
[78] Bohren C F and Huffman D R 1983 Absorption and Scattering of Light by Small Particles (Wiley, New York, USA)