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Citation for the original published paper (version of record):

Granqvist, C., Bayrak Pehlivan, I., Ji, Y., Li, S., Niklasson, G. (2014)

Electrochromics and thermochromics for energy efficient fenestration: Functionalities based on nanoparticles of $\text{In}_2\text{O}_3:\text{Sn}$ and VO_2 .

Thin Solid Films, 559: 2-8

<http://dx.doi.org/10.1016/j.tsf.2013.10.033>

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N.B. When citing this work, cite the original published paper.

Permanent link to this version:

<http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-227175>

Electrochromics and Thermochromics for Energy Efficient Fenestration: New Functionalities Based on Nanoparticles of $\text{In}_2\text{O}_3\text{:Sn}$ and VO_2

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Abstract

Windows incorporating electrochromic (EC) and thermochromic (TC) materials are of great interest for today's and tomorrow's buildings and can create energy efficiency jointly with indoor comfort. This paper summarizes several recent studies and shows that nanoparticles of transparent conducting oxides—specifically $\text{In}_2\text{O}_3\text{:Sn}$ (ITO) and thermochromic VO_2 —can lead to new functionalities. We consider three examples: (i) the use of ITO nanoparticles in conventional polaronic EC devices in order to suppress near-infrared solar transmittance, (ii) performance limits for novel plasmonic EC devices based on ITO nanoparticles, and (iii) ITO– VO_2 -based nanocomposites combining low thermal emittance with TC properties. We also consider Mg doping of VO_2 to enhance the luminous transmittance and $\text{Al}_2\text{O}_3/\text{VO}_2$ double layers with improved durability. Both experimental and theoretical results are reported.

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1. Introduction

Electrochromic (EC) and thermochromic (TC) fenestration make it possible to control the inflow of visible light and solar energy into buildings and can create energy efficiency along with indoor comfort. The purpose of this paper is to summarize some very recent work in which transparent conducting nanoparticles have been used to achieve new and improved functionalities.

Electrochromics and thermochromics lie in the realm of “green nanotechnology” [1] which enjoys intense current interest. In order to understand this interest, we first contemplate the World’s population and its ties to our common environment. The population has grown from roughly one billion in 1800 to about 2.5 billion in 1950 and is somewhat above seven billion at present (2013). The growth is not forecast to level off until around the year 2100, and then it has reached ten billion or more [2]. At the same time there is an improvement in the general living standard, and people in the poor countries expect, as they should, to have the same qualities of life and amenities as those in the richer countries. The growth of population *and* living standards leads to rapidly rising demands on Earth’s resources and an unsustainable demand on energy, water, minerals, etc. The energy is largely based on coal, oil, gas, and firewood, which release carbon dioxide into the atmosphere and lead to global warming, rising sea level, and other strains on our biosphere [3]. The effects of a growing average global temperature are aggravated since about half of the world’s population now lives in cities which act as “urban heat islands” with temperatures several degrees above those of the surrounding countryside [4]. The increasing temperatures have a clear connection to human mortality due to cardiovascular, cerebrovascular and respiratory diseases [5], and even to violent human conflict [6].

About 30 to 40 % of the World’s primary energy is spent in buildings sector and is used for heating, cooling, lighting, ventilation, and appliances [7]. The fraction of electricity that goes into buildings is even higher and can amount to as much as ~70 % [8,9]. For the US, where detailed information is available [10], the buildings’ part of the primary energy consumption was 41 % in 2010, which can be compared with 34, 36, and 38 % in 1980, 1990, and 2000, respectively. The high fraction for space cooling is connected with what has been fondly termed “America’s romance with air conditioning” [11].

The energy use in buildings is huge, but so is the savings potential and a recent study for the USA argues that as much as 70 % could be saved in new buildings by the year 2030, and perhaps more than 90 % in the long term [9]. It is essential to note that energy efficiency in buildings can be decoupled from discomfort, which is of the greatest importance since we spend of the order of 80 to 90 % of our time indoors, in buildings and vehicles [12], in the rich countries. Another important observation is that good energy performance may come with a financial premium, and recent market transactions in the USA indicated that “green” buildings can command higher rental rates and selling prices than comparable “non-green” buildings [13].

We now turn to windows, which are important for the considerations above since they are weak links in the buildings’ energy system and more often than not let in or let out too much energy which must be compensated by space cooling or space heating. Making the windows small (or non-existent) is not a solution since they are needed for visual indoors–outdoors contact and for day-lighting, which are precious qualities and essential for human well-being and for good task performance [14].

Energy efficient windows must operate in harmony with Nature and we consider the electromagnetic radiation in our natural ambience [1,15]. It is natural to start with thermal radiation, which is governed by a black-body spectrum multiplied by a materials-dependent emittance. Fig. 1 shows that black-body radiation lies in the $3 < \lambda < 50 \mu\text{m}$ wavelength range for the relevant temperature bracket, between -50 and $+100 \text{ }^\circ\text{C}$. Solar radiation, as also shown, comes at $0.3 < \lambda < 3 \mu\text{m}$, i.e., at wavelengths that are shorter and almost not overlapping with those for thermal radiation. Solar irradiation at Earth’s ground level essentially is the black-body spectrum for the Sun’s surface temperature multiplied by the spectral transmittance through the atmosphere. The human eye detects only the short-wavelength portion of the solar spectrum and has a bell-shaped sensitivity curve at $0.4 < \lambda < 0.7 \mu\text{m}$ with a peak at $0.55 \mu\text{m}$ as illustrated in Fig. 1.

Quantitative data on the luminous and solar transmittance of a surface—denoted T_{lum} and T_{sol} —will be used repeatedly in the discussions below. They are derived by averaging according to

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

where $T(\lambda)$ is spectral transmittance, φ_{lum} is the sensitivity of the light-adapted human eye [16] and φ_{sol} is solar irradiance for air mass 1.5 (i.e., the sun at 37° above the horizon) [17].

Ambient radiation is different during the day and year. To account for, or compensate for, this variability, one needs materials with properties that can be changed reversibly and persistently via some external stimulus. These materials are called “chromogenic” [18,19]: the most well known may be the *photochromic* ones, whose optical transmittance decreases under ultraviolet irradiation and increases to the original value in the absence of such irradiation. *Thermochromic* materials have different optical properties depending on their temperature, and *electrochromic* materials are able to change their properties in response to an applied electrical current or voltage. There are also *gasochromic* materials with optical properties depending on whether they are exposed to oxidizing or reducing gases.

Windows with chromogenic materials can impart energy efficiency and comfortable indoor environments, as discussed in numerous studies which also highlight other benefits such as downsizing of air conditioning systems, natural lighting, and occupant satisfaction [20–23]. It was stated recently that well-insulated EC windows used in commercial and residential buildings in USA would be able to save as much as ~4.5 % of the annual energy expenditure [24]. The energy benefits of the EC smart windows are critically dependent on their control strategies [25,26] and should consider whether persons are present or not in rooms equipped with such fenestration. The energy boon of TC windows has not received as much attention, but some recent investigations point at substantial savings [27,28].

The purpose of this paper is to summarize a number of recent studies involving nanoparticles of transparent electrical conductors, specifically $\text{In}_2\text{O}_3:\text{Sn}$ (i.e., indium tin oxide, known as ITO) and thermochromic VO_2 . The first study considers a standard (“polaronic”) EC device with a transparent polymer electrolyte and demonstrates experimentally as well as theoretically that the near-infrared (NIR) part of the solar irradiation can be absorbed very efficiently by ITO nanoparticles dispersed in the electrolyte, and that this functionality does not interfere much with the optical properties of visible light [29]. The second investigation regards a novel (“plasmonic”) EC device based on ITO nanoparticles and reports computed performance limits on the optical modulation [30]. Thirdly, we study nanocomposites of ITO and VO_2 and demonstrate that a temperature-dependent modulation of the NIR transmittance can be combined with low thermal emittance and electrical conductivity irrespectively of the temperature [31]. The latter study also regards the durability of VO_2 during extended heat treatment as well as recent work [32] on $\text{VO}_2:\text{Mg}$ which demonstrates that this doping can lower the luminous absorption in VO_2 to a significant degree. The present paper is an extension of two recent conference presentations [33,34].

2. Polaronic electrochromism: A polymer electrolyte with near-infrared-absorbing ITO nanoparticles

The standard “battery-type” EC window has a centrally positioned electrolyte, which can be an inorganic thin film, a polymer electrolyte layer, or an ionic liquid. The electrolyte joins two EC thin films, ideally one coloring under ion insertion (“cathodically”) and another coloring under ion extraction (“anodically”), and this three-layer stack is surrounded by transparent electrical conductors [35–37]. Reversible and persistent transmittance modulation occurs when a voltage is applied to the transparent electrical conductors. The physical mechanism responsible for the electrochromism is generally believed to be polaronic and based on electron transfer between adjacent transition metal ions [35,36]. The polymer-based construction permits long open-circuit memory and uniform color changes, and it is also advantageous for large-scale manufacturing [37,38]. We earlier considered a PEI–LiTFSI model electrolyte and investigated ion relaxation [39,40], mechanical properties [41], and the addition of SiO₂ nanoparticles for improving ionic conductivity without deteriorating the optical performance [42].

In the present work we used PEI–LiTFSI with maximum ion conductivity [39,40] to which we added up to 7 wt.% of ITO nanoparticles with a Sn/In ratio of 5 at%. The nanoparticles were prepared through collaboration with the Lawrence Berkeley National Laboratory [29,43]. Transmission electron microscopy studies of colloidal ITO nanoparticles—prior to ligand exchange being part of the preparation procedure—showed diameters D of 13 ± 3 nm. The spectral absorbance for these ITO nanoparticles had a strong peak at $\lambda \approx 1830$ nm.

Temperature-dependent ionic conductivity $\sigma(\tau)$ was determined by impedance spectroscopy in the $10^{-1} - 10^7$ Hz frequency range and at $23 < \tau < 70$ °C, as described in earlier papers [39–42]. Fig. 2 reports σ at six temperatures for samples with the shown ITO contents and demonstrates that the ionic conductivity is practically independent of the ITO nanoparticles and goes monotonically from $\sim 1 \times 10^{-6}$ S/cm at 23 °C to $\sim 2 \times 10^{-5}$ S/cm at 70 °C.

Spectral total and diffuse transmittance and reflectance were measured at $300 < \lambda < 2500$ nm for 70 ± 10 μ m thick (PEI–ITO)–LiTFSI layers. The diffuse spectral components were < 1 % in transmittance and < 0.3 % in reflectance and therefore negligible. The solid curves in Fig. 3 show $T(\lambda)$. In the absence of ITO, the transmittance is large for $\lambda < 1500$ nm, and

absorption features caused by PEI can be observed at $\lambda > 1500$ nm. When ITO is added, one finds a strong decrease of the NIR transmittance while T_{lum} remains high, which is caused by an absorption band with an intensity depending on the amount of ITO. T_{lum} drops marginally from 91.7 to 83.3 % when the ITO content goes from zero to 7 wt.% while the associated drop of T_{sol} is much larger and it goes from 88.9 to 56.3 %.

The optical data shown in Fig. 3 could be interpreted from effective medium theory since $D \ll \lambda$. There are several formulations of such theories, and those by Maxwell-Garnett [44,45] and Bruggeman [46] are frequently used; predictions from them coincide in the dilute limit which is applicable here. The Bruggeman (Br) theory yields an effective dielectric function ϵ^{Br} from

$$f \frac{\epsilon_{ITO} - \epsilon^{Br}}{\epsilon_{ITO} + 2\epsilon^{Br}} + (1-f) \frac{\epsilon_m - \epsilon^{Br}}{\epsilon_m + 2\epsilon^{Br}} = 0 \quad , \quad (2)$$

where ϵ_{ITO} and $\epsilon_m = 2.25$ are the dielectric functions for ITO and the polymer electrolyte, respectively, and $f \equiv f_{ITO}$ is the “filling factor” (i.e., volume fraction) for ITO. The calculation of ϵ_{ITO} was performed as reported before [47] and assumed a free electron plasma with singly charged tin impurities screened as described by the random phase approximation [48] with exchange represented by Hubbard’s approach [49].

We first modeled spectral absorbance using an empirical free electron density n_e —which is a basic parameter in the theory for ϵ_{ITO} —of $0.98 \times 10^{21} \text{ cm}^{-3}$. This value is of the expected magnitude [47] and was subsequently used to produce the data in Fig. 3. Theory and experiment are found to be in good semi-quantitative agreement in all of the studied samples.

3. Plasmonic electrochromism: Approximate performance limits

A novel approach to electrochromism, fundamentally different from the one discussed above, was put forward recently by Milliron et al. [50,51], and it was demonstrated that transmittance modulation—especially in the NIR—can be obtained electrochemically in layers with nanoparticles of ITO and of the closely related material ZnO:Al. This discovery opens ways to employ plasmonic effects, rather than the earlier discussed polaronic one, to modulate T_{sol} while T_{lum} remains high.

Conduction electrons in ITO constitute a free-electron plasma with a density n_e and a (screened) plasma frequency ω_p at

$$\omega_p \approx [n_e e^2 / (\epsilon_0 \epsilon_\infty m_c^*)]^{1/2}, \quad (3)$$

where e is electron charge, ϵ_0 is permittivity of free space, ϵ_∞ is high-energy dielectric constant, and m_c^* is effective conduction-band mass for the electrons. ITO films can display electron densities as high as $\sim 2.5 \times 10^{21} \text{ cm}^{-3}$ [52] and similar values of n_e have been reported for ZnO-based films [52]. The corresponding plasmon resonance at ω_p lies in the NIR or red end of the luminous spectrum. The interesting recent discovery by Milliron et al. [50,51] is that the plasmon frequency of ITO and ZnO:Al nanoparticles can be tuned by electrochemical post-treatment, which modulates n_e most probably via dynamic accumulation and depletion layers on the surfaces of the nanoparticles. The plasma absorption can then be swept across the NIR range, implying that a variable part of the solar radiation is absorbed while the luminous absorption is much less affected.

The optical properties of ITO nanoparticles in a dielectric medium can be calculated as indicated above, and the upper panel of Fig. 4 shows spectral absorptance for a 5- μm -thick layer of ITO nanoparticles in a medium with $\epsilon_m = 2.25$; the latter value is characteristic for typical solvents, polymers and glasses. It is obvious that the peak moves from long wavelengths to $\sim 1300 \text{ nm}$ when n_e is increased to $2 \times 10^{21} \text{ cm}^{-3}$. The lower panel of Fig. 4 shows absorptance for $n_e = 1 \times 10^{21} \text{ cm}^{-3}$ and layer thicknesses in the $1 \leq d \leq 100 \mu\text{m}$ range and demonstrates that high absorptance extends over a large part of the NIR for the largest values of d while the luminous absorptance is low.

Quantitative data on $T_{\text{lum}}(d, n_e)$ and $T_{\text{sol}}(d, n_e)$ were derived from Eq. (1) and are reported in Fig. 5, which shows that each value of T_{lum} has a corresponding well-defined minimum solar transmittance, denoted $T_{\text{sol}, \text{min}}$. The relationship can be fitted to an empirical expression, given by the curve in Fig. 5, as $T_{\text{sol}, \text{min}} \approx -1.03 + 5.94T_{\text{lum}} - 9.26(T_{\text{lum}})^2 + 5.27(T_{\text{lum}})^3$, which is an approximate performance limit for a device with plasmon-induced electrochromism based on transparent conducting nanoparticles.

The performance limit is valid not only for ITO but the same theory can be used also for transparent conductors based on ZnO [53] and SnO_2 [54], implying that there is significant freedom in the choice of material. A limitation to dilute nanoparticle composites is important, though, since otherwise particle–particle interactions widen the plasmon absorption compared to the data in Fig. 4 and strong NIR absorption extends into the luminous range. Similar broadening is important if nanoparticle clustering or non-spherical shapes are prevalent. The maximum layer thickness was put to $100 \mu\text{m}$, which is arbitrary, and by going to much thicker layers it is possible to reach values of $T_{\text{sol}, \text{min}}$ that are 0.01 to 0.02 lower than those in Fig. 5

for a given T_{lum} . Furthermore, the optical properties of the layers are considered to be isotropic, but strongly anisotropic properties—obtained for example via aligned nanorods—might yield somewhat improved performance limits, and the same would be the case for a judicious choice of nanoparticles with different electron densities.

4. Thermochromics: ITO–VO₂ nanocomposites with low thermal emittance

Vanadium dioxide is a well known TC material which has been considered for energy efficient fenestration for decades [1,27,52,55,56]. Bulk VO₂ is monoclinic, semiconducting and infrared-transparent for $\tau < \tau_c$, where τ_c is a “critical” temperature at about 68 °C, and is tetragonal, metallic-like and infrared-reflecting at $\tau > \tau_c$ [57]. This material has to be modified in order to be of interest for applications in practical fenestration [56], specifically (i) τ_c should be decreased to a value around room temperature, (ii) the film should have a high enough T_{lum} , and (iii) T_{sol} should drop significantly for $\tau > \tau_c$. This change in solar energy transmittance is denoted ΔT_{sol} and defined by

$$\Delta T_{\text{sol}} \equiv T_{\text{sol}}(\tau < \tau_c) - T_{\text{sol}}(\tau > \tau_c) \quad . \quad (4)$$

Requirement (i) can be met by doping with tungsten and some other metals [52,56,58], but (ii) and (iii) have remained challenging. However we recently demonstrated by computation that a VO₂-based material comprising nanoparticles—rather than being a thin film—enhances T_{lum} and ΔT_{sol} and makes thermochromics much more promising for windows in buildings than it was before [56,59,60].

Coatings which combine low thermal emittance E_{therm} and thermochromism irrespectively of temperature have not attracted much attention, although some recent studies have dealt with VO₂ films with extremely thin top layers of Pt [61] or ZnO:Al [62]. The best films of this kind attained a modest combination of $T_{\text{lum}} \approx 46$ %, $\Delta T_{\text{sol}} \approx 4$ %, and $E_{\text{therm}} \approx 30$ %. However, there are other possibilities [31], and we next report computed data for a heavily doped wide band gap semiconductor incorporating VO₂ nanoparticles. ITO is used, as in the studies of electrochromism in Secs. 2 and 3 above, as this material can produce an excellent combination of high T_{lum} and low E_{therm} [47].

The computations consider a random mixture of nanoparticles of VO₂ and ITO and employ Bruggeman theory [46] to derive an effective dielectric function ε^{Br} by

$$f \frac{\epsilon_{VO_2} - \epsilon^{Br}}{\epsilon_{VO_2} + 2\epsilon^{Br}} + (1-f) \frac{\epsilon_{ITO} - \epsilon^{Br}}{\epsilon_{ITO} + 2\epsilon^{Br}} = 0 \quad , \quad (5)$$

with $f \equiv f_{VO_2}$. We took ϵ_{VO_2} from earlier work on 50-nm-thick sputter deposited VO_2 films [63], while ϵ_{ITO} was based on measurements on high-quality ITO films with $n_e = 6.2 \times 10^{20} \text{ cm}^{-3}$ [47]. These data are almost identical to the theoretical values on ϵ_{ITO} used above.

Spectral and temperature-dependent transmittance and reflectance were calculated from ϵ^{Br} at $300 < \lambda < 2500 \text{ nm}$. Specifically, Fig. 6 reports data for ITO- VO_2 composites with an ITO mass thickness kept at 200 nm and a VO_2 mass thickness varied so that the filling factors lay in the range $0.1 \leq f \leq 0.5$. The ITO nanoparticles are then percolating—i.e., electrically connected—and they approach the properties of an ITO film with a moderately strong plasma absorption in the NIR [47]. A TC effect can be seen in the full spectral interval, and the reflectance rises monotonically for $\lambda > 1000 \text{ nm}$ and attains $\sim 60 \%$ at $\lambda = 2500 \text{ nm}$ for $\tau > \tau_c$. The results for $\tau < \tau_c$ and for films with low values of f agree with earlier determinations of spectral reflectance for 200-nm-thick ITO films [47], which showed $E_{\text{therm}} \approx 20 \%$. An addition of VO_2 increases E_{therm} but the ITO- VO_2 films nevertheless are low-emittance coatings, especially for small contents of VO_2 .

Values of T_{lum} and T_{sol} were calculated from Eq. (1), and ΔT_{sol} was derived from Eq. (4). Fig. 7 shows data for these parameters at $\tau < \tau_c$ and $\tau > \tau_c$ vs VO_2 content. It is found that T_{lum} and T_{sol} decrease monotonically when f is increased. The integrated transmittance is larger for $\tau < \tau_c$ than for $\tau > \tau_c$, and the differences are similar for T_{lum} and for T_{sol} . It then follows that the TC effect is significant in the entire solar range. It is seen that $\Delta T_{\text{sol}} = 10 \%$ occurs at $f \approx 0.196$ and is consistent with $T_{\text{lum}} \approx 59.7 \%$ at $\tau < \tau_c$ and $T_{\text{lum}} \approx 51.1 \%$ at $\tau > \tau_c$. A broad maximum of ΔT_{sol} occurs at $\sim 12.8 \%$ for $f \approx 0.35$.

5. Further considerations of thermochromic VO_2 : Band gap widening and durability

It is evident from Fig. 6 that the transmittance drops sharply at $\lambda < 500 \text{ nm}$, which is caused by the main optical band gap of VO_2 being undesirably low. Mg doping can widen the band gap, however, as discovered recently [64]. This effect is elaborated in Fig. 8, taken from a recent paper by Hu et al. [32], where panel (a) reports spectral optical absorptance for different Mg contents and indicates that a main optical band gap E_{g1} is shifted from 1.67 to 2.32 eV when the Mg content is increased, while a lower band gap E_{g2} remains at $\sim 0.5 \text{ eV}$. The data for VO_2 are consistent with results in the literature [65–67] and can be understood

from Goodenough's work on the electronic structure of VO_2 [58] as shown in the inset of Fig. 8(a). Crystal-field-induced splitting of the $\text{V}3d\ t_{2g}$ band into $d_{||}$ and π^* sub-bands, and dimerization of the V atoms in the otherwise tetragonal lattice, divides the $d_{||}$ band into two components; the lower $d_{||}$ band is filled and the π^* band is empty, and E_{g1} is the band gap between $\text{O}2p$ and π^* and E_{g2} the band gap between the lower $d_{||}$ and π^* .

A deeper understanding of the role of Mg doping on the electronic band structure and optical properties was accomplished through calculations with spin-polarized density functional theory using the Heyd–Scuseria–Ernzerhof hybrid functional [68] and accounting for doping via supercells [32]. Fig. 8(b) shows data for two Mg contents and demonstrates that the doping-dependent lowering of the luminous absorption can be reconciled with theory.

Practical TC fenestration obviously requires long-term durability, which is an essential observation especially since VO_2 is not thermodynamically stable and may convert to non-thermochromic V_2O_5 under oxidizing conditions. However, the stabilization of VO_2 -based thin films and nanoparticles has received surprisingly little interest in previous work. We have recently made some preliminary studies of sputter deposited VO_2 films with top layers of Al_2O_3 . Fig. 9 shows data for 80-nm-thick VO_2 films at $\tau < \tau_c$ and $\tau > \tau_c$ in as-deposited state and after one hour of heat treatment in a tube furnace at 300 °C. It is evident that the VO_2 film has deteriorated and is no longer thermochromic after the heating. Such a film with a 10-nm-thick top layer of Al_2O_3 has a radically different performance, though, and Fig. 10 shows that thermochromism prevails for heating times up to 30 h. Some minor degradation was noted after the longest heat treatment, but this effect was no longer observed for a 30-nm-thick Al_2O_3 top coating.

6. Summary and conclusions

This paper summarized several recent studies [29–32] on new uses of nanoparticles in electrochromics and thermochromics. Concerning the first topic, we included ITO nanoparticles in the transparent polymer electrolyte of a conventional, polaronic EC device and demonstrated that high and haze-free luminous transmittance could be achieved together with strong near-infrared absorption without deteriorating the ionic conductivity. Furthermore we demonstrated that reliable performance limits could be stated for novel, plasmonic EC devices based on ITO. Concerning the second topic, thermochromism, we showed that good luminous transmittance, low thermal emittance, and significant thermochromic modulation of the solar energy throughput could be accomplished in composite ITO– VO_2 films. It was also

found that Mg-doping of VO₂ decreases the luminous absorptance which otherwise tends to be an obstacle for thermochromic fenestration, and that VO₂ films with a top coating of Al₂O₃ can sustain prolonged heat treatments in air.

The present work is exploratory, and there are many options for further development. For example, there are numerous alternative transparent conducting nanoparticles, such as ZnO:Al [51], SnO₂:Sb [69], M_xWO₃ (with M being Na, K, or Cs) [70,71], and LaB₆ [72–75]. There is also a huge number of techniques for nanoparticle and nanowire fabrication, as recently surveyed with regard to ITO [76].

Acknowledgements

The ITO nanoparticles included in the polymer electrolyte were prepared through collaboration with E. L. Runnerstrom and D. J. Milliron at the Molecular Foundry of the Lawrence Berkeley National Laboratory, Berkeley, CA, USA. The computational work on Mg-doped VO₂ was performed by Shuanglin Hu and K. Hermansson at the Department of Chemistry, The Ångström Laboratory, Uppsala University (K. H. is also at the Department of Theoretical Chemistry, Royal Institute of Technology, Stockholm, Sweden), and by R. Ahuya and R. H. Scheicher at the Department of Physics and Astronomy, The Ångström Laboratory, Uppsala University. Financial support was received from the European Research Council under the European Community's Seventh Framework Program (FP7/2007–2013)/ERC Grant Agreement No. 267234 ("GRINDOOR"). Additional support was obtained from the Swedish Research Council (VR) and the Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (FORMAS).

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Figure captions

Fig. 1. Upper panel shows black-body spectra for four temperatures and the Sun's surface temperature. Lower panel illustrates a typical solar irradiance spectrum during clear weather and at ground level, and the eye's sensitivity.

Fig. 2. Temperature-dependent ion conductivity vs ITO content in wt.% and volume fraction f . Symbols denote experimental data and connecting lines were drawn for convenience. From Ref. [29].

Fig. 3. Spectral transmittance for different ITO contents as measured (solid curves) and calculated (symbols) for ~ 70 - μm -thick layers of (PEI-ITO)-LiTFSI. From Ref. [29].

Fig 4. Calculated spectral absorptance for a 5 - μm -thick layer with electron densities of $0.1 \times 10^{21} \leq n_e \leq 2 \times 10^{21} \text{ cm}^{-3}$ (upper panel) and for layers with thicknesses of $10 \leq d \leq 100 \mu\text{m}$ and $n_e = 1 \times 10^{21} \text{ cm}^{-3}$ (lower panel). The layer has 1 vol.% of dispersed spherical ITO nanoparticles. From Ref. [30].

Fig.5. Calculated luminous and solar transmittance (T_{lum} and T_{sol} , respectively). The curve shows an approximate performance limit for plasmonic EC devices. From Ref. [30].

Fig. 6. Calculated spectral transmittance and reflectance for ITO-VO₂ composites, where f is the volume fraction of VO₂. Data are given for $\tau < \tau_c$ (semiconducting VO₂) and $\tau > \tau_c$ (metallic VO₂). From Ref. [31].

Fig. 7. Calculated luminous and solar transmittance (T_{lum} and T_{sol} , respectively) and TC modulation of the solar energy transmittance (ΔT_{sol}) vs VO₂ fraction (f) for ITO-VO₂ composites. Data are shown for $\tau < \tau_c$ (semiconducting VO₂) and $\tau > \tau_c$ (metallic VO₂).

Circles indicate data and connecting lines were drawn for convenience. From. Ref. [31].

Fig. 8. Experimental (panel a) and calculated (panel b) data for $(\alpha\hbar\omega)^{1/2}$ vs photon energy $\hbar\omega$, where α is absorption coefficient, for Mg-doped VO₂ with the shown Mg/(V + Mg) atomic ratios. Inset shows a schematic band structure for monoclinic, semiconducting VO₂ according to Goodenough [58]. E_F denotes Fermi level. The shaded bell-shaped regions signify relative luminous efficiency of the eye, as also given in Fig. 1. Reproduced from Hu et al. [32].

Fig. 9. Spectral transmittance for an 80-nm-thick VO₂ film before and after heating at 300 °C for one hour. Data were taken at $\tau < \tau_c$ (panel a) and $\tau > \tau_c$ (panel b).

Fig. 10. Spectral transmittance for an 80-nm-thick VO₂ film with a 10-nm-thick Al₂O₃ top layer before and after heating at 300 °C for the shown times. Data were taken at $\tau < \tau_c$ (panel a) and $\tau > \tau_c$ (panel b).

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Fig. 9.

Fig. 10.