

Innovative approaches to thermochromic materials for adaptive building envelopes

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# Innovative approaches to thermochromic materials for adaptive building envelopes

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**Abstract.** Thermochromic (TC) materials are characterized by a change of their optical response at a specific temperature. They can work based on both, the alteration of solar reflection by temperature, or the change of photoluminescence intensity. In building applications, this type of smart materials enhances the rejection of solar heat for high temperatures to favour cooling of the envelopes and reduces this rejection for low temperatures to improve surface heating. This adaptive optical response improves energy efficiency and reduces environmental impact of urban areas. Most of the current advances in this area are related to TC glazing based on Vanadium oxide, while opaque TC materials have been developed as based on Leuco dyes. The main drawback of these last materials is their significant aging in outdoor applications due to a photo-degradation process. The present work shows the recent results of a multidisciplinary and multinational consortium for research on innovative approaches to thermochromic materials for adaptive building envelopes. Next steps will be focused on building simulation to evaluate material choices across different performance aspects, while physical prototypes will be used for inter-laboratory evaluation of such performance and material durability.

## 1. Introduction

Thermochromic materials are smart materials characterized by a change in optical properties with temperature. Their adaptive optical response to solar radiation has proven to be useful when implemented in building envelopes for improvement of energy efficiency, occupant comfort and mitigation of environmental impact of urban areas, such as heat island effect (UHI) [1,2]. Current approaches to implement thermochromic (TC) functionality in building materials are mainly based on vanadium oxide for glazing and organic pigments for paints and cement-based coatings. However, there is a clear need for research in innovative approaches to improve their energy conservation potential, optical contrast and, especially, durability of TC functionality when directly exposed to outdoor conditions [3], as well as their building integration.

Promising strategies based in nanotechnology for development of both opaque and transparent TC materials have been identified [4]. These materials offer the unique possibility of tailoring their optical properties through fine-tuning and controlling several input factors (e.g. physical and/or chemical



properties) to achieve the best energy efficiency, occupant comfort and urban overheating mitigation. For opaque building materials, the implementation of nanotechnologies that have been developed for other applications represents a clear research and technology challenge. Conversely transparent promising TC materials need to be identified for optimal building integration as far as occupant comfort and energy efficiency is concerned.

The present work shows the recent results of a multidisciplinary and multinational consortium for research on innovative approaches to thermochromic materials for adaptive building envelopes.

## 2. Thermochromic transparent materials and glazing

TC glazing are able to reversibly change their optical properties (keeping specularly) by varying the micro-structure of the material induced by the temperature variation. This allows to achieve passive smart glazing which can be adopted in buildings to improve building performance aspects and occupant comfort and wellbeing by suitably controlling solar gains, daylight and view-out.

To date the main research focus in this field has been on deposition of thin films on glass substrates, by means of expensive vapour deposition and magnetron sputtering processing, while currently more cost effective roll-to-roll manufacturing techniques are being explored. Thin TC films are based on monoclinic Vanadium-Oxide ( $\text{VO}_2(\text{M})$ ) and its Semiconductor-Metal phase Transition (SMT). Given its relatively high critical temperature for glazing applications ( $68.5^\circ\text{C}$  when pure), most of the research efforts have focused on optimising the material with various approaches such as doping, nanocomposites and antireflective layers [5]. The main aims have been to i) reduce the critical temperature and the optical hysteresis between heating and cooling cycles [1]; ii) widen the solar switching range, and iii) improve colour neutrality. Nevertheless, the potential of integrating  $\text{VO}_2$ -based TC in buildings may be limited by limited transmittance modulation, only achievable in the near IR region.

On the contrary, TC polymer systems based on the doping of a polymeric transparent matrix with TC additives, provide the advantage of achieving modulation both in the visible and the near IR region of the solar spectrum [6]. Table 1 collects the capability for temperature modulation of optical properties corresponding to different approaches for TC glazing, including the following polymeric systems:

- Leuco-dyes (LD). Their TC functionality is based on proton transfer reactions. They present limited modulation capability and are heavily affected by photo-degradation in outdoor applications.
- Ligand Exchange (LETC). Polymeric compounds which are able to vary the coordination environment around a central metal ion. They can be embedded into a transparent polymeric matrix (adopted for glass lamination) and their optical response is very wide and distributed over a large set of temperatures.
- Twisted Nematic Liquid Crystals (TNLC). They exploit the variation between a cholesteric and a disorganised structure below and above a clearing point temperature. They can be embedded as well on flexible substrates and present a sharp transition of optical properties at a specific programmable temperature. However, due to the necessity of using polarising filters, they present a limited switching range and visible transmission.

**Table 1.** Range of Temperature Modulation capabilities of optical properties for thermochromic smart glazing materials (after [6]).

Thermochromic smart glazing (specular – specular)	$\Delta\tau_{\text{sol}}$ [%]	$\tau_{\text{sol max}}$ [%]	$\Delta\tau_{\text{vis}}$ [%]	$\tau_{\text{vis max}}$ [%]	$T_{\text{crit}} (\text{SMT})$ [ $^\circ\text{C}$ ]
<b><math>\text{VO}_2</math> thin films/nano composites</b>	10 ÷ 40	20 ÷ 80	2 ÷ 9	10 ÷ 80	25 ÷ 70
<b>LETC</b>	15 ÷ 25	40	57	62	25 ÷ 75
<b>Leuco-Dyes</b>	5 ÷ 6	50 ÷ 70	7 ÷ 30	30 ÷ 60	60 ÷ 80
<b>TNLC-TC</b>	15 ÷ 20	55	30	35	30 ÷ 40
<b>Hybrids <math>\text{VO}_2</math> LETC</b>	10 ÷ 20	80	5 ÷ 10	60	40 ÷ 50

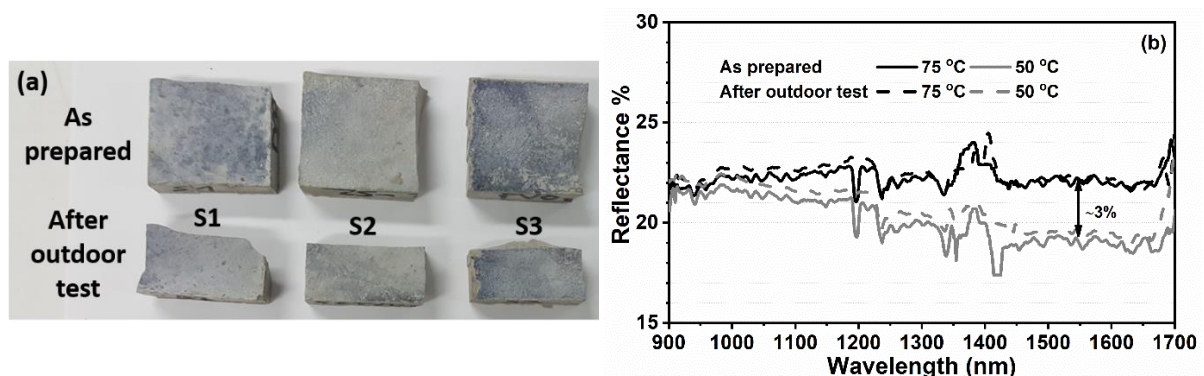
### 3. Thermochromic cement-based material based on VO<sub>2</sub> nanoparticles

Research on opaque materials with TC functionality for building envelopes has been mainly based on Leuco dyes [4]. However, given their rapid photo-degradation under solar radiation, innovative approaches are necessary within this field. One of the approaches addressed by the authors is the use of the vanadium dioxide TC phase (VO<sub>2</sub>(M)), considering that the lack of modulation in the visible range transmittance is not an issue in the case of opaque envelope elements.

VO<sub>2</sub>(M) nanoparticles were considered for the first time for the implementation of TC functionality in cement-based opaque materials. Cement paste specimens (3x1x6 cm<sup>3</sup>) were prepared with an ordinary Portland cement and a water to solid ratio of 0,4. Commercial VO<sub>2</sub>(M) particles were mixed with water at a concentration of 100 mg/ml and dispersed by magnetic stirring. The dispersion was sprayed onto the fresh paste, so as to cover its surface, immediately after compaction in specimen 1 (S1) and after 30 min and 1 hour in S2 and S3, respectively.

The near IR reflectance of the specimens was measured using a fiber-optic spectrometer with an integrating sphere after 56 days of curing in a humidity chamber. Spectra were measured for the samples heated to two different temperatures (50 °C and 75 °C) that are clearly below and clearly above the transition temperature of TC vanadium oxide (68.5 °C). The measurements were repeated after exposure of the specimens to outdoor conditions for 11 days in Madrid (3 rainy, 2 cloudy and 6 predominantly sunny days with temperatures between 3 and 15 °C).

The specimens show a dark surface consistent with the black color of VO<sub>2</sub>(M) dispersion, with no sign of delamination (figure 1 (a)). The near IR reflectance of the specimens is clearly lower for the lower temperature with a contrast increasing with wavelength (figure 1 (b)). Although further analysis is necessary, these results indicate that VO<sub>2</sub>(M) particles are properly bound to the cement paste during its hydration and their TC behavior is stable within the cementitious matrix.



**Figure 1.** Appearance of the specimens (a) and near IR reflectance spectra of S3 (b)

Moreover, neither the surface appearance of the specimens nor the change in optical response with temperature are observed to be affected by the exposure to outdoor conditions. This preliminary result suggests a better durability of this cement-based TC material, as compared to those based on leuco-dyes [3].

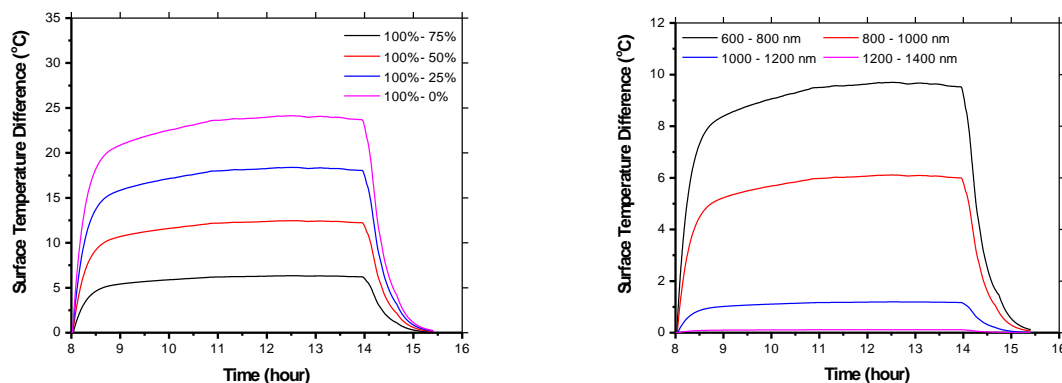
### 4. Thermochromic quantum dots

A cutting-edge approach for TC envelope materials under development by the authors is based on quantum dots (QDs). These are light emitting nano-scale semiconductor materials capable of re-emitting a portion of absorbed light through so-called photoluminescence (PL) effect [7]. Two main fluorescent properties determining the PL effect cooling potential include: 1. PL quantum yield (PLQY) (i.e. the number of re-emitted photons divided by the number of absorbed photons) and/or 2. Absorption edge wavelength ( $\lambda_{AE}$ )/PL peak wavelength (PL effect occurs at wavelengths shorter than  $\lambda_{AE}$  only) [8].

One of the interesting features of QDs is their tuneable fluorescent properties caused by quantum confinement effect at nano-scale [4]. Some QDs are reported to demonstrate interesting temperature-

sensitive/thermochromic (TC) fluorescent properties including temperature-sensitive PLQY (thermal quenching or thermal anti-quenching) and/or  $\lambda_{AE}/PL$  peak wavelength red-shift as well [4,7]. PLQY reduction by temperature, known as thermal quenching, is the commonly observed phenomenon [9,10]. However, thermal anti-quenching effect caused by thermal rectification of surface defects is also reported in some QDs with specific capping agents [11,12]. In addition, some QDs may demonstrate  $\lambda_{AE}/PL$  peak wavelength red shift due to temperature-dependant bandgap shrinkage effect. In this paper, an advanced deterministic numerical model was developed to study the thermal performance of TC QDs. Results of this research is of high importance as it provides a very useful insight at the early stages of experimental design of temperature sensitive QDs.

The predictive model proposed in this study is an extended version of our currently developed fluorescent cooling model for TC fluorescent materials [7]. To study the impact of PLQY variation, a comparative analysis of surface temperature difference between TC and conventional QDs was performed. Fluorescent samples are assumed to demonstrate a PLQY variation between 0-100%, 25-100%, 50-100%, and 75-100% at a transition temperature of 30 °C. The reference samples are assumed to have 0%, 25%, 50%, and 75% PLQY at all times, respectively. In parallel, the impact of PL peak wavelength red-shift for fluorescent samples with various PL peak wavelengths at 600 nm, 800 nm, 1000 nm, and 1200 nm was examined. The PL peak wavelength red-shift is assumed to be 200 nm for all TC fluorescent sample at temperatures above 30 °C. The corresponding conventional fluorescent samples have a constant PL peak wavelength at 600 nm, 800 nm, 1000 nm, and 1200 nm, respectively. As can be seen in figure 2, TC QDs with a PL peak at the blue end of the spectrum showed a more significant temperature difference compared with conventional QDs. Likewise, TC QDs with PLQY variation between 0-100% demonstrated the highest temperature difference of around 24.1 °C compared with conventional QDs.



**Figure 2.** Surface temperature difference between conventional and TC QDs in a typical summer day in Sydney. Left: PLQY of TC QDs varies between 100%-75%, 100%-50%, 100%-25%, and 100%-0% at a transition temperature at 30 °C, PL peak wavelength: 1200 nm; Right: PL peak wavelength varies between 600-800 nm, 800-1000 nm, 1000-1200 nm, and 1200-1400 nm for TC QDs at transition temperature at 30 °C, PLQY: 100%.

## 5. Discussion

Simulation analysis clearly show that TC materials implemented in building envelopes can provide important benefits in terms of energy efficiency enhancement and of urban heat island effect mitigation.

The main requirements for the real application of this technology in the building sector are:

- Adequate modulation of the optical properties with temperature. An optimum management of solar energy is necessary to provide significant benefits in the reduction of building energy demand.
- Durability in the conditions expected at building envelopes. The TC functionality must be stable upon incidence of solar radiation and at different climate conditions to ensure, at least, a similar service life as in conventional envelopes.

- Feasibility of fabrication at industrial scale. TC building envelopes must be obtained with scalable and reproducible processes and also at a competitive cost.

Unfortunately, the initial TC materials did not fulfil these three requirements. TC glazing based on VO<sub>2</sub> thin films show limited transmittance modulation, while the approaches based on leuco-dyes are not durable in outdoor conditions. Taking this into account, innovative approaches are necessary to optimize thermochromic materials for adaptive building envelopes.

As far as TC transparent materials are concerned, Ligand Exchange and Twisted Nematic Liquid Crystals TC are already available on the market. Nevertheless, very few real world example exists, as optical properties modulation would need further improvement for optimal integration for building application. On the other side, a lot of research is currently ongoing to develop more cost-effective VO<sub>2</sub> based transparent TC, based on roll-to-roll manufacturing techniques, so to balance the small building performance improvements due to limited solar modulation.

Regarding VO<sub>2</sub>-based cementitious materials, specimens have been produced and characterized at laboratory scale. Next steps in their development must be devoted to the optimization of their optical performance for varying temperatures and more complete outdoor performance tests.

Finally, the TC devices based on quantum dots represent a cutting-edge approach at the first development stages. The next challenge in this case is to synthesize, characterize, and perform outdoor thermal performance testing of the temperature-sensitive QDs with the desired temperature-sensitive fluorescent properties.

Apart from this, there are other challenges to be tackled, whichever approach is considered to achieve the TC functionality. It is necessary to improve building simulation implementing the dynamic properties of the TC envelopes. This will be fulfilled by the enhancement of the simulation tools, as well as by the monitoring of physical prototypes for validation of the digital models. Also necessary is to perform a cost analysis, to assess the balance between the increase in the production cost and the benefits from the building energy demand reduction.

## 6. Conclusions

A multi-scale, interdisciplinary and inter-laboratory approach for TC building materials is presented in this work, supporting the development of opaque and transparent thermochromics from laboratory scale to building integration. A brief description is given of the fundamentals and the current development stage of different opaque and transparent TC materials, representing the state of the art in the topic.

To date, research efforts have mainly focused at solving specific issues at the material scale, improving different features of opaque and transparent thermochromic functional materials with different techniques, aimed at maximising their optical and solar switching range, tuning the switching temperature range towards building façade applications, improving colour neutrality, ensuring material stability and durability, as well as reducing the overall costs of the functional material and of the processing necessary for building integration. Although, due to their passive working principle, temperature dependent modulation mechanism need to be effectively designed and tuned, so that it is able to optimise the required aspects of building performance when building integrated.

Understanding the effect of the tuning of the functional material properties on the overall building performance (i.e. energy uses, visual and thermal comfort, etc.) and the effectiveness of material design choices on building performance and integration aspects is not a trivial task. First, it is a crucial step to gain a profound understanding on the impact of optical and fluorescent properties on the thermal performance of TC materials. Second, it is necessary to evaluate the TC functional material behaviour at a building scale. Therefore, advanced numerical modelling and experimental tests will be adopted by the authors to understand the effect of material features on overall building performance. Building performance simulation will be adopted to evaluate the effect of different materials across different performance aspects (energy efficiency, thermal and visual comfort requirements, urban microclimate effect), while physical prototypes will be used to evaluate such performance and material durability across exploiting the inter-laboratories facilities among the different institutions.

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