

# Chromogenic Technologies for Energy Saving

Subjects: Energy & Fuels

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Chromogenic materials and devices include a wide range of technologies that are capable of changing their spectral properties according to specific external stimuli. Several studies have shown that chromogenics can be conveniently used in building façades in order to reduce energy consumption, with other significant effects. First of all, chromogenics influence the annual energy balance of a building, achieving significant reductions in consumption for HVAC and artificial lighting. In addition, these technologies potentially improve the indoor level of visual comfort, reducing the risks of glare and excessive lighting.

Keywords: chromogenics ; electrochromics ; thermochromics ; pho

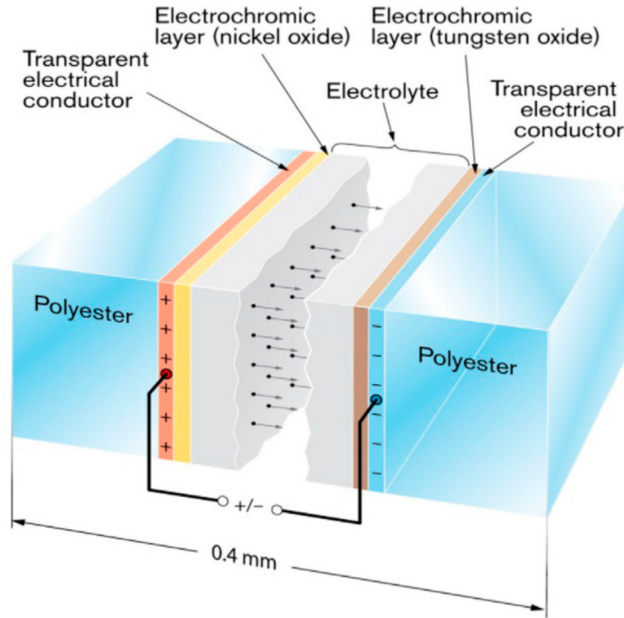
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## 1. Introduction

In recent years, awareness of global warming has grown a lot and this has pushed research groups all over the world to find new solutions to reduce the anthropogenic fingerprint on ecosystems <sup>[1]</sup>. A plethora of studies has highlighted the significant impact that the construction sector has on the global consumption of primary energy and, at the same time, on carbon dioxide and greenhouse gas emissions. It is possible to estimate that in the most developed countries, about 40% of primary energy is used for commercial and tertiary residential buildings <sup>[2]</sup>. In particular, in the last decades, the vast and multidisciplinary field of nanotechnologies has made available a large number of new materials with surprising properties that allow us to design systems, devices, and components that are capable of reducing impacts and manufacturing costs and of increasing performance as well. An extensive family of materials and devices of this kind is represented by so-called smart materials, i.e., materials with adaptive properties that change according to the application of an external *stimulus* <sup>[3]</sup>. Among smart materials, the so-called chromogenic materials are still under investigation: among them, electrochromic (EC), photochromic (PC), and thermochromic (TC) materials are of particular importance for use in buildings <sup>[4]</sup>. The vast class of chromogenics includes materials not considered in this work, such as gasochromics or liquid crystals <sup>[4][5][6][7]</sup>. In all cases, these materials undergo an alteration of their spectral properties in the visible and/or infrared wavelengths due to the application of a specific external *stimulus*. Consequently, chromogenic materials owe their name to the physical *stimulus* that triggers the activation of their mechanism. While in the case of EC materials and devices <sup>[8]</sup>, the stimulus is represented by a voltage applied by means of an external circuit, PC <sup>[9]</sup> materials change color according to irradiation with precise wavelengths; on the other hand, TC materials <sup>[10]</sup> change their optical behavior due to the achievement of a precise critical temperature ( $T_c$ ). As mentioned above, EC materials change color depending on the application of an external bias to the device in which they are embedded. They have always been thought of as optimal for integration into buildings within the so-called "smart windows" <sup>[11]</sup>. In fact, windows are still considered a thermodynamically weak point of a building façade. Nowadays, increasing attention is paid to the design of materials capable of controlling and optimizing the energy flux, mainly through glazing. Windows allow the penetration of a wide range of thermal radiation, including visible and infrared wavelengths, with several thermal transfer mechanisms (conduction, convection, and irradiance) between the glass, surrounding gases, and sky. If, on the one hand, free heat gains are welcomed in winter (for example, reducing heating loads), in the summer season, they turn into undesired cooling loads <sup>[12]</sup>. For this reason, chromogenic glazing, with adaptive or adjustable spectral properties, can be a very useful tool to reduce energy consumption in several fields: automotive, transportation, and construction. EC materials, differently from PCs and TCs, work only if inserted within the architecture of a more complex device, embodying one or two transparent and conductive substrates, an electrolyte, and one or two EC materials with complementary behavior. EC materials can be organic <sup>[13]</sup> or inorganic; there is abundant scientific literature that investigates the properties of these materials under different profiles. Several companies, in recent years, have brought some types of EC devices to the market <sup>[13]</sup>. On the other hand, TC and PC materials do not allow, differently from EC ones, any type of control of their feature by users since the presence of the external light (or thermal *stimulus*, respectively) activates the chromatic modulation, at least until the *stimulus* itself is applied. It seems clear that these differences could be fundamental in finding the potential applications for these materials inside buildings or in other contexts.

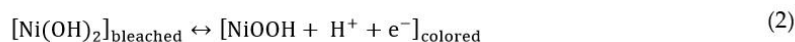
## 2. Electrochromic Materials and Devices

The seminal studies by S. Deb <sup>[5][6]</sup> and C.G. Granqvist <sup>[7]</sup> have catalyzed the interest of numerous research groups worldwide towards the achievement of the dynamic behavior of glazing. An EC glass can be viewed as a battery embodying several materials in the form of thin films. The charge inserted can be related to the degree of transparency of an EC device. Typically, an EC device (Figure 1) includes two transparent conductive substrates; an EC film is deposited on top of each of them, with complementary behavior; the two substrates are separated by an electrolyte (liquid, gel, or solid). The electrolyte conducts ions, also acting as an insulator for electrons. It contains small cations ( $H^+$ ,  $Li^+$ , or  $Na^+$ , in general <sup>[14]</sup>) that can be shuttled through the electrolyte by applying an external bias.



**Figure 1.** Web-coated electrochromic (EC) devices in the form of large flexible sheets, as a foil for glass lamination. Reproduced from <sup>[15]</sup>, Elsevier: 2018.

Coloration takes place as a consequence of redox reactions involving the EC films and the cations moving across the electrolyte. The most widely investigated EC materials are inorganic transition metal oxides, such as tungsten oxide ( $WO_3$ ), molybdenum oxide ( $MoO_3$ ), titanium dioxide ( $TiO_2$ ), and nickel oxide ( $NiO$ ). EC material color, due to simultaneous cation and electron intercalation, is named "cathodic", whereas color due to cation extraction is called "anodic". The most investigated cathodic and anodic inorganic EC materials are  $WO_3$  and  $NiO$ , respectively <sup>[16][17]</sup>. Their complementary behavior allows for the simultaneous coloration/bleaching of both the materials being deposited on the two opposite substrates, oppositely charged during the processes. EC materials show "double conduction" of ions and electrons; for this reason, they have been defined as "mixed conductors". When cathodic EC materials are charged with electrons, due to the external bias (in general, very low voltages, 1–5 V dc) applied to the device, they tend to attract small cations inside the complex network of channels within their structure. Following this intercalation, EC materials undergo a reversible modification of absorption. Simplified forms of the complementary redox equations are as follows <sup>[18]</sup>:



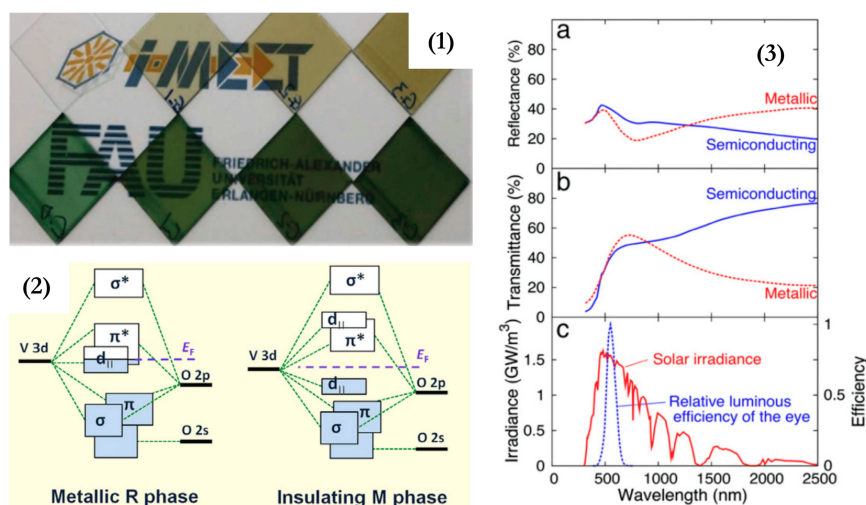
In some cases, the anodic EC film can be replaced by a material providing ion storage to allow safe and full bleaching processes. The state of aggregation of an electrolyte influences the performance and durability of an EC device <sup>[19][20]</sup>. Liquid electrolytes containing volatile solvents may undergo evaporation and leakage, affecting the durability of devices <sup>[21]</sup>. They can be solid, as in the case of tantalum oxide ( $Ta_2O_5$ ) <sup>[22][23]</sup>, liquid <sup>[24][25]</sup>, or gel <sup>[26][27]</sup>. Electrolytes based on polyethylene oxide (PEO) <sup>[28]</sup> or polymethyl methacrylate (PMMA) raise their ion conductivity by adding specific amounts of salts, such as lithium perchlorate  $LiClO_4$ , LiTF, lithium iodide (LiI), or lithium sulfide ( $Li_2SO_4$ ). Transparent conductive oxides <sup>[29][30][31]</sup> typically used are indium tin oxide (ITO) and fluorine-doped tin oxide (FTO). There are recent studies reporting the adoption of graphene and metal meshes, used effectively as conductive materials. Typically, the substrates used to make EC devices are made of glass. However, there are several studies using flexible substrates such as polyethylene terephthalate (PET). In this case, the weight of EC devices can be minimized. PET-based EC devices have also been used for lamination. EC devices may also be deposited on polyethylene terephthalate (polyester, PET), as

reported in recent work by Granqvist et al. [15]. In this case, a gel polymer electrolyte was solidified by crosslinking; EC devices could be laminated in an insulated glass unit (IGU) using polyvinyl butyral (PVB) or ethylene vinyl acetate (EVA). Additionally, polyethylene naphthalate has been adopted for flexible EC devices [32]. The most widely studied EC materials are transition metal oxides and organic materials; more recently, ITO nanoparticles have shown relevant plasmon absorption within the near-infrared wavelength range, as demonstrated by Llordes et al. [33][34], who reported the independent tuning of infrared and visible light in a "dual-band" device. Organic EC molecules also undergo reversible coloration (and bleaching) upon specific redox processes. The most widespread organic EC materials are bipyridilidium systems, conducting polymers, quinones, cyanobiphenyls, and phthalocyanines [4]. Jensen et al. [35] reported a relevant demonstration of flexible solid-state EC devices, fabricated using continuous roll-to-roll processing based on photo-crosslinking of an acrylate-based electrolyte. Dyer et al. [33] demonstrated a solar-powered EC device that includes PProDOT-(CH<sub>2</sub>OEtH<sub>x</sub>)<sub>2</sub> and PProDOP-N-C<sub>18</sub>H<sub>37</sub>. The device includes PV cells that produce net positive energy, which is only partially used to modulate the thermal energy flux of windows.

Piccolo et al. adopted a lithium-conducting polymer made of PEO-PEGMA:Li to fabricate a large-scale EC window (12 by 12 cm) embodying two complementary inorganic EC materials: WO<sub>3</sub> (cathodic) and NiOH:Li (anodic/ion storage). The device reported switching times of 5–6 min, with (visible transmittance) T<sub>vis</sub> varying from 70% to 30%. Sibilio et al. [36] reviewed commercial EC glazing and made an examination of their average acceptable properties: minimum visible transmittance values in the clear state of 0.4–0.5; minimum solar heat gain coefficient from 0.29 to 0.32; T<sub>vis</sub> and SHGC of the colored state ranging from 0.09 to 0.1 and from 0.1 to 0.13, respectively. Switching times may range from 7 to 20 min.

### 3. Thermochromic Materials

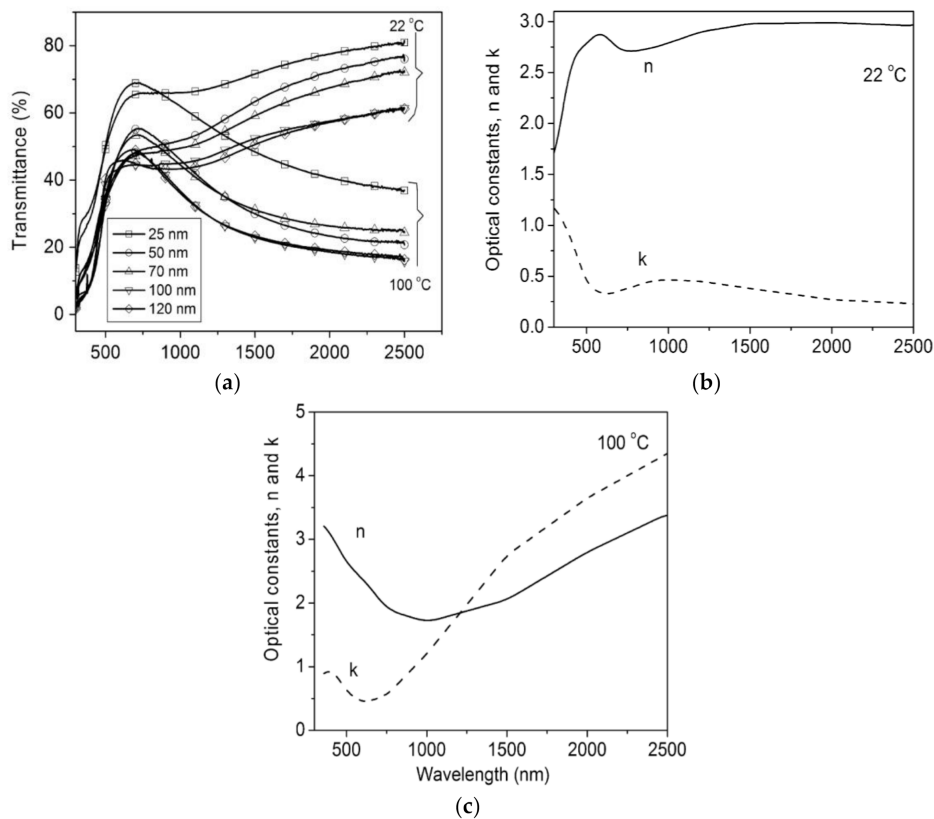
TC materials undergo reversible phase transition when a T<sub>c</sub> is reached, with relevant changes in physical properties (transmittance and resistivity, for instance). TC behavior has been reported in organic compounds, ionic liquids, and composite materials [18][37]. Inorganic materials have reported higher stability even at temperatures higher than 200 °C. For example, Liu et al. have reported metal-doped Ca<sub>14</sub>Zn<sub>6</sub>Ga<sub>10</sub>O<sub>35</sub>-based TC materials, achieving reversible thermochromism in a wide temperature range (25–460 °C). The most widely investigated TC material is, by far, vanadium dioxide (VO<sub>2</sub>). If it reaches its T<sub>c</sub> (68 °C), a strong modulation of near-infrared transmittance takes place. VO<sub>2</sub> can be obtained by several methods: physical vapor deposition [37][38][39] has been the most studied method, though nanostructured VO<sub>2</sub> has also been studied recently [40]. On the contrary, the modulation of visible transmittance (T<sub>vis</sub>) is quite moderate (less than 10%). Cao et al. [41] have reviewed the open challenges and possible strategies for improving the properties of VO<sub>2</sub>. The open issues regarding VO<sub>2</sub> were also summarized in work by Li et al. [42]: limited solar modulation (10%); luminous transmittance (T<sub>lum</sub>) should not be higher than ~40%; ΔT<sub>sol</sub> should take place not so far from ambient temperature, but the T<sub>c</sub> of VO<sub>2</sub> is as high as 68 °C (Figure 2). TC materials indeed represent a chance to control solar radiation and thermal radiation passing through transparent façades, for various applications, according to the temperature variations.



**Figure 2.** (1) Pictures of VO<sub>2</sub>-based thermochromic (TC) samples, (2) Band structures of the metallic rutile and insulating monoclinic phases of vanadium dioxide (VO<sub>2</sub>). Reproduced from [43], Elsevier: 2018. (3) Spectral reflectance (a) and transmittance (b) for a 50 nm VO<sub>2</sub> film. Panel (c) illustrates spectra for the luminous efficiency of the human eye and solar irradiance. Reproduced from [42], Elsevier: 2012.

VO<sub>2</sub> shows a monoclinic structure (insulator) in its transparent state, which turns rutile (metal) upon reaching its T<sub>c</sub> (Figure 2, left side). In its basic form, the T<sub>c</sub> is too high for building fenestrations. For this reason, several methods have been adopted to decrease it (40 °C is considered an acceptable value). Other issues in the development of TC coatings for industrial applications include the stability of performance in time and increasing the modulation of visible and infrared transmittance. To reduce the T<sub>c</sub>, doping with cations larger than vanadium (such as tungsten, molybdenum, and niobium) and anions smaller than O<sup>2-</sup> (like fluorine) is the most adopted strategy [44][45][46]. In fact, it was observed that the direction of the change in T<sub>c</sub> could be related to the relative size of the doping ion compared with vanadium [47] or to the charge-transfer mechanism associated with the introduction of extra electrons into the vanadium d bands [48]. On the other hand, to increase the luminous transmittance of VO<sub>2</sub> films, antireflection coatings or structures are adopted. For instance, Kolenaty et al. reported a three-layer structure, with ZrO<sub>2</sub> antireflective layers acting as a protection layer and structure template [49]. Several works have used SiO<sub>2</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub> antireflective layers [37]. A more sophisticated approach was proposed by Liu et al. [50], who reported the design of nanocone antireflective layers made of TiO<sub>2</sub>, biomimicking moth-eye morphology and reaching a T<sub>lum</sub> of 55.4%, with ΔT<sub>sol</sub> of 11.3%. Moreover, the stability of VO<sub>2</sub> coatings is limited by chemical and physical deterioration issues. Durability is indeed a special figure of merit for TC coatings: at least 10 years of service life is required. Several forms of VO<sub>2</sub> exist, but, unfortunately, the most stable is V<sub>2</sub>O<sub>5</sub>. Moisture and acidic environment tend to affect the original TC properties of VO<sub>2</sub>. From the physical point of view, a small volume change (roughly 0.3%) takes place upon each phase-transition process, and this point may result in cracks and deterioration of TC performance [41]. This fact may influence the durability of core-shell structures embodying VO<sub>2</sub>.

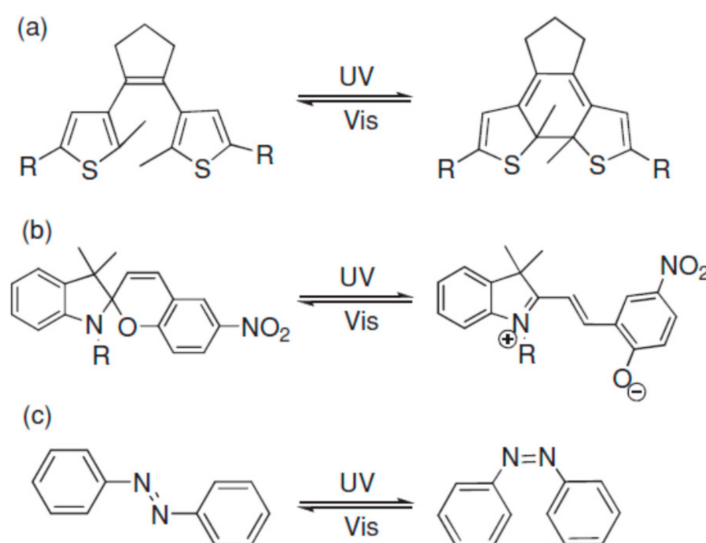
Figure 3 shows spectral transmittance for VO<sub>2</sub> films at different temperatures, lying below and above the T<sub>c</sub>. Mlyuka et al. [51] used computations to optimize multilayer films and demonstrated that TiO<sub>2</sub>/VO<sub>2</sub>/TiO<sub>2</sub> structures may report higher transmittance than bare VO<sub>2</sub> films. VO<sub>2</sub> transmittance drops at λ < 600 nm: such a feature is due to inherent band-to-band absorption. This issue can be partially solved by Mg doping, leading to a band-gap widening. Doping strategies of VO<sub>2</sub> have led to much lower T<sub>c</sub> ≈ 25 °C [42]. Zhan et al. [39] reported the TC performance of VO<sub>x</sub>-based multilayer films that are effectively controlled by annealing pressure: the T<sub>c</sub> was reduced to 54 °C by changing the annealing pressure, without doping. Xu et al. reviewed a recent advance in TC composites for smart windows [52], with special reference to multilayer composite structures that improve the VO<sub>2</sub> properties. A synthesis of the three main challenges of TC materials' performance, which limit their building integration, was offered by Li et al. [42]: VO<sub>2</sub> should accomplish high solar transmittance modulation (ΔT<sub>sol</sub> >> 10%), high luminous transmittance modulation (T<sub>lum</sub> >> 40%), and low critical temperature (T<sub>c</sub> ≈ 25 °C).



**Figure 3.** (a) Spectral transmittance for VO<sub>2</sub>, measured above and below its precise critical temperature (T<sub>c</sub>); (b) spectral optical constants, n and k, for VO<sub>2</sub> films, measured above and below its T<sub>c</sub>; (c) Spectral optical constants, n and k, for VO<sub>2</sub> films, above the T<sub>c</sub>. Reproduced from [51], Elsevier: 2009.

## 4. Photochromic Materials

Photochromic (PC) materials undergo reversible photoinduced switching (Figure 4) between different states (or isomers) that have remarkably different absorption spectra [53]. The word PC derives from the transliteration of the ancient Greek words "φῶς" (light) and "χρῶμα" (color). To activate the coloring process, PC materials must be exposed to certain wavelengths of light. Just like TC materials, PC devices can be fabricated without any extra energy input for use in and maintenance of windows. In these materials, light acts as a free, energy-efficient, and fast power source, activating the photoswitching. PCs can be exploited not only for optical lenses and smart windows, photonics, and optoelectronics, but also in molecular switches, optical data storage, molecular electronics, and sensors [53][54]. The interconversion between different states is also witnessed by parallel changes in chemical and physical properties upon light irradiation of PC materials (refractive index, polarizability, as well as electric, magnetic, and mechanical properties). As reported by Barachevsky, a current goal in the design of PC nanoparticles is represented by the development of PC nanoparticles or hybrid core-shells of PC compounds based on noble metals, silica, and PC organic compounds [55]. The relevant potential of organic synthesis allows for an unlimited fine-tuning of molecules, according to specific design choices. In organic PC materials, coloration is the result of a chemical bond rearrangement, effecting changes in structural and electronic properties. They can be fabricated by embedding active PC materials into a transparent matrix [56]. Several classes of PC organic molecules exhibit the phenomenon named as photochromism: fulgides, diarylethenes [57], spiropyrans [58], spirooxazines [59], naphthopyrans [60], and azobenzenes [61]. The main figures of merit for these materials, as reported by Ke et al. [62], are fast kinetics, high contrast, and, above all, photochemical stability. Azobenzenes can undergo trans-to-cis isomerization when UV-irradiated and the cis isomer may be bleached back to the trans form by visible light as well as thermal relaxation. They photoisomerize upon UV exposure and show opposite properties compared with other PCs. In fact, azobenzenes are originally opaque and turn transparent when UV-irradiated. When UV-exposed, spiropyrans will isomerize, showing a transition to dark blue—such photo-induced process of coloration is thermally unstable; for this reason, it gives rise to spontaneous bleaching after UV exposure ceases. Spiropyrans are generally used for transitional PC sunglasses.



**Figure 4.** Photochromism of dithienylethene (a), spiropyran (b), and azobenzene (c). Reproduced from [53], WILEY-VCH: 2013.

On the other hand, the coloration of diarylethenes [63] is due to reversible photoinduced valence isomerization between the colorless ring-open state and the colored cyclic form. Four kinds of diarylethenes are reported in the literature, depending on the benzofuran and benzene moieties contained by the molecules. They can turn from colorless to red, purple, or orange. The colored form is thermally stable and cannot be bleached in the dark (simply leave the material at room temperature). On the contrary, the bleaching process—also observed in fulgides [64]—requires exposure under visible light (or elevated temperatures) to recover its original color. As reported by Nakamura et al. [65], the colored ring-closed forms of diarylethenes tend to remain stable for more than 12 h at 80 °C and can be reversed to their original colorless form only by exposing them to visible light.

This is typical behavior reported of the so-called "thermally irreversible" PCs. On the other hand, spiropyrans, spirooxazines, azobenzenes, naphthopyrans, and dipyrrolylethenes show "thermally reversible" PC behavior [66][67], i.e., their bleaching may be activated by visible light or heating. They are used for eyeglasses due to their behavior. Naphthopyrans embedded in a solgel matrix [68] demonstrate a relevant reduction (50%) of the visible transmittance upon



coloration. Bleaching back occurs after 30 min from ceasing UV irradiation [68]. Fulgides doped in PMMA showed stable and multilevel photoisomerization due to UV irradiation and consequent absorption at 382 nm [69]. As reported by Wang et al. [70], a recent trend of research in PC materials is represented by the challenge to obtain more color states by designing specific functional groups in order to tune the HOMO–LUMO gap of PC molecules. However, organic PCs require complex syntheses and, in some cases, do not show thermal stability [71]. Some authors have also highlighted the persisting drawbacks: cost of synthesis, limited thermal stability, and toxicity issues [72]. Orta [73] reviewed a series of PC systems (spirooxazines, chromenes, and diarylethenes), investigating the effect of temperature on their behavior. Temperature may increase the bleaching rate in thermo-reversible molecules and also decrease the coloration due to the light stimulus; on the other hand, for spirooxazines and chromenes, a description was made by considering a combination of the TC and PC data obtained. Another phenomenon under wide investigation in PC materials is represented by the upconversion process: two or more near-infrared photons can convert into visible or ultraviolet light, generating high energy luminescence, absorbing two or more photons of low frequency [72][74]. Kang et al. [75] observed that the range of the UV is quite limited in the solar spectrum (about 5%), and this fact limits the maximum theoretical efficiency of PC windows, which are typically triggered by UV absorption. For this reason, they suggested the use of phosphor materials (i.e., lanthanide metal ions like  $\text{Pr}^{3+}$ ,  $\text{Tm}^{3+}$ ,  $\text{Eu}^{3+}$ , and  $\text{Er}^{3+}$ ) to upconvert visible or IR wavelengths. They suggested praseodymium-doped yttrium silicate ( $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$ ,  $\text{YSO}:\text{Pr}^{3+}$ ) as a suitable phosphor material that is capable of absorbing nm light with a wavelength of  $\sim 505$  and emitting UV light (between 270 and 380 nm). In their work, they proposed a hybrid double-layer film embodying a phosphor devoted to upconversion and a PC layer ( $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}/\text{H}_3\text{PW}_{12}\text{O}_{40}$ ). The PC effect and kinetics that resulted increased several times compared to a single layer due to the upconversion effect. Reversible PC modulation has also been reported in inorganic materials and hybrid organic–inorganic films, showing, on the other hand, chemical stability, mechanical strength, and oxidation resistance. Inorganic materials that have also been reported to have PC properties, such as transition metal oxides ( $\text{WO}_3$ ,  $\text{TiO}_2$ ,  $\text{MoO}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$ ), are considered cost-efficient for large-scale applications; other materials like metal halides and rare-earth complexes are typically used for lenses. Fair photochromism in  $\text{WO}_3$  takes place due to the electron transfer between tungsten atoms, with different valence states, if the material is in contact with water and irradiated with light. Poor revisability of its PC behavior has compelled researchers to improve its properties, adopting different strategies.  $\text{TiO}_2$  has also been reported to have PC behavior in the form of gels and nanoparticles. Similar to  $\text{WO}_3$ , an electron–hole pair is created by light irradiation of the material. Titanium ions undergo reduction due to electron insertion, producing colored  $\text{Ti}^{3+}$ . Zuo [76] reported the PC postannealing properties of RF magnetron-sputtered  $\text{TiO}_2$  thin films with embedded silver nanoparticles. These films can also be deposited using other techniques (solgel, spin-coating, photoreduction by UV irradiation). As well known,  $\text{WO}_3$  exhibits PC properties due to  $\text{W}^{6+}$  to  $\text{W}^{5+}$  reduction upon UV irradiation, activating a charge transfer from oxygen to metal.  $\text{WO}_3$ —with a bandgap ranging from 2.7 to 3.1 eV—can suitably work as a PC component in a cellulose matrix, being deposited by the solvent casting method, reporting full cycles of coloration/bleaching, from pale yellow into dark blue in about 1 min, and gradually recovering its bleached form in the dark within 20 min, lasting about 20 min [77].

Several studies have recently demonstrated the benefits associated with the building integration of chromogenic devices, mainly ECs [16][78][79][80][81]. Sibilio et al. [36] observed that EC devices may allow high energy savings (up to 39–59%, in some cases), but such benefits are indeed influenced by orientation, the control strategy adopted, climatic conditions, and location. As to the building integration of TC materials, it is claimed that they have the ability to reduce both heating and cooling energy demand from 5.0% to 84.7% when compared to clear glass as a reference. Nevertheless, such performance was strongly dependent on film type and location [82]. On the other hand, Giovannini et al. [83] tested large-scale samples of TC layers laminated in glazing and compared them to standard selective glass. They found a strict dependence of the results on latitude and location; in the case investigated, TC glazing required lower energy use than selective glazing, although cooling demand was higher because of secondary heating flows towards the interior of the building, associated with increased TC glazing absorption in its dark state. The number of studies concerning the integration of PC glass in buildings is significantly lower. A recent work by Tällberg et al. [84] reported a comparison among the chromogenic technologies studied in this work. They observed that the performance of PC glazing was affected by the narrower interval between the clearest and darkest state (i.e., 0.40–0.36 in the case investigated in their work). Moreover, TC and PC glass showed low values for both the bleached/colored states compared to EC glass, which had higher modulation of SHGC in the bleached and colored states, respectively (0.46–0.09). Ke et al. [62] also observed that just like TC glass, PCs allow simple fabrication without extra energy input. Moreover, according to their outcomes, they suggested that PC windows should have high contrasts and fast reversible kinetics to be suitable for building integration; moreover, they stated that PC windows would not be desirable in "four-seasoned countries" since they could impede energy flow through the glazing even in winter in the colored state.

Piccolo et al. observed that EC layers have intrinsic low-e properties due to the ITO conductive layer. Moreover, they suggested placing EC films in Surface 2, i.e., the inner side of the outer glass pane of a standard argon/air-filled IGU. Such placement allows the reduction of high rates of secondary heat gain, as well as glass overheating.

Many studies have dealt with the potential benefits deriving from chromogenic systems used in glazing [48]. Some of them were carried out using numerical simulation software; others were based on in-situ measurements of prototypes made on a large scale. In any case, the significant modulation of  $T_{sol}$  and  $T_{vis}$  of glass entails a dramatic opportunity to control the energy flow that passes through the windowed component, according to seasonal requirements, to achieve indoor comfort. This can translate into the possibility of reducing energy consumption in the construction sector and, at the same time, an improvement in the conditions of comfort in offices and homes. Moreover, they may allow for a relevant downsizing of HVAC systems, with further economic and environmental advantages. In this brief review, the most common chromogenic systems (thermochromic, electrochromic, photochromic) have been described, as well as the fabrication techniques typically used to manufacture them, although in a nonexhaustive way. The current research trends have been reported for each class of materials. The interest in chromogenics is very high in the scientific field as they offer significant economic, comfort, and environmental benefits for users. What unites TC and PC glass is the fact that the modulation in these cases is not controllable or customizable by the user. On the contrary, the user can overrun the modulation of EC glass or activate it at different degrees, according to specific needs. On the other hand, the fact that EC glass requires activation by users strongly relates their advantages to the management strategy adopted for such devices. For example, it has been observed that the degree of coloration of EC glazing should ideally depend on the degree of illuminance required on a work surface: such a strategy offers the maximum energy benefit in the face of an optimal condition of visual comfort. Other strategies, such as the one based on glare control, allows the maximization of visual comfort at the expense of energy consumption [5][12][78].

In recent years, beyond the strategies aiming at improving device performance and new optimization processes for materials on the nanoscale, there has been a clear trend to design devices with extended functionalities, coupling several functions; in the case of photoelectrochromic devices [85][86] and photovoltachromic ones [24], this would allow the separation of the control of optical modulation from photovoltaic conversion. A further approach, aiming at a separation of visible and near-infrared modulation, has been adopted in the design of so-called dual-band devices, produced by the research group of the LBNL [33][34]. It allows a wide customization of device features, according to the varying external conditions. DeForest et al. analyzed the energy savings associated with the building integration of such devices in the US, reporting fair output that was strictly related to the climatic zone [87][88][89]. One more suitable strategy would be represented by the combination of more chromogenic technologies in a single device. For instance, Detsi et al. [90] have recently proposed a combination of EC and TC materials, demonstrating an 18.5% and 8.1% reduction in annual primary energy use for Athens and Stockholm, respectively. Multistage coloring devices could also be of particular interest for precise practical applications [42]. The application of the devices, in each case, is finally one of the main points to be carefully evaluated for each technology. For example, a system that does not allow users to control the optical properties (such as TC and PC glazing) could be applied in contexts where the illuminance on a worktop may not be relevant, while the control of incoming radiation and visual comfort are, thus preferring the energetic aspect. For these reasons, the choice of the most suitable chromogenic technology to be used will be made on the basis of specific design needs and constraints, case by case.

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