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Mini Review

Smart Window Technologies: Electrochromics and Nanocellulose thin film Membranes and Devices

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ABSTRACT:

Strategies for incorporating energy-efficiency requirements into building standards have been implemented by governments in developed countries in order to introduce the concept of green nanotechnology. Substituting regular glass windows in residential/commercial buildings with smart windows is the objective. The smart window is to function as electric dimming glass that is to be built with innovative nanomaterial based membranes/ coatings. Currently, the regular windows are made of glass and curtains/blinds are used to block sun light; eliminating such elements is of importance due to its limited functionality. Though these curtains/blinds blocks UV and prevents sun light illumination inside the rooms, but there are additional issues such as health hazards (e.g. dust and germ collection especially in hospitals) relating to asthma problems, disposal/recycling issues, regular cost, and maintenance which are some of the possible glitches. The smart window is expected to block harmful UV light and provide controlled privacy while also eliminating the problems related to curtains/blinds. Electrochromic (EC) smart windows are already in use that varies the throughput of visible light by electrical voltage or by solar energy application and are able to provide energy efficiency and indoor comfort. These smart windows comprises of electrochromic materials such as LixWO2.89 and HxNiO2 as cathodic and anodic oxide films, respectively, and other complex polymers, which are complicated to create, expensive and some are hazardous in nature. Nanocellulose (achieved from wood/pulp product) is already being used in flexible electronics, so nanomaterial membrane based suspended particle device (SPD) technology for smart window is a probable alternative to EC devices, but still under research. This paper reviews, introduces and discusses the present situation of both (EC and SPD) options for the state-of-the-art smart windows and its applications while also provide ample references to current literature of particular relevance and thereby, hopefully, an easy entrance to the research field. Also the paper presents an outlook for an innovative technology for smart-windows with SPD-EC technology to work as dimming glass on voltage application while also induce the capability of solar applications in smart windows leading to green nanotechnology in buildings.

Keywords: Nanocellulose, electrochromic, electric dimming glass, smart windows, nanomaterial

INTRODUCTION

The smart windows based on electric dimming glass (EDG) are able to control the quantity of visible light and solar energy radiation into buildings while it can transport energy efficiency as well as human comfort by changing the transmittance levels depending on dynamic needs. Smart windows are currently being used in some high-tech commercial buildings, as shown in Figure 1 with two examples of multi-pane installations in which some panes are in their fully colored state and others are bleached. Thus the smart windows in Figure 1 induce both colored and bleached states simultaneously presenting switchable and controlled privacy. These smart windows utilize electrochromism and prompt the concept of "green" nanotechnologies that are very much in focus in today's scientific community [1–3].

The smart windows developed with integrated technology and photovoltaics can provide advantage of around 20 % savings in energy consumption while having the transmittance similar to regular glass windows [4-7]. In regular glass windows direct sunlight enters the premises during summer months leading to increase in indoor temperatures; while in winter the glass absorb the cold from outside and cool the premises more than desirable. To maintain comfortable temperature, climate controlling is done by air conditioning and heating thus increasing power consumption. And especially in countries where extreme weather presumes, power consumption is a major issue. So, climate control based smart windows that can maintain comfortable and suitable temperature in buildings are desired. The smart windows operate on the basic concept of EDG, a technology used to control transmission of daylight and provide privacy [5]. The major technologies that emerge for smart windows are: suspended-particledevice (SPD) and electrochromic (EC) device [7].

Figure 1 Two examples of electrochromic smart windows each are having both the fully colored and the bleached state [3].

SPD smart window is constructed by using two panes of glass separated by a conductive film with suspended light absorbing nanoparticles. This technology is under research. Nanoparticles like iron oxide along with nanocellulose may be used to be suspended in liquid/film such as in acetone/silicone oil/propylene carbonate. At no electrical bias, nanoparticles absorb light, making the glass dark [8, 9]. On application of bias, particles align and light passes through. The amount of light passing through the SPD-window is precisely controlled with electrical voltage. Figure 2, illustrates the working concept of SPD. However, the major advantage is that SPD switches ―ON‖ in 1-3 seconds and is expected to provide ~99% UV blockage promising energy saving [6].

A competing technology with SPD smart windows is the electrochromic smart window. Electrochromic windows consist of two glass panes with several layers sandwiched in between (as shown in Figure 3 (a) and (b)) under Offand-On conditions. The most commonly used electrochromic materials in between glass panes are tungsten oxide (WO3), niobium oxide (NbOx) or even violegens with titanium oxide (TiO2). On application of electrical bias across nanoscopically-thin coating on the glass surface the electrochromic layer is activated, which changes color from clear to dark i.e translucent states (usually dark blue), and the transparency level changes with bias [4, 8]. Different from SPD, electrical charge is applied one time (~ 1 Volt) to change the property of the thin film. Applying a reversed charge the glass returns to its original state. This dimming process moves slow from the edges taking a time that is varied between many seconds to minutes (depending on windows size) [8, 10]. Electrochromic glass window provides comforting level of visibility even in the darkened state. These smart windows require electricity to change its opaqueness and are energy based solution, so cost involved and difficult to commercialize for regular buildings [4, 8]. Though, electrochromic material based smart window is still in the developing state and further research is needed, these materials are extremely expensive hence being difficult to commercialize. Also the construction of this window is complex and the material has low life time thus again increasing cost.

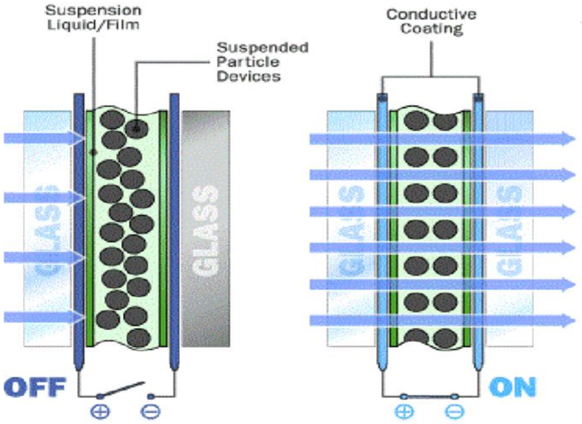

Figure 2 SPD based smart technology presenting the on/off process [8].

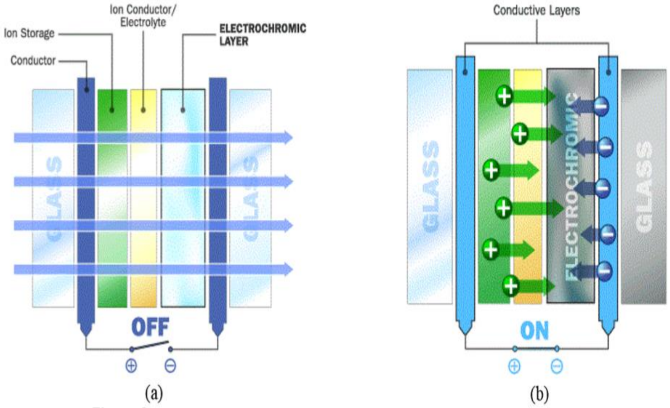

Figure 3 Electrochromic smart windows presenting the (a) off and (b) on processes [8].

As much as 30 to 40% of the primary energy in the world is spent in buildings, for heating, cooling, lighting, ventilation and appliances, and developed countries lie at the top of this bracket; the fraction of the electricity used in buildings is even higher and can amount to ~ 70% [3, 11]. The need for smart energy efficient window is clear and must function in harmony with nature and make good use of what nature offers in terms of light and energy. Hence, we review and describe a fully functional electrochromic material technology based smart window consisting of

LixWO2.89 and HxNiO2 as cathodic and anodic oxide films that work as electric dimming glass. Also the alternative SPD technology based on nanocellulose material for smart window application has also been reviewed in this paper. Finally, a combined (SPD-EC) technology utilizing nanocellulose fiber and electrochromic materials forming conductive nanomembrane to develop an innovative energy-efficient smart-window is proposed as an alternative option.

2. Electrochromic Smart Window

The electrochromic smart window is designed based on a generic model of EC device that consists of electrochromic material oxide layers along with electrolytic and ionic conductors to transfer charged ions and electrons across the device. An EC device design introduces a consistent construction to that of a thin film electrical battery whose charging state corresponds to a certain level of optical absorption. Figure 4 presents a generic EC device with five layers positioned between two transparent substrates (glass) [3, 12]. The five layers principally comprises of three different kinds of layered materials: the ion conductor (electrolyte) separates the two EC films (active electrochromic layer and counter electrode) that conducts ions and electrons and the two transparent conductors (TC) that conducts pure electron. The counter electrode EC film is also known as the optically passive ion storage electrochromic film. The electrons move into the EC films from the transparent conductors while the charge balancing ions enter the EC films from the electrolyte leading to optical absorption in the device. This optical absorption alters as the EC films have a variability of optical transmittance, when ions are inserted or extracted via a centrally positioned electrolyte. In all practical EC devices ion transport occurs with help of small ions and protons (H+) or lithium ions (Li+) which form the majority [3]. Previously, transparent liquid electrolytes and ion-containing thin oxide films were used [13], but following the development of electrical battery technology polymer electrolytes are in use in electrochromic devices [3]. A minimum of 1 V DC is needed to power the electrochromic device integrated photovoltaics for functioning. The EC smart windows being small in size, the voltage can be applied directly to the transparent conductors leading to evenly distributing the current thereby leading to reasonable uniform coloring and bleaching of the smart window.

The EC smart windows are expected to operate under strong solar irradiation, leading to the device being photochromic in addition to being electrochromic. Resulting in deeper coloration due to increased charge transfer; while also, the device may degrade especially due to formation of excess polymeric components for consistent resonant tunneling effects [14-20]. The EC devices have open circuit memory, and can function without energy for long periods; optical absorption can be tuned between states, but the optical change is slow depending on device size varying from seconds to tens of minutes [3]. In the EC windows the optical properties are in the atomic scale, so the windows are not hazy [21], a vital feature for windows used in building applications. Due to optical transmittance better color neutrality has also been achieved by using two EC films in a single smart window [3].

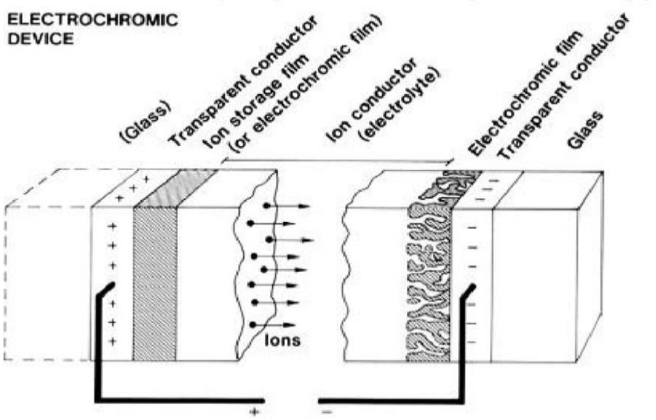

Figure 4 Generic five-layer electrochromic smart device on application of bias [12].

2.1 Electrochromic thin film

The EC device shown in Figure 4 forms the basis of today's practical EC smart window, but the device is still far from being introduced for mass production due to the device's complex construction and extremely costly materials needed for manufacturing. Though there are few prototypes of EC smart windows only some can be practically used. These are some full-scale products and prototypes that were recently (2014) delivered to customers, or at least evaluated together with potential customers [22-24]. A view of existing device designs and a brief discussion of their pros and cons are explained. A significant part of the EC functionality for all of these devices is provided by the tungsten oxide thin films [3]. The five layer EC device smart window comprises of two electrochromic oxide layer films where one supports ion insertion while the other is to allow for ion extraction across the device as per the operation needed for the EC device. Thus the two most popularly used EC oxide layers in general are referred as ―cathodic‖ that color under ion insertion, and as ―anodic‖ that color under ion extraction [3]. Cathodic oxide layers are formed by electrochromic materials such as W, Mo, Ti or Nb while the ―anodic‖ oxide layers are Ni or Ir. The two different polarity EC films used in the operation of the smart window provides to be highly advantageous for coloring and bleaching of the device indicating high optical transmittance as on applying bias ions transport between the two EC films in one direction making both of these films color, while ion transport in the other direction makes both films to bleach as has been termed by the lithium battery technology [3, 25, 26]. W and Ni exhibiting cathodic and anodic electrochromism, respectively, are the most commonly used oxides for EC smart window devices as described by the proton insertion/extraction while electrons are donated as electron (e-).

The crystalline nature and the EC properties of these oxide layers are to be analyzed. These oxide based layers in the device form a unified framework with MeO6 octahedra (where Me denotes metal) structure that are connected via joint corners and/or joint edges [12, 27, 28], which is associated with some amount of octahedral distortion [3]. The two oxides that do not fall in this situation are: the vanadium pentoxide (V2O5), which is formed either from heavily distorted VO6 octahedra or from square pyramidal VO5 units [29, 30]; and the hydrous nickel oxide (HxNiO2) that contains layers of edge-sharing NiO6 octahedra —the actual EC material [31, 32].

One of the most important features of electronic properties in the EC oxide layer is the octahedral organization [12, 28], where the 2p bands in oxygen are separated from the metal d levels and an octahedral equilibrium leads to splitting of these d levels in the bands and are denoted as eg and t2g. A schematic of the band structures for different EC oxide layers are illustrated in Figure 5. On addition of proton to this anodic oxide HxNiO2 is formed that provides coloring to the EC device anodically. This Ni based oxide layer is characterized by the partially empty t2g state (d level as per the energy band structure is split in two upper state eg and lower state t2g), which when added to the proton, these states fill due to insertion of ions and electrons, exhibiting a gap between the eg and t2g levels. The material is then transparent, considering that the band gap is wide enough, thus in turn increasing optical absorption adequately for the device [3, 12]. Pure tungsten oxide (WO3), the cathodic oxide of the EC device has full O2p band while an empty d band and is transparent, as is applicable for any wide band gap semiconductor. Addition of protons and charge balancing electrons to this tungsten oxide, HxWO3 is produced that provides a partial filling of the d band at the t2g level, leading to optical absorption as in the case for proton added nickel oxide [3].

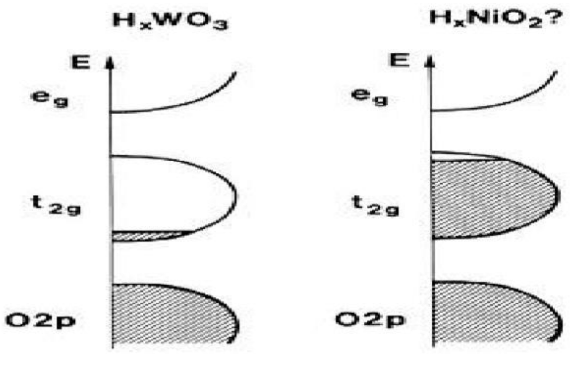

Figure 5 Schematic band structures for W and Ni based EC oxides added with proton. E denotes energy, while filled states are the shaded regions. [12].

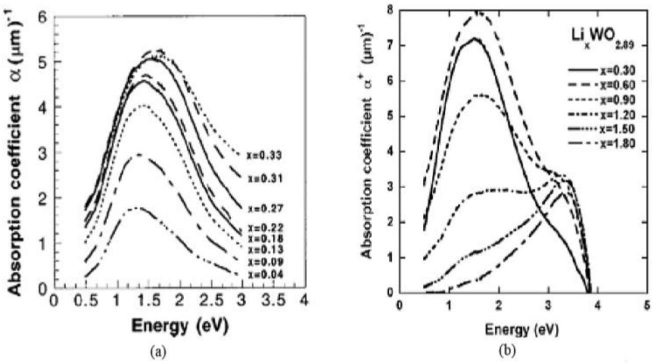

Figure 6 (a) W oxide films with different intercalation levels showing spectral absorption coefficient, where x is the Li+/W ratio [34]. (b) Spectral absorption coefficient at higher x values for Li+/W ratio when unintercalated film absorption is subtracted [36].

Optical absorption of the W based EC oxide is often associated with charge transfer and polaron absorption captures, so a close study has been performed to understand the principle. Electrons when inserted with ions enter the localized states, lying 0.1 to 0.2 eV below the conduction band, on metal ions changing W6+ sites to W5+, initiating a displacement of the atoms surrounding them thereby inducing a potential well, leading to charge transfer between the sites. The creation of small polarons with a physical extent of 0.5 to 0.6 nm is observed with the strong electron–phonon interaction [3, 33]. This WO3 film is electrochemically intercalated with Li+ ions to several levels x (defined as the number of Li+ ions per W atom) and the optical absorption coefficient is presented in Figure 6 (a) by Berggren et al. [34]. With Li+ the peak becomes broader and asymmetric around an energy of ~1.3 eV and on increase of Li+ intercalation the optical absorption is seen to increase while the peak position also shifts towards higher energies. The integrated absorption strength is observed to be proportional to x for x < 0.1 and levels off at larger intercalation levels [3]. At x = 0.04 and x = 0.36, the experimental optical absorption coefficient from Figure 6 (a) provides an excellent match with Bryksin's theory of polaron absorption [612] considering intraband transitions between localized energy levels in a Gaussian density of states. With various levels of Li+ intercalation into sputter deposited WO3 films was conducted to investigate the optical properties [36], which were quite similar to the ones for hydrogen containing material [37], and a substoichiometric film was achieved from the spectral optical absorption coefficient for Li+ intercalation [3]. At energy ~1.5 eV for lower values of x, a broad absorption band develops while the dominant absorption moves to higher energies for larger intercalation levels [3, 38]. A sharp increase in optical absorption above ~3.5 eV exists due to transitions across fundamental band gap of WO3 for unintercalated film absorption. To extimate the exact spectral absorption unintercalated film absorption is subtracted and presented in in Figure 6 (b), clearly showing highest optical absorption occurs at for Li+ with x varying between 0.3 and 0.6 [36]. The peak created due to the unintercalated film absorption is submerged and inexistent at lower x; as at x = 0 the states are empty so states will be singly occupied in the beginning of the intercalation, and electron transitions between empty and singly-occupied states will be common. But with increase in x the peak shift is observed leading to doubly-occupied states and then site saturation which in turn changes the absorption strength per transition. Thus, optimizing the Li+ intercalation and peak shift due to unintercalated film absorption, LixWO2.89 is possibly the most effective for x in between 0.3 to 0.35 for a practical EC smart window considering the long-term cycling durability [3, 36, 39]. So from the study outlined the cathodic oxide (active electrochromic) film used is LixWO2.89 for x in between 0.3 to 0.35, while the anodic oxide (counter electrode) film used is HxNiO2 for x ~ 0.3 in present EC smart windows, respectively, are best suited for their reliability, performance and durability [3].

2.2 Transparent Electrical Conductors and Electrolytes

The EC device as described by Figure 4 consists of two ion conductors also known as electrical conductors. These electrical conductors needs to be transparent and are of large interest not only in electrochromics but also in variety of devices such as thin film solar cells, light emitting devices, display devices of various types, etc., thus there are numerous reviews covering the field of transparent conductors [40, 41, 42, 43, 44–53], and here we focus on the materials related work to be used in EC smart window. In the EC smart windows two transparent conductors are required on either side between the glass substrate and the electrochromic layer and is possibly the most expensive part of the EC window, so lots of attention is needed [3]. Thin films of heavily doped transparent conducting oxides are used in EC devices such as In2O3:Sn (ITO), In2O3:Zn (IZO), In2O3:Nb, ZnO:Al (AZO), ZnO3:Ga (GZO), ZnO:Si (STO), SnO2:F (FTO), SnO2:Ta, SnO2:W, and various other doped substitutes.

A low resistivity as low as ~1 × 10−4 Ωcm is desired as this can provide a luminous transmittance (Tlum) in few percent in a film with a thickness of ~300 nm to give an adequate resistance per square, and excellent durability. The oxide based metal conductors such as films of ITO, FTO, AZO and GZO that are prepared by reactive dc magnetron sputtering onto glass are able to produce resistivity of ~2 × 10−4 Ωcm [3]. Though nanoparticle based deposition to produce films may be an alternative for low-cost applications but, so far no films that can achieve sufficient electrical contact between the clusters [3, 54, 55]. Figure 7 clearly shows the transparency level across the spectrum of solar radiation and also the front and back reflectance for FTO based coating, which is quite similar to most of the other oxides [56].

In EC windows glass being the substrate, thus cracking and accompanying loss of electrical conductivity is ruled out which are highly probably for deposition onto flexible substrates that are bended to a radius smaller than a few centimeters [57-59]. Indium being highly expensive the ITO films that are widely used increases the cost of the smart windows and also this ITO film deposition requires careful process control [3]. Films such as AZO and GZO also provide similar optical and electrical properties, but process supervision and control is more stringent, while good FTO and TiO2:Nb films must be deposited onto hot glass nearly ruling out these options for regular EC smart windows [3]. Health related pulmonary disorders are developed only on careless handling in preparation of Incontaining oxides for ITO films [60-63]. But ITO is still the only suitable option as a transparent conductor film in EC smart window.

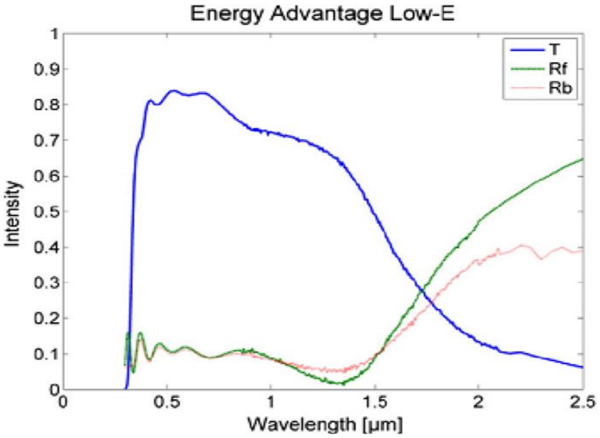

Figure 7 Spectral transmittance T and reflectance from the front (Rf) and from the back (Rb) for a FTO film [56].

2.3 Electrolyte for EC device

In an EC device an electrolyte or an ion conductor is used as the material layer at the junction of the two electrochromic (anodic and cathodic oxide) films. The main functionality of the electrolyte is to allow the conduction and transport of ions and electrons across the device while also works as an excellent adhesive so as to have both sides of the device well connected. Thin film based electrolytes such Ta oxide that are co-deposited with H+ or Li+ have been studied and applied for usage in EC devices for ion conduction [64-68]. The proton-conducting film display ion-conductivity of ~ 10-9 S/cm but when the film prone to heat conductivity decreased [3], presenting a clear view for the film to be not suitable for EC smart windows in warm climate. In EC devices, polymers and ionic liquids have also be used and studies exists with boronate esters [69], ormolytes [7072], Li-doped poly-trimethylene carbonate /PEO [73], poly-methylmethacrylate (PMMA) based electrolyte [74], ionic liquids [75, 76–79] and gel electrolytes plasticized with ionic liquids [80]. For EC smart windows in situ polymerization may aid in delineating sealing difficulties so polymerization of polymer electrolytes [81] as well as ionic-liquid-based gel electrolytes [82] are being researched [3].

Nanoparticles are added to polymer electrolytes and ionic liquids and a model electrolyte of polyethyleneimine– lithium bis-trifluoromethylsulfonyl (PEI–LiTFSI) [83-87] is developed for use in EC smart windows. SiO2 nanoparticles when added to the electrolyte ion conduction occurs introducing coloration and bleaching in an EC device; with increase in number of particles the ion conductivity rises monotonically but diffusion transmittance decreases over 6 wt%. Nanoparticles of a transparent electrical conductor such as ITO, when added to the electrolyte near-infrared absorption is obtained, and solar transmittance (Tsol) is diminished without significantly lowering Tlum. This optical property for EC smart window is needed in warm climates [3]. Spectral transmittance of ITO based (PEI–LiTFSI) electrolyte is presented in Figure 8 [84] and even with 7 wt% of ITO, Tlum = 83.3% and Tsol = 56.3% is achieved while the electrolyte is not hazy, thus presenting excellent optical transmittance with dilute suspensions of nanoparticles and inducing (PEI–ITO):LiTFSI electrolyte as the most suitable option for EC smart window.

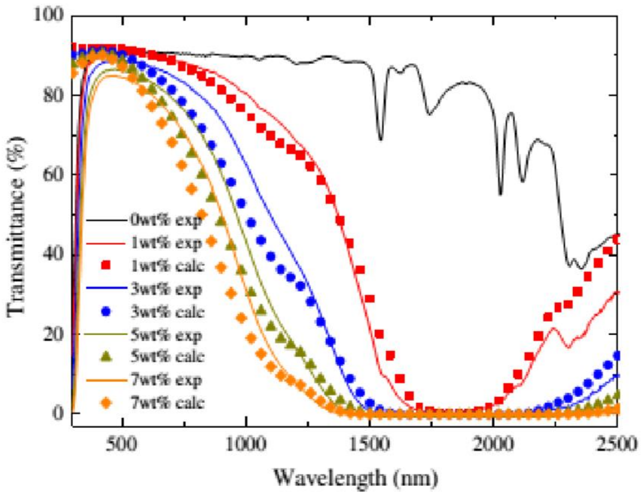

Figure 8 Spectral transmittance of ITO nanoparticles in (PEI–ITO):LiTFSI electrolyte compared for experimental to calculated data. [84].

2.4 EC device smart window

The five layered EC device which forms the basis of the EC smart window can be used as a foil based device that can be laminated on glass panes or may also be used to place in between a pair of glass panels. Considering the basis of the structure of the EC device the basic principle of operation of the EC smart window is shown in Figure 9 (a). The W based oxide that forms the cathode electrochromic oxide layer is the most extensively used in today's EC devices while Ni is used as the anodic electrochromic oxide. This EC smart window based on W oxide and Ni oxide works quite similar to that of electrochromic battery device and numerous studies have been reported for glass based devices [88-102] as well as for PET (foil)-based devices [14, 33, 103-108].

Figure 9 (a) demonstrates a design of an EC smart window: the first glass is coated with ITO and W oxide, a second glass of the same kind is coated with ITO and Ni oxide, and the oxide layers are joined via an ion conducting adhesive. Electrical charge is inserted and extracted through ITO films from the device. This EC device is also used as a foil to laminate of glass windows and Figure 9 (b) shows the spectral transmittance modulation in the luminous wavelength range for these EC films when different amounts of charge are transported [108]. In the long-wavelength part of the spectrum the W-oxide-based film colors, while in the short-wavelength part the Ni-oxide film colors [3]. For the EC smart window the coloration/bleaching dynamics is an essential property so the device can serve as a proper window application [12, 109]. Recently data is published on a 5 × 20 cm2 EC smart window with a structure similar to Figure 9 (a) at a transmittance at λ= 532 nm for different distances from the current contact [110]. The transmittance was observed to change much faster closer to the current contact than far away. It has also been observed that the colored-state transmittance can be reached by placing two or more EC foil based devices on top of each other thus indicating optical modulation with double layer device [3]. The EC based windows whether used as foil or glass based window are of interest and is on the verge of commercialization except for the major fact of cost due to which alternative options are needed for smart windows. The EC foil based devices can be produced by roll to-roll deposition followed by lamination [111] with only post-deposition application of electrical contacts which will have shape and size consistent with the primary foil manufacturing, thus an easy concept to be implemented at

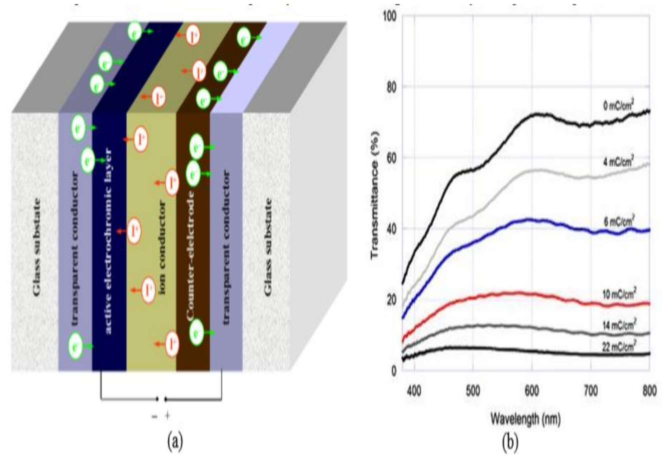

Figure 9 (a) EC smart window showing the principle of operation. (b) Spectral transmittance of the EC foil based device [108].

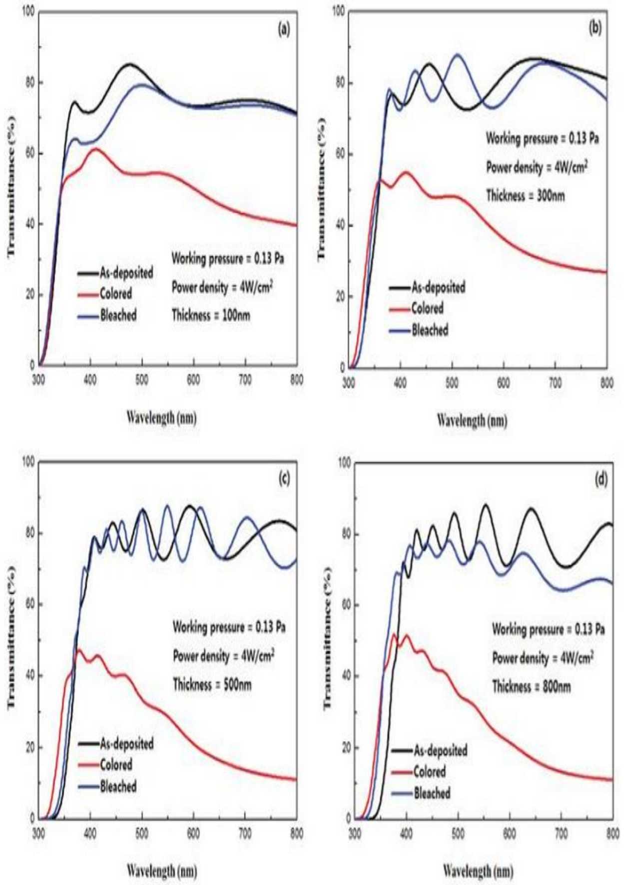

Figure 10 Optical transmittance of EC smart window for WO3-x thin films (a) 100 nm, (b) 300 nm, (c) 500 nm, and (d) 800 nm for as-deposited, colored and bleached condition [112].

possibly lower cost, but cannot be a substitute for glass windows. It has already been observed that the WO3 doped with Li+ ions forming LixWO3-x is best suited for the purpose of cathodic oxide in the EC smart window. The EC smart window with WO3-x thin films of various thicknesses (100 nm, 300 nm, 500 nm, and 800 nm) has also been characterized for optical transmittance and presented in Figure 10 [112]. The spectral transmittance of various thicknesses of the thin-film deposited on glass substrate in the three conditions as-deposited, colored and bleached in the visible wavelength range is observed for all four thicknesses in Figure 10 [112]. The transmittance varies with the film thickness, though the films remain transparent at x below 0.3 [113]. Due to the existence of the fundamental absorption edge, as previously reported in the literature, the reduction in the transmittance spectra at the wavelength of ~350 nm is observed [114] and this is seen to be almost similar for different thickness of WO3-x films [112]. The oscillation of the film is directly related to the film thickness which is from the optical interference due to the multilayered components [115]. With injection of Li+ ions to the film the original color transforms to dark blue and the device's optical properties change from transparent to dark blue and vice versa with application of an external voltage.

The EC smart windows that is a five-layered device with HxNiO2 and LixWO3-x as anodic and cathodic oxide layers, respectively, developed till date are suitable for practical installation and usage, though there are some issues such as these electrochromic materials are somewhat hazardous in nature so, protective measured to taken. These EC smart windows are extremely expensive so, replacing for regular windows in residential/ commercial buildings is not being suitable. Research is still underway in manufacturing EC smart window with low-cost is the present initial objective, which may be possible only when large area technology development can be implemented for EC windows.

3. SPD Smart Window

The suspended particle device (SPD) smart window is an alternative for the EC smart window that is designed based on a generic model of EC device consisting of electrochromic material oxide layers along with electrolytic and ionic conductors to transfer charged ions and electrons across the device. Looking into SPD based windows as an alternative is mainly due to minimizing of the huge cost related to EC materials. A SPD smart window has a long history of development since 1930s by Edwin Land's ―light valvesǁ leading to series of patents [116]. In the SPD two sheets of glass or plastic coated with transparent electrically conducting thin films are used to sandwich a polymer layer consisting of a large number of polarizable particles. These nanoparticles are in size of less than ~200 nm to avoid the visible haze and are polyiodide/ polyhalide that have strong optical anisotropy such as herapathite (i.e., quinine bisulfate polyiodide) [117, 118]. High optical transmittance is an important aspect of proper functioning of an SPD, thus these nanoparticles in the polymer needs to be aligned in order to yield higher transmittance [3]. An electrical bias is applied to the polymer layer via the transparent conducting films to adjust and increase the optical transmittance in an SPD. With decrease in applied voltage the particle alignment disassembles the device becomes darker and a bluish-black appearance is attained. Barrios et al. [119] presented in figure 11 the spectral direct and diffuse transmittance of an SPD with bias voltage varying from 0 V to 100 V ac, thus directly indicating change of Tlum with voltage [3]. It has also been observed that the SPD based smart windows exhibit noticeable haze and modulate the transmittance in luminous range while solar range modulation is limited, which is a contrast to the functionality of EC smart window devices [3]. SPD based windows are still in the developing state and research is going on in improving the transparent conducting film with a membrane of nanoparticles or most probably nanocellulose again an easily and abundantly available material [120]. Nanocellulose based SPD window if possible will be quite cheap and be comparable to the regular windows. So, developing a SPD smart window that will be cheaper than a practical EC window is the major objective, while it is also expected that the SPD window can also provide optical transmittance.

3.1 Nanocellulose conducting film

The transparent conductive film that is used in a SPD smart window can be replaced by nanocellulose fibers and crystals when made conductive in nature. The nanocellulose fibers (CNC/NFCs) that is available abundantly from wood/paper pulp and from damaged/unused parts and portions recycling a share of bio-waste is a kind of inexpensive material, and is possibly best fit material for SPD smart windows. Paper is a product of cellulose providing fast printing and strong binding of other materials is also a low cost, flexible and porous substrate. Recently, thin film transistors, solar cells and batteries have been demonstrated using paper substrate thus exploring electronics and power applications [121, 122]. The cellulose fibers that forms the basis of paper is of ~20 □m diameter which is larger than the wavelength of visible light, so regular paper is not transparent and not suitable for window applications. But, each of these cellulose fibers that make up this paper consists of millions of nanofibrils cellulose (NFC) with diameter of ~4 nm and length of ~2 mm [120]. Now disintegrating these nanofibrils using high pressure in a solution and reforming the paper without the solvent as a membrane is called nanopaper [123-125]. As the diameter of the NFCs is smaller than the wavelength of visible light, nanopaper is highly transparent and the light scattering effect is significantly reduced compared to the regular paper. Figure 12 (a), shows the schematic of optical transmission through a transparent nanopaper where the backscattering effect is nearly negligible and each individual nanofiber leads to forward scattering presenting superior optical properties of the nanopaper. Though the nanopaper consists of number of layers of 1D nanostructure light propagates resulting in highly transparent substrate making nanopaper different from regular paper or plastics and possible to be used in window based technologies [120].

W˚agberget al. [126] fabricated nanopaper by disintegrating the wood based cellulose fiber to create carboxymethylated NFC which forms the nano-membrane paper. Atomic force microscopy (AFM) was used to study the diameter and length of the nanocellulose fibers that was then drained and compressed dried to form the NFC paper sheets. Any additional water was removed to form a smooth gel-like substance that was then sandwiched between two paper carrier boards and placed into the drying unit of the paper sheet. The nanopaper thus formed is ~40 □m thick, and is highly transparent when placed close to the substrate (Figure 12b) and substrate cannot be observed clearly when the nanopaper is around 2 inches away being hazy (Figure 12c). So, the optical transmittance is witnessed to decrease when the substrate is moved away from the nanopaper

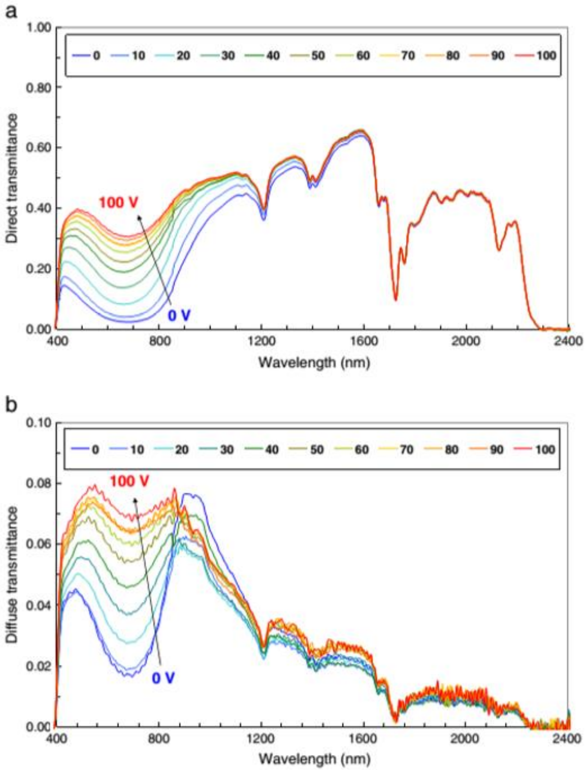

Figure 11 SPD smart window for spectral (a) direct and (b) diffuse transmittance with applied voltage varied between 0 V and 100 V ac. [119].

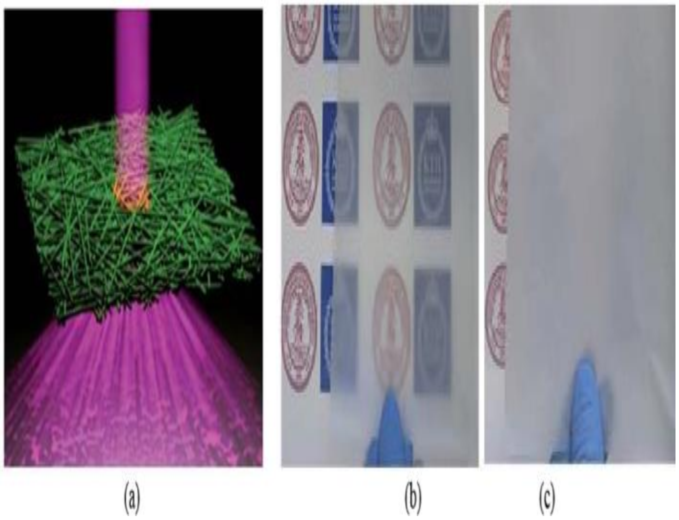

Figure 12 (a) Schematic of a nanocellulose paper indicating its light scattering effect. (b) Transparent nanopaper held close to the below object indicate high optical transparency. (c) Same nanopaper at a distance from object rarely visible indicating large light scattering [120].

The optical transmittance being the major issue in nanopaper for its usage in windows polyethylene terephthalate (PET) plastic substrate and the nanopaper were simultaneously compared for their optical properties. In the experiment the light detector was moved away from the substrate, and the fraction of the light collected showed the divergence of the transmitted light; so the distance between the collector and the substrate was set 0 mm, 25 mm, 50 mm and 75 mm. The optical transmittance observed from the transparent nanopaper is shown in Figure 13 (a) which was extremely different from the PET substrate [120]. The transmittance for the plastic substrate remains constant when detector is moved away, but in case of nanopaper the transmittance changes intensely. This is mainly because the nanopaper is a 1D nanostructure with high porosity and is non-uniform leading to large light scattering while plastic is dense uniform structure larger than the wavelength of light [120]. Nonetheless, the amount of light scattered from a nanopaper is small and in forward direction due to its building blocks are of few nanometers thus a significant improvement is observed compared to regular paper. The back-scattering is lessened by reducing the cellulose fibers to nanofibrils and also closely packing them creates a dense film, which also decreases the scattering of light. As these NFC fibers used in nanopaper is smaller than the wavelength of light, light scattering is isotropic, i.e. the scattering in the forward and backward directions is equal. Using Mie [127] method the scattering crosssection is calculated for the NFC fibers and is compared to experimental data for nanopaper and is presented in Figure 13 (b) [120]. The overall transmittance of nanopaper was observed to be ~90% quite close to plastic substrates.

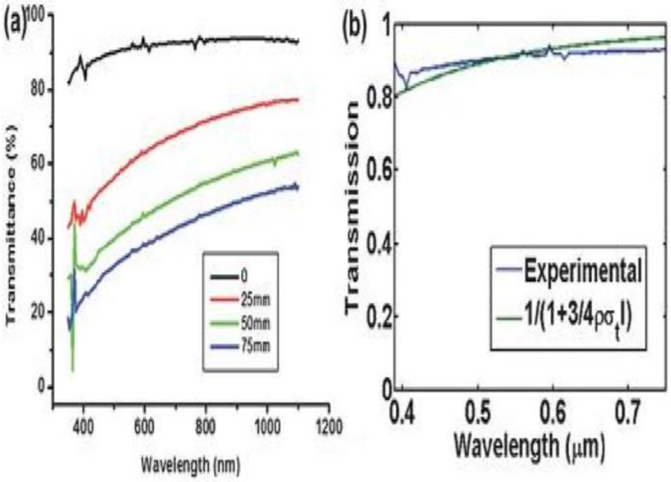

Figure 13 (a) Optical transmittance of transparent nanopaper when detector placed at varied distances. (b) Experimental and optical modeling comparison of spectral transmittance of nanopaper. [120].

To use nanopaper in smart window applications transparent conductors such as tin-doped indium oxide (ITO), carbon nanotubes (CNTs) or silver nanowires (AgNWs) are deposited [128-132]. With the use of nanopaper instead of plastic or glass substrates problems such as (i) the mechanical instability of ITO on plastic or glass would be partially resolved as there will be negligible stress (ii) the printing capability will be excellent using porous nanopaper and (iii) the nanopaper's high optical transmittance and large forward light scattering can bring new developments in the usage [120]. ITO films of ~300 nm are deposited on nanopaper, which becomes conductive and transparent as shown in Figure 14 (a) with a sheet resistance of 12 □sq-1. This doped membrane decreases the reflection due to light scattering improving the visibility in bright environments such as in sunlight. The binding of the nanopaper with ITO is robust leading to somewhat low sheet resistance even after repeated bending of the membrane. The overall transmittance of the nanopaper is then compared with the membrane that is doped with CNT/ITO/AgNWs and presented in Figure 14 (b) [120]. The performance observed is analogous with that of plastic or glass based substrates.

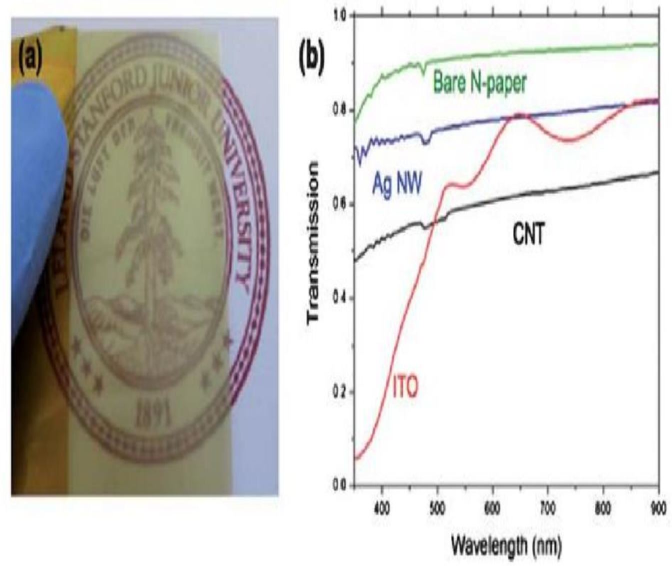

Figure 14 (a) Optical transmittance of ITO doped conductive nanopaper. (b) Comparison of transmittance of bare-nanopaper to that of doped ones for ITO, CNT and AgNW. [120].

There has already lots of development in the research leading to the applications of nanocellulose based nanopaper as a membrane that can transmit light as well as be conducting. This conductive membrane can be suspended in a transparent liquid such as acetone/silicone oil and when bias is applied the light throughput can be controlled, thus developing the SPD technology appropriate for smart window applications [3, 120]. Based on this aspect of the nanopaper membrane the material has high probability of being used in SPD technology based smart window, but still research work needs to be carried out to be able to implement nanopaper membrane for both conditions of high transparency and also blackened out under bias to perform proper electric dimming effect needed in a smart window. On developing SPD based smart window with nanocellulose based membrane will be of high advantage as it can replace the only existing option of EC smart windows which are to some extent prone to health hazards and also extensively costly for regular usage.

Innovative Technology Smart Window

The foremost objective of smart window is to have electric dimming effect providing control of privacy as and when needed by the inmates of the building and also to guard furniture and related items from direct exposure to sunlight. Research has gone a long way in developing various kinds of technology related to the development of smart windows. The most common and well established option is the EC smart window that we have already reviewed, but the major issue with this is its cost which is sky rocketing compared to regular glass windows. The other alternative is the SPD technology based window, but this is still under research and long way to go before it can be commercialized as an option. To this effect of the review we introduce an innovative technology based smart window that will combine both the EC device and SPD technologies and is expected to less costly and less hazardous while will suffice the electric dimming cause for the smart window. This innovative smart window is expected to have the similar glass substrate on both sides while the inner side of both the glasses will be coated with ITO to function as transparent electrode as is the case in both EC devices and SPDs [3, 120]. The nanocellulose fibrils that were doped with CNT/AgNWs to form the conductive nanopaper membrane in SPD technology smart window [120] will also be used in this technology. But, instead of using one conductive nanopaper membrane as in SPD, here two nanopaper membranes will be used and each will be doped separately to form two different membranes. One will be doped with LixWO3-x while the other nanopaper will be doped with HxNiO2 to form the cathodic and anodic electrochromic oxide membranes, respectively, thus forming the SPD-EC films. Due to the electrochromic materials used here will be only be used for doping the hazardousness of the material in EC smart windows will be minimized. As these thin nanomembrane films will have the electrochromic material as in an EC device, the SPD-EC device is expected to function similarly on application of bias. Also as the NFCs form a conductive nanopaper will support the functionality of the EC device thus requiring less amounts of electrochromic materials in this innovative technology based smart window design. The advent of nanopaper in this smart window which will be a conducting membrane as well will possibly be able to work as a solar panel as has already been experimentally observed [120]. This concept of conserving solar energy by the smart window will bring forth the concept of green technology into building standards. The solar energy conserved can possibly generate enough electricity needed for the purpose of electric dimming by the smart windows. This innovative smart window will thus be less costly having an innovative approach in the technology development as it is expected to function not only as electric dimming glass but also as an energy sustainable device due to the integration of nanopaper, thus conserving, transforming and utilizing the solar energy (introducing green energy). This innovative technology based SPD-EC smart window is probably the future of smart window that can possibly be cost effective while bring forth the electric dimming as is desired for regular residential/commercial buildings.

Social and Environmental Benefits

It is expected that the application of smart windows in regular residential/commercial buildings will potentially meet the international as well government's demands for heat and sound resistant dimming smart windows.

The innovative technology based smart window as will also be comprising of the solar panel due to the involvement of conductive nanopaper will probably be able save ~20% of energy usage especially in Canada that have extreme winter and summer climates [5, 6]. This will be possible by not letting the rooms to be extremely heated in summer months as electric dimming will protect over-heating, thus lees consumption of hydro (electricity) due to negligible usage of air conditioners [5-8]. So the smart windows will suffice the government demand for energy efficient buildings reducing energy use in Canada, US and other countries, thus indicating its significance on economic, social, and environmental benefits. The evaluation of the multi-functional solar panel based on conducting nanocellulose membrane will help determine the technical feasibility (temperature control, stability) of using the SPD-EC smart glass technology for residential buildings. The field measurement of these smart windows will result in practical guidelines based on real time performance of climate control due to dimming effect while also have relatively comparable transmittance as compared to regular glass windows [3, 5-7, 120]. The improved innovative solution will be using doped nanocellulose fiber (CNC/NFC) based conducting nanomembrane film that is expected to benefit and will encourage the development of products produced from nanocellulose crystals forming nanopaper. CNC is a wood byproduct, thus the membrane developed for smart windows will be from an abundantly available substance that has nearly negligible cost; utilizing these unused portions of the timber industry process will in a way recycle the share of bio-waste a favorable and remarkable way of enriching the environment. This conductive nanopaper will modify and enhance the existing smart window technologies with the expectation of developing next generation system to meet the need of cost efficiency. The nanopaper is also expected to function as a solar panel inbuilt in the SPD-EC technology based smart window thus will be generating electricity from the sunlight that will be used for the electric dimming of the smart windows thus no additional usage of electricity and will be conserving green technology in the building standards, most effective social and environmental benefit. Using smart windows will directly eliminate the use of window curtains and blinds in buildings, a major advancement, as disposal/recycling issues, cost, and maintenance are a distress for the consumers. Also the window curtains/blinds gather dust, which relates to health problems (asthma), especially in hospital buildings, a major health risk [6, 7]. CNCs are used in medicine/pharmaceuticals and even in some food products, therefore assumed devoid of health hazards, thus using these nanopaper based smart windows in place of regular glasses and curtains will definitely benefit socially, environmentally and also be cost effective. By facilitating appropriate use of multi-functional panel technologies in smart windows, long term renewable usage can be achieved as the smart windows will last long enough performing the electric dimming effect and save consumer's money in replacing blinds and curtains for the windows; thus will reduce negative impacts on the environment as well as mark positive impact on the country's economy.

Summary

Technologies for smart window applications such as electrochromism and suspended particle though not mature but are already there for some time now and can be used for fenestration in energy efficient buildings introducing ―green‖ nanotechnology which is of larger interest [1]. Global warming being the most alarming issue in today's scientific community, energy efficiency in the built environment is of greatest importance for combating, as is discussed with the introduction of the proposed SPD-EC based smart window in this review.

The existing electrochromic material based multi-layer EC device for the smart window is reviewed that resemble a thin-film electrical battery. The optical transmittance, electrical conductivity and stability of the device for smart window application are presented. The electron and ion transfers across the device layers and their interaction for the electric diming are well versed for further research. The review also covered details of different transparent electrical conductors and electrolytes, which are the most essential part of the EC smart window. The EC materials have the capability of functioning as thin-film solar cells, which may possibly supplement for generating electricity from sunlight and can supply the voltage required for dimming. Issues related to health hazards and manufacturing cost is noticed as the major drawback for regular usage so, research needs to be performed in enhancing the material properties or raise an alternative in reducing cost while maintaining the similar or higher throughput of smart window.

The SPD technology based smart window an alternative to the EC based window is still under research. Nanocellulose based nanopaper doped conductive nanopaper is used as a suspended membrane, though a challenge, but is being possible to function dimming effect. This technology is less costly compared to EC technology, but far from commercialization. The optical transmittance of the materials used is a hindrance when compared to EC device, so extensive research to be performed.

An innovative SPD-EC technology based smart window with nanopaper (CNCs) doped with electrochromic materials is proposed as the future outlook in the smart window development that can function as electric dimming as well as solar panels generating electricity sufficient for the dimming purpose from the acquired sunlight. This device is expected to be less costly and not prone to hazards due to minute usage of electrochromics, which led to the discussion of social and environmental benefits of smart window by utilization of bio-waste and elimination of regular glass windows along with curtains/blinds, thus reducing maintenance and replacement costs. This SPD-EC technology based smart window will be energy efficient and is expected to induce green nanotechnology standards in structural building designs.

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