



## A photoactive layer in photochromic glazing



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### ABSTRACT

Different approaches have been studied to evaluate the efficiency of the photoactive layer in a photochromic (PC) device. The studied device combines materials typically used in dye-sensitized solar cell (DSSC) and an electrochromic (EC) layer of WO<sub>3</sub>. First, we examine if the dye could be attached directly to the EC layer forming an efficient photoactive layer to colour the PC device. Further, different TiO<sub>2</sub> layers have been coated on the EC layer to enhance dye loading and two different sol-gel TiO<sub>2</sub> layers and the post-treatment of the EC layer with a titanium(IV) chloride tetrahydrofuran complex have been studied. The dye loading of different photoactive layers and their efficiencies in DSSC have been evaluated and discussed with regard to the performance of the PC devices. The results confirmed that the dye could be attached to the WO<sub>3</sub> layer, but that the voltage of the DSSC is too low to colour the device. To realize a functioning PC device, the addition of TiO<sub>2</sub> is necessary. The best performance (deep and fast colouration) is obtained for a PC device with a TiO<sub>2</sub> sol-gel layer; the solar transmittance of the PC device decreases from 57% to 7.5% in under three minutes. According to our knowledge, this is the first study of the impact of the photoactive layer on the photochromic glazing's response.

### 1. Introduction

A photochromic (PC) system can be used as a simple smart window; its transmittance is dimmed upon solar illumination but returns to its original value in the dark similar to photoreactive sunglasses. In general, photochromism brings a dynamic function to glass enabling the control of the amount of direct sunlight entering a building, i.e. it gives control over excessive illumination in a room (glare protection) and avoids an over-heating of the building, which reduces the cooling load and improves comfort. Especially for an efficient glare protection a transmittance below 5% should be reached, which is still a challenge for devices as they are described in this paper. According to our knowledge, there is limited literature on a photochromic system that have an electrochromic layer (EC) and a thin transparent dye sensitized solar cell (DSSC) [1–3]. So far, most of laboratory research has been performed on the photoelectrochromic (PEC) system. Both systems, PEC and PC, combine an EC layer with component of a DSSC (TiO<sub>2</sub>-dye/electrolyte/Pt) and colours under solar illumination. The difference between them is that PEC can be either fully or partially bleached under solar illumination, but requires the use of transparent conductive electrodes (TCO), wiring, a power supply and a regulation unit. Alternatively, a PC device is a fully passive device whose transmittance depends only on illumination intensity.

The PEC device was first described in a US Patent [4] and in [5,6],

but its main disadvantage is its slow bleaching kinetics due to the photoactive layer and EC layer being positioned at separate electrodes. The device has been significantly improved by Hauch et al. [7] who proposed a novel device structure in which the TiO<sub>2</sub> layer is positioned directly above the EC layer (glass-TCO/EC/TiO<sub>2</sub>-dye/electrolyte/Pt-TCO-glass). This configuration allows the device to be rapidly bleached by short circuiting of the electrodes under solar illumination. Details about the PEC device configuration, material development and its performance can be found in [7–9]. This structure (glass/Pt/EC/TiO<sub>2</sub>-dye/electrolyte/glass) using similar sol-gel materials as in a PEC is also appropriate for producing an efficient PC device [1]. Recently, a PC device with sputtered WO<sub>3</sub> and TiO<sub>2</sub> layers showing excellent visual (solar) transmittance modulation from 74% (63%) down to 30% (20%) has been reported [3].

In this study, we present a similar device structure based on sol-gel materials that combine the components of a DSSC with an EC layer, but without a Pt layer on the photoactive electrode (Fig. 1). It consists of two glass substrates of which one is coated with a photoactive layer (dye-covered nanoporous TiO<sub>2</sub> layer) situated on an EC layer (porous WO<sub>3</sub>), and an electrolyte containing lithium ions and a redox couple (I<sup>-</sup> and I<sub>3</sub><sup>-</sup>). The pores of the TiO<sub>2</sub> and WO<sub>3</sub> layers are filled with the electrolyte. Although not applied in this study, a Pt layer could be added on the photoactive electrode at different positions [10] to further tune its colouring/bleaching characteristics by catalysing

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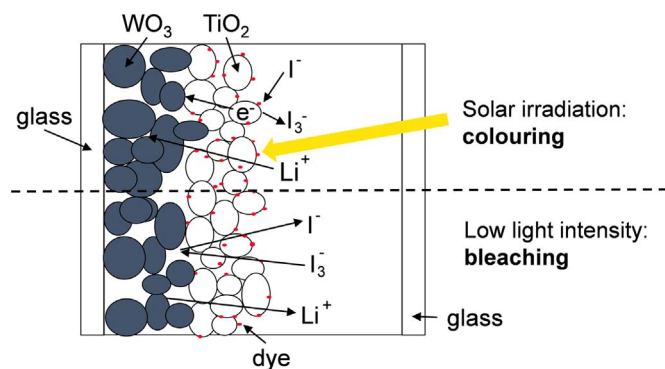


Fig. 1. Schematic of a photochromic device with an iodide/triiodide redox couple electrolyte, colouring when irradiated by the sun (high intensity) and bleaching in the dark (or at low light intensity).

recombination losses. During illumination, a dye molecule absorbs a photon of the incident light whereupon an electron is rapidly injected from the excited state of the dye into the conduction band of the  $\text{TiO}_2$  and intercalates into the  $\text{WO}_3$ . Ionized dye molecules are then reduced by the (tri-)iodide ions in the electrolyte while  $\text{Li}^+$  ions intercalate into the  $\text{WO}_3$  keeping the charges balanced. This injection of electrons, colours the  $\text{WO}_3$  blue. Under low light intensity or in the dark recombination reactions prevail,  $\text{Li}^+$  ions and electrons leave bleaching the  $\text{WO}_3$ . Bleaching is governed solely through these recombination reactions. A more detailed explanation about colouring and bleaching is given in detail in [1].

The optical contrast of a PC device is limited by the efficiency of the photoactive layer, e.g.  $\text{TiO}_2$ -dye, exposed to solar irradiation and by the thickness, colouration efficiency and redox potential of the EC layer [2]. In our PC device the integrated photoactive layer ( $\text{TiO}_2$ -dye), together with the redox electrolyte, represents the “inner” power supply for colouring the EC layer in the PC device. The requirements for an efficient photoactive layer in the DSSC are a large inner surface area and good connectivity between the  $\text{TiO}_2$  grains. A large inner surface area enables a high dye loading for efficient light harvesting while good connectivity between the  $\text{TiO}_2$  grains assures good transport of the generated electrons [11,12]. An increase in thickness of the  $\text{TiO}_2$  layer improves electron generation and leads to a deeper and faster colouration, and results in a more efficient solar cell; both in terms of the open circuit voltage ( $V_{OC}$ ) and short circuit current ( $J_{SC}$ ). The photoactive layer needs to be thin, so that it remains transparent and the “inner” DSSC provides the potential for overcoming the redox potential of the EC layer necessary to colour the PC device, while the current influences the colouration kinetic. We have previously studied the influence of the photoactive layer (dye-coated  $\text{WO}_3$  and  $\text{TiO}_2$  layer) on the performance of a PC device and to the best of our knowledge there exist no published studies describing the influence of different nanostructured  $\text{TiO}_2$  layers on the performance of a PC device. To bridge this gap in the knowledge, we examined two different sol-gel  $\text{TiO}_2$  layers and a thin  $\text{TiO}_2$  coating formed by treating an EC layer with a titanium (IV) chloride tetrahydrofuran complex ( $\text{TiCl}_4$ -THF). Two sol-gel syntheses were developed both based on titanium isopropoxide ( $\text{Ti}(\text{OiPr})_4$ ) while two different complexants (acetyl acetone and ethylene acetoacetate) were used to stabilize the sol. In addition, into an ethylene acetoacetate based sol a “softener” poly(propylene glycol) bis(2-amino propyl ether) – 2-APPG 4000 was added to reduce the brittleness of the  $\text{TiO}_2$  layers. A third approach is based on  $\text{TiCl}_4$ -THF treatment that previously has been used to prepare a highly efficient photoactive layer in a DSSC [13–19]. The method involves post-treatment of the  $\text{TiO}_2$  layer in which a thin layer of  $\text{TiO}_2$  is grown onto the  $\text{TiO}_2$  nanoparticles creating a double layer and increasing the connectivity between the  $\text{TiO}_2$  grains. Different explanations of the impact of this coating have been reported: (i) improved electron transport due to improved connectivity between the  $\text{TiO}_2$  grains [13–17], (ii) increased amount of dye

adsorbed on the  $\text{TiO}_2$  layer due to increased number of specific binding sites [14], (iii) better dye anchoring due to improved binding of the dye [16] and (iv) improved performance of the DSSC due to increased light scattering [18]. Several  $\text{TiO}_2$  precursors have also been used for post-treatment including titanium tetrachloride [13–18],  $\text{Ti}(\text{OiPr})_4$  [19] and a  $\text{TiCl}_4$ -THF complex [20]. In this study, we use a  $\text{TiCl}_4$ -THF post-treatment method to prepare the photoactive layer on top of the EC layer.

One question that arises is whether or not a  $\text{TiO}_2$  layer is needed in a PC device or could the dye itself be attached directly to the  $\text{WO}_3$  layer. Zheng et al. [21] successfully adsorbed a  $\text{N}_3$  dye (cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II)) directly on the  $\text{WO}_3$  layer and then fabricated and evaluated a  $\text{WO}_3$ -based DSSCs (TCO/ $\text{WO}_3$ -dye/electrolyte/Pt-TCO) using a 12  $\mu\text{m}$  thick dyed  $\text{WO}_3$  layer. The DSSC maximum efficiency was 0.75%,  $J_{SC}$  4.6  $\text{mA}/\text{cm}^2$ ,  $V_{OC}$  390 mV and fill factor ( $FF$ ) 0.38 (AM 1.5, 90  $\text{mW}/\text{cm}^2$ ). The low  $V_{OC}$  is due mainly to the unfavorable conduction band position of  $\text{WO}_3$ , which limits the  $V_{OC}$ . The low  $J_{SC}$  can be attributed to the acidic surface of  $\text{WO}_3$  that reduces the dye's adsorption and leads to an increase in the amount of charge recombination reactions at the  $\text{WO}_3$ /electrolyte interface [21,22]. In PC and PEC devices, a typical thickness of the  $\text{WO}_3$  layer is around 600 nm [1,5,23,24], which is sufficient to maintain its transparency and high optical contrast. The limiting factor when omitting the  $\text{TiO}_2$  layer in a PC device configuration is the too low potential i.e., it cannot reach the redox potential of the  $\text{WO}_3$  layer. Nevertheless, we have attempted to adsorb a Ruthenium complex dye N719 (di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II)) onto the EC layer ( $\text{WO}_3$ ) in order to determine whether or not the  $\text{TiO}_2$  layers could be omitted from either the PC or PEC device.

## 2. Experimental

UV–vis spectroscopy has been used to determine the amount of dye molecules attached to different photoactive layers ( $\text{TiO}_2$  layers) and double layers consisting of a photoactive layer deposited on an EC layer and on an EC layer post-treated with a  $\text{TiCl}_4$ -THF complex. In this study, we deliberately use TCO coated glass as a substrate in order gain information about the colouration processes taking place. In addition, the Pt-coated TCO has been used as a counter electrode in PC device coloured electrochemically to avoid the high overpotential when evaluating a redox potential of the EC layer. In this case, the counter electrode (Pt-TCO) serves as a quasi-reference electrode in the presence of  $\text{I}^-/\text{I}_3^-$  redox couple.

The differences in structure and morphology of the  $\text{TiO}_2$  layer, prepared by sol-gel synthesis and a post-treated EC layer are best discerned by scanning electron microscopy (SEM). We tested the photoactive electrodes in DSSCs that have the configuration TCO/X-dye/electrolyte/Pt-TCO, where X is either an EC layer or sol-gel based  $\text{TiO}_2$  layers. We also used cyclic voltammetry to evaluate the redox potential of the EC layer. And finally, we used different layers to assemble PC devices and evaluate their performance under solar illumination (1000  $\text{W}/\text{m}^2$ ).

### 2.1. Preparation of the electrochromic (EC) layer

The EC layer used in this study was a highly symmetric crystalline, cubic  $\text{WO}_3$  the symmetry of which was induced by incorporating titanium into the  $\text{WO}_3$  matrix (c- $\text{WO}_3$ ). The details are described in full in [2]. The first step in the preparation of the sol was the synthesis of a peroxo-tungsten acid, while  $\text{Ti}(\text{OiPr})_4$  was used as a precursor for titanium ions. The atomic ratio between tungsten and titanium atoms in the sol was 10:1, which is the most suitable molar ratio to achieve optimal performance of the EC layer [2]. Finally, 6 wt% of 2-APPG 4000 (Aldrich, average Mw ~ 4000) was added to the sol to obtain a thick crack free EC layer (c- $\text{WO}_3$ ).

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