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Photoelectrochromic devices based on sputtered WO_3 and TiO_2 films

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ABSTRACT

The photoelectrochromic (PEC) device, a combination of a dye solar cell and an electrochromic film, can be used for the dynamic solar control of buildings under illumination or with an external voltage. Typically, titanium oxide (TiO_2) and tungsten oxide (WO_3) films are being prepared from colloids or sol-gel chemistry with high porosity and high surface area as functional layers for a photoelectrochromic device in lab scale. We have, for the first time, successfully developed a PEC device with conventionally sputter deposited TiO_2 and WO_3 films. This coating technique is attractive due to the well documented upscaling capability and industrial viability for window applications. The functional layers WO_3 and TiO_2 were deposited onto fluorine doped oxide ($F:SnO_2$) coated glass . Characterization of WO_3 and TiO_2 was performed in an electrochromic cell and in a dye solar cell, respectively. Three types of PEC devices with different layer configuration were constructed and their performance based on visual transmissions was compared. In best case, the visual transmission could be switched from 61 down to 15% in 30 min under 1.5 A.M. illumination.

1. Introduction

Photoelectrochromic (PEC) systems comprise an electrochromic film e.g., tungsten oxide (WO_3) together with a dye-sensitized titanium oxide (TiO_2+dye) film, a thin platinum (Pt, thickness about 1 nm) counter electrode and an electrolyte containing redox couples, e.g., iodide/triiodide and a lithium salt. They can be used for the dynamic solar control of buildings under illumination of light [1].

Fig. 1(a) explains the coloration (under illumination at open circuit (upper half)) and bleaching (under illumination or dark at short circuit (lower half)) processes of a PEC device. On the right hand side of Fig. 1(b) shows schematic diagram of the redox potentials vs. standard hydrogen electrode under illumination at open circuit condition in a PEC device. Under illumination photons are absorbed by dye molecules, which excites the electrons from the HOMO (highest occupied molecular orbital) to the LUMO (lowest unoccupied molecular orbital) level of dye. These excited electrons of the dyes are injected into the conduction band of TiO_2 and further to the WO_3 creating a blue colour. In parallel, Li^+ ions are intercalated into WO_3 to keep the charge balanced. The oxidised dye molecules are reduced again by the reduced form of redox couple ($3I^- \rightarrow I_3^- + 2e^-$). In the meantime, the recombination of electrons from the TiO_2 or the WO_3 to the redox electrolyte occurs reducing the triiodide to iodide ($I_3^- + 2e^- \rightarrow 3I^-$). However, this process is very slow. This results in a very slow bleaching when switching from illumination to dark in open circuit condition [2]. For bleaching, the electrode with WO_3 and TiO_2 is connected externally to the counter electrode, where the electron transfer back to the triiodide is catalysed by a thin layer of Pt. This can also allow intermediate coloration steps by adjusting an external resistance between the electrodes.

So far, the most common TiO_2 and WO_3 thin films have been prepared by sol-gel chemistry for photoelectrochromic [1–8] and photochromic devices [9]. This work was focused on the development of PEC devices using the magnetron sputtered WO_3 and TiO_2 thin films. This coating technique is attractive due to the well documented upscaling capability and industrial viability for window applications. The application of sputtered TiO_2 film for dye adsorption to be used in solar cells was already investigated many scientists [10–16] despite of its high production cost for the thickness of around 10 µm, as it is needed in dye sensitized solar cells. However, a thin film of around 180 nm of TiO_2 is sufficient for the photocatalytic activity to drive the coloration process of the PEC device, which makes sputtering cost effective. Furthermore, sputter coating process of WO_3 thin film was also investigated for the electrochromic devices based on redox electrolyte [17–19].

In this regard, initially, the WO_3 and the TiO_2 films are coated onto TCO (transparent conductive oxide) coated glass and characterized individually. The WO_3 film was characterized in EC device based on redox electrolyte considering the redox potential of lithiated tungsten oxide with respect to the redox potential of iodide/triiodide electrolyte and its coloration performance. The redox potential of WO_3 at bleached state should be lower than the redox potential of redox electrolyte to

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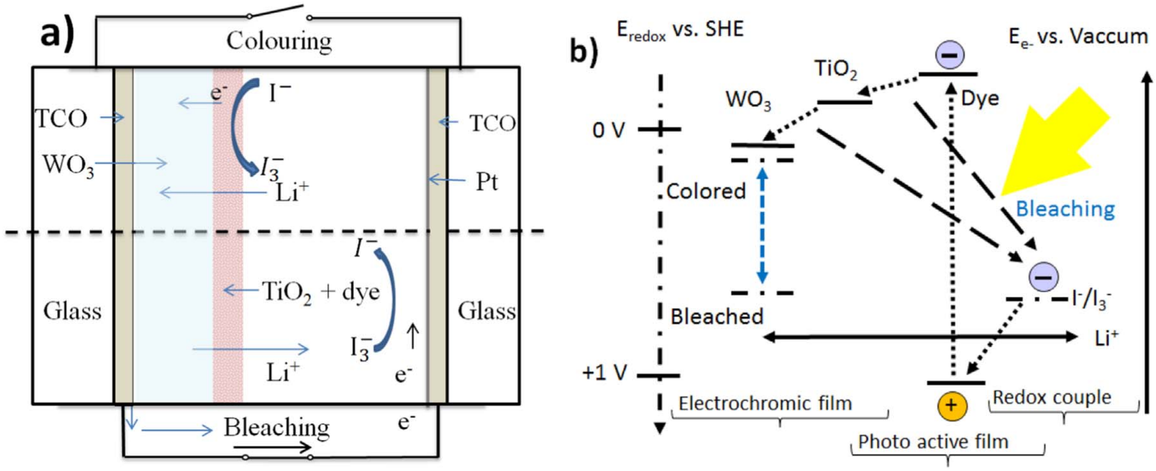

Fig. 1. The layer configuration of PEC (type-A) device showing coloration (upper part) and bleaching (lower part) (a), and schematic of the redox potentials, E, vs. standard hydrogen electrode (SHE) in a photoelectrochromic cell under illumination at open circuit (b) as described by Hauch et al. [1].

Layer configurations:

Type-A

Glass – TCO – WO_3 – TiO_2 – (dye) / Electrolyte / Pt – TCO – Glass

Type-B

Glass – TCO – TiO_2 – (dye) – WO_3 / electrolyte / Pt – TCO – Glass

Type-C

Glass –TCO – TiO_2 (annealed) – (dye) – WO_3 / electrolyte / Pt – TCO – Glass

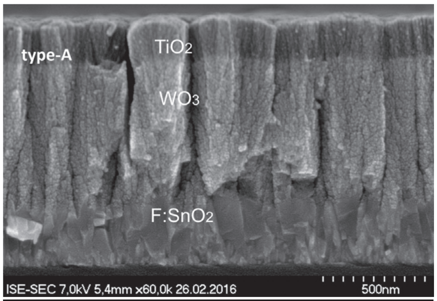

Fig. 2. SEM image of a PEC layer type-A comprising a TCO layer (bottom), WO_3 layer (middle) and TiO_2 layer (top).

prevent a self-coloration of PEC device upon short circuit in the dark. Similarly, the TiO_2 film was characterized in dye sensitized soar cells (DSSCs) evaluating the open circuit potential and the short circuit current as well as photovoltaic efficiency and fill factor of the cells. Finally PEC device were investigated with respect to their coloration and bleaching properties. As shown in Fig. 2 three different types PEC were prepared, sputtering first the WO_3 followed by TiO_2 (type-A), sputtering of TiO_2 followed by sputtering of WO_3 (type-B) and sputtering of TiO_2 followed by annealing step and sputtering of WO_3 (type-C).

2. Materials and methods

2.1. Materials

The transparent conducting oxide (TCO), fluorine doped tin oxide ($F:SnO_2$) in our case, coated glass having a sheet resistance of 16 Ω/□ was purchased as k-glass™ from Pilkington, UK and used as substrates for the all experiments. Lithium iodide (LiI), Iodine (I_2) and gamma-butyrolactone (GBL) were supplied by Sigma Aldrich, Germany. Dye N917 (Ru(II)L2(NCS)2:2TBA, where L=2,20- bipyridyl-4,40-dicarboxylic acid) was supplied by Solaronix, Switzerland. Electrochemical characterization work station (Zennium) was purchased from Zahner, Germany. The solar simulator (300 W Xe LSU306) was purchased from LOT-Quantum Design GmbH, Germany. A low temperature 100 µm thermoplastic foil (DuPontTM Surlyn® functionalised E/MAA resin) was purchased from Dyesol, Switzerland. The electrolyte composed of 0.5 M lithium iodide and 5 mM iodine in gamma-butyrolactone was used for all experiments. The active area of cells was 6 cm^2. Absorptive neutral density (ND) filters with the optical density of 2 were purchased form Edmund Optics GmbH, Germany.

2.2. Coating and characterization of WO_3

A metallic tungsten (W) target was used to deposit the WO_3 films by reactive magnetron DC-sputtering. The film thickness was measured by atomic force microscopy, and adjusted to be 600 nm. The redox potential of WO_3 with respect to the iodide triiodide redox electrolyte was compared. For that, an electrochromic test cycle was designed as shown in Fig. 3. In this cycle, 2 coloration, 2 bleaching voltages as well as 5 intermediate short circuit steps are used. The resulting transmission of the cell was measured at 655 nm wavelengths applying a red led (λ=655 nm) and a photodiode (OP301) [18]. The measured data converted into visual transmission. This possible as there is a unique relation in between the transmission for each wavelength and change in colored Li_xWO_3 layer. Therefore, spectral measurement of full transmission spectra T(λ) can be done for a certain set of degree of coloration (x, as in Li_xWO_3) of an electrochromic device and related to the corresponding signal of the photodiode with solar simulator and electrochromic device with identical coloration. This also considers the electrochromic coloration of redox electrolyte (LiI/LiI_3). The distance between the working and counter electrode was maintained to be 1.5 mm by a silicon frame with the effective area of 6 cm^2.

2.3. Coating and characterization of TiO_2

A ceramic dual rotary target was used to deposit the TiO_2 onto k-glass™ substrate. For the higher porosity of TiO_2 film and better dye adsorption [14], a high pressure (20E-3 mbar) is maintained during the coating. As suggested by Pjevic *et al.* [20] a deficiency of oxygen in