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Photoelectrochromic devices: Influence of device architecture and electrolyte composition

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ABSTRACT

Solar energy harvesting and chromogenic technologies can be integrated together to give self-powered and wireless photoelectrochromic devices (PECD). Due to the similarity in the architecture of both dye-sensitized solar cells (DSC) and electrochromic devices (ECD), it is possible to merge these two devices into one combined solar-powered electrochromic device known as DSC-EC. The present work describes the preparation and characterization of electrochromic solar cells using PEDOT:PSS (poly(3,4-ethylenedioxythiophene) polystyrene sulfonate) as electrochromic material in the counter-electrode. Different configurations and liquid and polymer-based electrolytes are studied. The resulting electrochromic solar cells were characterized focusing on the determination of solar to electricity conversion efficiency and the color contrast was assessed using color coordinates under simulated solar irradiation. The best DSC-EC configuration originates a color contrast of ($\Delta E = 30$) at a potential difference of 0.4 V and energy conversion efficiency of 4.9% at V_{OC} of 0.66 V and J_{SC} of 11 mA cm^{-2}, when using the liquid electrolyte. On the other hand, the best performing DSC-EC using the polymer-based electrolyte showed a very good color contrast of ($\Delta E = 47$) at short circuit and an energy conversion efficiency of 1% at V_{OC} of 0.63 V and J_{SC} of 4.5 mA cm^{-2}.

1. Introduction

A photoelectrochromic device (PECD) combines synergistically photovoltaic (PV) with electrochromic functions in a single device. When the photovoltaic function is given by a dye sensitized solar cell, the combined device is known as (DSC-EC) [1]; a DSC-EC is self-powered, changing color when illuminated by sunlight. In the last two decades, considerable research efforts have been directed towards materials and devices intended for a dynamic solar control such as smart windows in buildings [2], automotive or aeronautic industries, helmet [3] and smart displays. In particular, buildings integrating "smart" windows are able to improve two features: i) energy efficiency since they reduce the air conditioning needs; and ii) indoor comfort because they attenuate high solar intensity glare [4]. On the other hand, electrochromic windows with no external wiring, powered by the sunlight, are of great interest.

DSCs are an important type of thin film photovoltaics, which have attracted much attention since the prominent work by Grätzel in 1991 [5]. These devices show very attractive advantages, like low-cost construct materials, efficient use of the diffuse light and transparency [5]. The working electrode of a DSC is a mesoporous oxide layer of nanometer size TiO_2 particles. Attached to its surface is a monolayer of dye responsible for light absorption. Upon light absorption dye injects an electron into the conduction band of the semiconductor that percolate through the semiconductor network until the electrical contact. The oxidized sensitizer is regenerated by the transference of electrons from the redox couple present in the electrolyte, which in turn receives the electrons from the counter-electrode, normally platinum [6].

Electrochromism is the phenomenon exhibited by some materials that change color when an electric potential is applied; the electrochromic (EC) material, which can be an organic or an inorganic substance, is able to convert between two or more color states upon oxidation or reduction [3]. To take advantage of this phenomenon, namely for smart windows and low electrical consumption displays, an electrochromic device (ECD) should be built. An ECD is composed of two electrodes separated by an electrolyte, where at least one of the electrodes is transparent, such as a TCO coated glass substrate; in the most common configuration, the EC material is deposited on top of this TCO coated substrate [3]. When applied a potential difference between the two electrodes, the electrochromic layer changes the oxidation state, reacts with the electrolyte, and in consequence changes color [3].

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For coupling a DSC with an ECD, several architectures can be considered. The most common and simple one considers a thin film of electrochromic material deposited on the photoelectrode or on the counter electrode of a DSC [7,8].

The DSC architecture used depends on the choice of the electrochromic material once the energy levels of the combined materials dictate the electron path through the device. For devices where the electrochromic material is applied on the counter-electrode (see Fig. 1), and upon light absorption, dye injects an electron into the conduction band of the semiconductor that percolates through the semiconductor network until the electrical contact. The oxidized sensitizer is regenerated by the transfer of electrons from the redox couple present in the electrolyte which in turn receives the electrons from the counter-electrode, the EC material film changes color during the process (by being reduced).

For electrochromic materials with transparent/colored states, it is possible to have normally transparent devices or normally colored devices depending on the electrochromic material used and on the cell architecture. If the ground state of the electrochromic material is transparent the DSC-EC should be named normally transparent; likewise, if the ground state of the electrochromic material is colored this state should be named normally colored. The first DSC-EC device was reported in 1996 by Bechinger et al. [9] and concerns an integrated photoelectrochromic device using DSC technology, instead of coupling a solar energy harvesting device followed by a full electrochromic device in a sequential arrangement, as described before [10,11]. This work successfully describes a simple architecture where the counter-electrode of the DSC was replaced by a tungsten oxide layer in a normally transparent arrangement; a transmittance variation of 17% was reported. After Bechinger's work, in 1999, Will et al., [12] reported a different DSC-EC architecture. These authors adsorbed the EC material (viologen) and the dye in the DSC photoelectrode; however, this architecture brought additional problems such as electron transfer between viologens adsorbed at the same or adjacent nanocrystals. In 2001, Hauch et al., [13] described a DSC-EC device where the electrochromic WO_3 layer was applied over the TCO glass substrate and under the TiO_2 photoelectrode. The color contrast obtained was good (transmittance variation of 40%) but no solar to electricity conversion efficiency was reported. Later, Hsu et al. [14] and Wu et al. [7] used electrochromic material PProDOT-Et_2 as counter-electrode (instead of the platinum layer). This arrangement exhibited a solar to electrical energy conversion efficiency below 1% and transmittance variations of c.a. 40%. In 2012, Yang et al. [15] reported a device using a PProDOT-Me_2 layer also as counter-electrode but now on top of the platinum layer; this arrangement exhibited a solar to electricity conversion efficiency of ca. 1% and a transmittance variation of 30%. More recently, in 2014, Cannavale et al. [16] described a micropatterned bifunctional counter-electrode made of platinum layer stripes intercalated with WO_3 over ITO layer stripes; both types of stripes are not electrically connected. The platinum and WO_3 strips were then electrically connected to the photoelectrode through different electric circuits. When the platinum circuit is connected, the cell displayed PV function, while when the WO_3 circuit is connected, the cell change color displaying an electrochromic function; this complex cell displayed a conversion energy efficiency of ca. 3% and the transmittance variation was c.a. 25%. In 2015, Cannavale et al. [17] also presented for the first time a perovskite-based photovoltachromic device with self-adaptive transparency. The combination of semi-transparent perovskite photovoltaic and solid-state electrochromic cells enabled fully solid-state photovoltachromic devices with 26% (or 16%) average visible transmittance and 3.7% (or 5.5%) maximum light power conversion efficiency.

The present work uses the well-known electrochromic material PEDOT:PSS (poly(3,4-ethylenedioxythiophene) polystyrene sulfonate) applied on the counter-electrode – Fig. 1. Despite being organic, PEDOT:PSS is quite stable and shows a high contrast color [18,25].

PEDOT:PSS layer was applied directly over the TCO glass substrate and over a platinum layer. Two electrolytes where considered, a commercial liquid electrolyte widely used in DSC devices (AN-50, Solaronix, Switzerland) and a semi-solid electrolyte (UV cured PEO (poly(ethylene oxide) based), used with various concentrations of lithium salts. UV-cured electrolytes are being extensively studied for applications such as in DSC devices [19], especially the UV-polymerization of PEO/PEG-based electrolytes [20–22]. This electrolyte was provided by company YD Ynvisible S. A. (http://www.ynvisible.com/) which works in the field of electrochromism; the exact composition of it is a trade secret. The electrolyte showed a quite good performance in electrochromic devices, [18,25,30]. The use of this electrolyte can be of

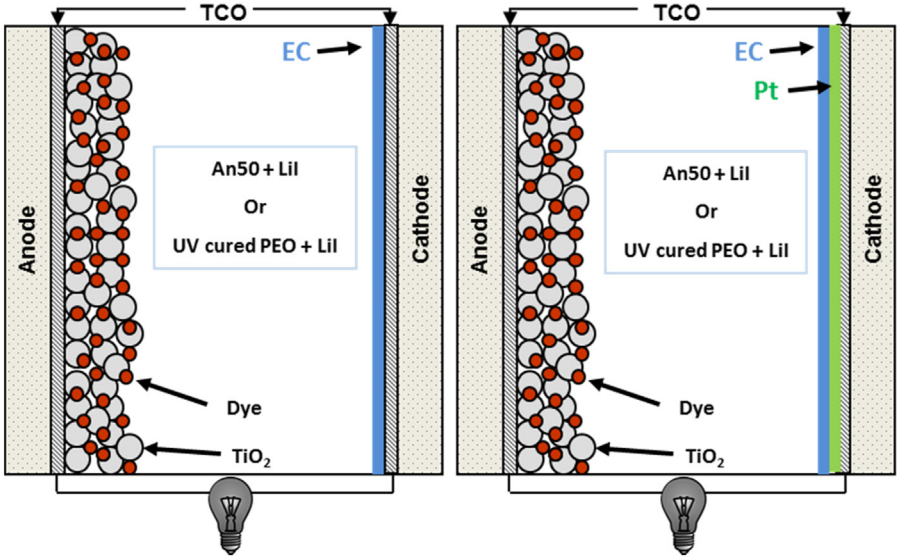

Fig. 1. EC-DSC device architecture with the PEDOT:PSS layer deposited on the counter-electrode: a) Applied directly on the TCO glass substrate; b) Applied on the platinum layer.