Multi-layer Anti-counterfeit Labels Based on Electrochromism: from Materials to Displays

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ABSTRACT
Electrochromic Displays (ECDs), known for their ability to modify their visual appearance under an applied voltage, are described as an efficient technology in smart anti-counterfeit labels. Fabricated on paper and produced from lab techniques including doctor blading and serigraphy to large scale depositions, multi-layer devices based on PEDOT are highlighted.

1 Introduction
Electrochromic materials, known for their ability to modify their visual appearance under an applied voltage, have promising applications in emerging technology. While traditionally used to alter transparency of glass to regulate the penetration of light in self-dimming rear mirrors for cars and in smart windows for energy-efficient buildings, the utilization of electrochromic materials to power low-energy displays is more recent and has found utility in various consumer electronics such as washing machines, smart cards and labels, and medical appliances. For the past ten years, our group has designed step by step, from the materials choice and optimization, to their integration in devices with unusual architectures, from lab prototypes further up-scaled in pre-commercialized products, anticounterfeit smart labels. Herein, this long term project will be described from earlier electrochemical and optical characterizations of single layers to the determination of the visual modulation through chromaticity parameters of pre-commercialized prototypes always based on paper substrates. Using poly(3,4-ethylenedioxythiophene) polystyrene sulfonate PEDOT-PSS conductive polymers as the main electrochromic material, a color palette was successfully achieved by the preparation of hybrid materials consisting of a mixture of PEDOT-PSS and pigments. As an overall concern of the current worldwild society, their environmental impact will be shortly discussed.

2 Experiment

Electrochromic Device Configuration

Electrochromic Devices (ECDs) are still often described as a stack of successive layers commonly represented by the TCO/EC/Elect./EC/TCO chain in which TCO lies for transparent conducting oxide, EC for electrochromic and Elect. for electrolyte. A step forward in the conception and production of smart labels, was the minimization of the number of layers from the five layers required in the battery-type architecture to four or even three layers. To achieve such a modification of configuration, also associated to the minimization of cost and ease of the process, the electrochromic material and/or the counter electrode needs to be conductive. Thus from earlier work on non conductive oxide, we move forward to the use of conductive polymer, and more precisely PEDOT.

3 Results

3.1. Four-layer lab scale ECD

Figure 1 presents a typical electrochromic characterization consisting of cyclic voltammetry and reflectance measurements of a four-layer ECD based on bar coated single layers. The ECD switches from a blue to a grey visual appearance. It is worthwhile mentioning that the blue coloration could be easily modulated by preparing hybrid inks based on the addition to the PEDOT ink of a proportion of oxide powders or pigments. The proof of concept was then extended to the use of paper as a substrate.

3.2. ECD on paper

Aiming at manufacturing all-printed devices on paper, the flexography tool for the PEDOT-PSS and silver inks was combined to screen printing of the electrolyte based on ionic liquid and UV polymerized. As a final proof of concept, an ECD was incorporated in a perfume packaging and activated thanks to a smartphone (Figure 2). Such device nicely switches from a colorless to a blue state. Further improvement were achieved by using NFC activation and modifying the deposition techniques.
aiming at up scaling the smart labels production.

Figure 1 : Cyclic Voltammograms recorded between 0.7 V and 0 V with a scan rate of 10 mVs⁻¹ of a four layer PET/ITO/ PEDOT/(0.3 M) LiTFSI/BMITFSI 40% PMMA/Ag/paper, visual appearance in the colored (-0.7V) and the bleached 0V states of 1cm² ECD. Reflectance curve of initial, bleached at 0V and colored at -0.7V and -1.0 V. Chronoampreograms in coloration (-0.7 V) and in-situ reflectance variation at a 550 nm wavelength.

Moving a step forward towards up-scaling, all layers were printed from R2R rotary screen printing. Details of the various printing steps of the device including the NFC antenna are reported in Haloka et al. 5 Figure 3 represents the visual appearance of complete devices including the NFC antenna and the electrochromic display. The colour change of the display was evaluated from the optical contrast \( \Delta E^* \). \( \Delta E^* \) is defined using the chromaticity parameters \((L^*, a^*, b^*)\) which belong to the CIE colourimetric space. For PEDOT:PSS, a cathodic coloration material, the colour change switches from the oxidized state \((L^{ox}, a^{ox}, b^{ox})\) which corresponds to the as-deposited colour, to a reduced state \((L^{red}, a^{red}, b^{red})\) (Equation (1)). The contrast \( \Delta E^* \) is equal to 

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\Delta E^* = \sqrt{(L^{red} - L^{ox})^2 + (a^{red} - a^{ox})^2 + (b^{red} - b^{ox})^2}.
\]

\( \Delta E^* \) values close to 30 were recorded for potential windows in between 0V to 3.8 V.

Figure 3 : Visual and optical performance of a PEDOT-based display switched from 0 to -3.8 V.

4 Discussion

Nowadays, the emergence of new products needs to be accompanied by the consideration of their environmental impact and their global warming potential. From deep investigations reported by E. Glogic et al. 6, the use of silver was identified as being the most detrimental as compared to any other layers of the ECDs.
raising the question of investigating new materials such as copper based ink. Additional questions concern the impact of the various deposition techniques favoring flexography instead of screen printing as an example. Further studies on the role played by the device architecture are in progress showing a reverse approach on using life cycle assessment as a predictive tool.

5 Conclusions

Anticounterfeiting smart labels, based on electrochromic technology, were developed on paper. Their activation using a smart phone was successfully achieved by combining suitable materials, including conductive polymer PEDOT:PSS, ionic liquid based electrolyte membrane, and silver as counter electrode. In the future, the aim is to develop and commercialize such labels as part of intelligent packages often mentioned as one of the most promising area for paper based electronics.

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