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A Planar Electrochromic Device using WO_3 Nanoparticles and a Modified Paper-Based Electrolyte †

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† Presented at the Eurosensors 2018 Conference, Graz, Austria, 9–12 September 2018.

Published: 19 November 2018

Abstract: Electrochromic devices are increasing its interest in the last decades due to the wide range of applications, from smart windows to biosensors or from smart labels to super-capacitors. So, the development of simple and cost-effective production technologies based on solution process and mask less approach is of great interest. In this work, a new planar and flexible electrochromic device based on tungsten oxide (WO_3) nanoparticles with a paper-based modified electrolyte was successfully produced, using a CO_2 laser technology for electrodes patterning and hydrothermal synthesis for the nanoparticles production. The devices were fabricated with a paper pad inserted in the sensor area for hydration on time of usage, thus replacing the electrolyte material of a typical electrochromic structure with a multi-layer stack, eliminating leakage problems, easy integration with other devices and enhancing the shelf life of the devices to several months. The produced device presents a low power consumption of only 2.86 $\mu A \cdot cm^{-2}$, with a deep blue color and an initial charge modulation of 11.5.

Keywords: tungsten oxide; electrochromism; hydrothermal synthesis; laser technology

1. Introduction

The interest in electrochromic (EC) materials has started to grow in the 1980's especially due to the application of tungsten oxide (WO_3) in smart windows for energy efficiency and indoor control [1,2]. WO_3 is one of the most studied EC inorganic materials due to its multiple oxidation states, high coloration efficiency and good cycle stability [3,4]. The case of nanostructured tungsten oxide shows even more advantages as: (i) the spatial size reduction which promotes a quantum confinement effect that will significantly influence charge transport, electronic band structure and optical properties; (ii) the large fraction of surface atoms and increased surface to volume ratio, which provides more surface area for chemical and physical interactions and (iii) the high surface energy and strong surface adsorption that allows materials properties engineering, as atomic species can bond to the surface of the nanostructure, thus conferring different properties to the material [4].

New smart applications as displays, labels, transistors [5,6], biosensors [7,8] and energy storage devices [9] have been associated to the need of developing easier and cost-effective manufacturing processes and materials.

Hence, in this work, we combine different technologies to produce a flexible, cost-effective, planar and freestanding EC device. For that, a computer-controlled laser machine is used to etch the indium tin oxide (ITO) layer from a commercial PET/ITO sheet, to negatively pattern the device. It allows the production of high-resolution electrodes, with freedom of design, in a mask less approach which significantly decreases the time of production and the fabrication cost, thus making it suitable to be easily applied to a roll-to-roll process for mass production manufacturing. This can be applied in several types of devices and can be combined with different power supplies due to the low operating potential.

2. Materials and Methods

2.1. Material Production and Characterization

The WO_3 nanoparticles (WO_3NPs) were produced according to L. Santos, et al. [10] by a hydrothermal synthesis process: 0.8 mL HCl 3 M was added to a $Na_2WO_4{\cdot}2H_2O$ 0.15 M aqueous solution and mixed together for 1 h. This solution was then transferred to a Teflon cup, set inside a stainless-steel autoclave and placed in an oven for 1 h at 180 °C. The final material was collected by centrifugation, washed with distilled water and dispersed in a 1:1 mixture of ethylene glycol butyl ether and distilled water. The morphological and structural characterization was supported by Scanning Electron Microscopy (Auriga SEM-FIB, Zeiss, Oberkochen, Germany) and X-ray diffraction (X'Pert PRO, PANalytical, Almelo, The Netherlands) techniques.

2.2. Device Production and Characterization

The EC device was designed as a planar structure with a 2-electrode configuration defined as working and counter electrode (WE and CE, respectively) using a vector image software (Adobe illustrator, Adobe systems software, San Jose, CA, USA). The electrodes, as well as the electrical tracks were negative patterned in a 30 Ω/sq PET/ITO sheet (Kintech Company, Shenzhen, China) by laser etching the ITO layer, on a computer-controlled CO_2 laser-cutting machine (VLS 3.50, Universal Laser Systems, Scottsdale, AZ, USA), with a 10.6 μm wavelength, at 10 W and 1.27 m/s. 1.5 μL of the WO_3NPs dispersion was deposited onto the WE after a 5 min UV-ozone treatment to better promote the adhesion of the dispersion.

Finally, the devices were encapsulated on PET lamination pouches using a home version laminator, with the hydrophilic paper (Whatman nº 4, GE Healthcare, Chicago, IL, USA) inside, covering the area of the WE and CE. A small pad was left outside the device to allow the impregnation of the electrolyte in time of usage.

For the electrochemical characterization the paper was impregnated with 20 μL of LiClO4:PC 1 M electrolyte and the electrochemical measurements were performed in a Potentiostat (Gamry 600, Gamry Instruments, Warminster, PA, USA). Chronocoulometry and cyclic voltammetry measurements were performed to fully characterize the devices.

3. Results and Discussion

In this work, laser technology was used to define the electrodes, for a planar EC device, on a commercial PET/ITO sheet.

Figure 1 shows the steps and important results of the material synthesis, device fabrication and device testing.

The produced WO_3NPs, with an average diameter of 10 nm and a hydrated orthorhombic crystallographic structure, are white and turn blue after lithium intercalation, where Li^+ is the ion present in the electrolyte and it can be replaced by other small cations like H^+ or K^+ [11]. This material was drop casted on the WE and its nanostructured nature is expected to enhance the performance of

the electrochromic device due to the increased surface to volume ratio with large fraction of surface atoms, high surface energy and strong surface adsorption [4,12,13].

The etching of the ITO layer with a CO_2 laser cutting machine is very effective as proven by the SEM EDX analysis, where it is possible to observe a complete absence of indium and tin on the etched PET/ITO separation gap between the two electrodes (WE and CE). So, this method allows a fast and high-resolution device patterning with freedom of design as the user can design its own device structure directly in the software.

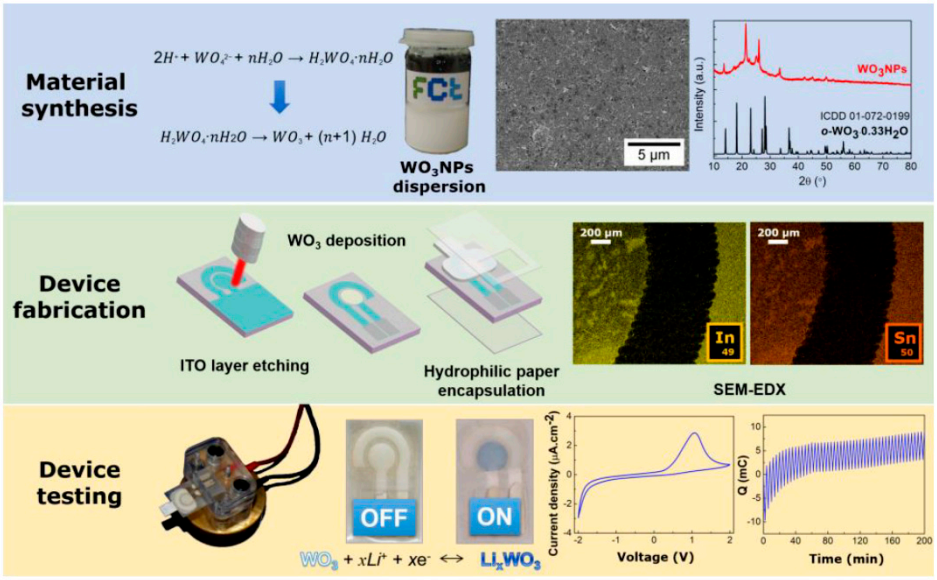

Figure 1. Schematic representation of the EC device workflow and some important results: SEM image and XRD diffractogram of the produced WO_3NPs; Scheme of the device fabrication with SEM-EDX analysis; Device testing showing the electrical interface for the measurements, real pictures of the devices on OFF and ON state, cyclic voltammogram at ±2 V and 50 mV/s and chronocoulometric results of stability cycles, performed for 200 min (50 cycles at ±2 V for 120 s).

Liquid electrolytes on EC devices allow a low power consumption together with fast and uniform coloration but present some drawbacks such as the leakage and environmental problems as well as a short shelf life. Therefore, in a way to overcome these concerns, the device was produced without any electrolyte and the hydration of the device was only performed at the time of usage with a minimal quantity of liquid. For that, a hydrophilic paper was encapsulated inside the planar device, covering both WE and CE, thus replacing the electrolyte layer of a typical stacked multilayer structure. Different types of hydrophilic papers were tested and from all papers, Whatman nº 4 showed the most promising results. This paper is highly absorbent and thus the hydration of the device that occurs by capillarity is quite fast, down to a few seconds.

The cyclic voltammetry of the devices was analyzed by applying ±2 V at a scan rate of 50 mV/s, where the results are in accordance with other reported studies where the redox peaks are not fully visible in this potential range [14,15]. Moreover, the devices produced present a very low power consumption of only 2.86 $\mu A \cdot cm^{-2}$.

Additionally, a stability test was performed by chronocoulometry. The results clearly showed that the device had a high charge modulation ($\Delta Q_{initial} = Q_{bleached} - Q_{coloured} = 11.5$), although the deterioration after 50 cycles was almost 50% ($\Delta Q50 = 5.9$).

In any case, for some applications proposed in this paper, as labels and biosensors, the cycling stability is not the most relevant figure of merit of the device but instead the shelf life can be a critical issue. Therefore, in this structure, since the hydration of the device only occurs prior to usage, the shelf life can be enhanced to several months as tungsten oxide in the dry form is quite stable. In fact, to attest the shelf life, the EC device was tested four months after fabrication, still showing an optimal optical modulation with just a small decrease on the charge modulation ($\Delta Q = 7.7$).

4. Conclusion

In this work, a WO_3 EC device with a new planar architecture was developed using laser technology for electrodes patterning. The method allowed a freedom of design, simple and cost-effective process for devices fabrication. The devices were fabricated with a paper pad inserted in the display for hydration on time of usage, thus enhancing the shelf life of the devices to several months. The EC devices presented a high optical modulation, with a fast response time and a stable behavior. This device structure, even if not fully optimized, can be easily adapted for several commercial applications just by choosing the best combination of materials.

Author Contributions: A.M. did the experimental work and wrote the manuscript; L.S. helped designed the experiments and on the writing of the manuscript; S.P. helped on the production of the devices; U.E. and S.S. designed and produced the interface for all the electrical measurements; R.I., G.S., R.M. and E.F. supervised the work and reviewed the manuscript.

Acknowledgments: The authors acknowledge funding from Symbiotic project (ref. 665046) and the project UID/CTM/50025/2013, funded by the FCT-MCTES and co-funded by the FEDER under the PT2020 partnership agreement. ACM acknowledges funding to National Foundation for Science and Technology, I.P., through the PhD Grant SFRH/BD/115173/2016.

Conflicts of Interest: The authors declare no conflict of interest.

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