Nanostructured metal oxides for printed electrochromic displays

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Abstract

Electrochromic devices are able to change their optical properties reversibly under the action of applied voltages. The conventional method of fabricating electrochromic devices utilizes a 'sandwich' configuration of electrodes. We developed a 'side-by-side' design for fabricating electrochromic display devices without the use of conductive, transparent electrodes. A simple printing technology can be used to produce commercial scale, flexible electrochromic displays. We have also discovered that tin oxide nanocrystallites heavily doped with antimony exhibit a high level of electrochromism. The high contrast ratio of nanostructured antimony–tin oxide (ATO) electrochromic displays is attributed to an accessible antimony energy state in the band gap of the mixed oxide. The fast switching rate can be attributed to the high surface area of, and high number density of grain boundaries in, the nanophase ATO materials. The interfacial regions between ATO nanocrystallites facilitate the transport of ions in and out of the electrochromic layer. The dynamics of the electrochromic displays is critically dependent on the nanostructure of the electrochromic layer. The design strategy for commercial production of printed, flexible electrochromic displays will be discussed. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Electrochromic devices, such as displays or smart windows, are able to change their color reversibly under the action of an applied voltage pulse. An electrochromic device is essentially a rechargeable battery with the electrochromic electrode separated by a solid, gel, or liquid electrolyte from a charge-balancing counter-electrode. When an external potential is applied between the working and counter electrodes the charge or discharge of this electrochemical cell induces color changes of the electrochromic device. The modulation of the optical properties of electrochromic devices is largely determined by the capacity of the electrochromic materials for charge injection and expulsion. The contrast ratio, which is an important parameter for evaluating the performance of display devices, is defined as the ratio of the intensity of light diffusely reflected through the bleached state of the display to the intensity of light diffusely reflected from the colored state. Commercial devices require electrochromic materials with a high contrast ratio, high coloration efficiency, long cycle life, high write–erase efficiency, and fast response time.

The conventional method of fabricating electrochromic devices utilizes a 'sandwich' configuration of electrodes [1]. The electrochromic electrode of these devices generally consists of a thin film of electrochromic materials deposited onto a conductive, transparent glass such as indium–tin oxide (ITO) coated glass substrate. Disadvantages of this type of device design include high cost, low conductivity, difficulty in fabricating sophisticated display designs, and electrochemical instabilities.

To overcome these difficulties, we developed an interdigitated electrode approach. The construction of display devices utilizes a low cost printing or coating process. The production of raw materials involves only simple solution and dispersion processes. With this new design approach electrochromic display devices can be commercially produced without the use of transparent electrodes. A wide range of device types has been demonstrated with an interesting range of colors and prototype electronic drivers [2].

A large number of electrochromic materials including transition metal oxides, conducting polymers, metallopolymers, Prussian Blue systems, etc. are now avail-
able [1,3]. Transition metal oxides such as WO$_3$, MoO$_3$, TiO$_2$, and V$_2$O$_3$ show considerable variations in stoichiometry and display inherent electrochromic properties [1]. Thin films of antimony–tin oxide (ATO) and indium–tin oxide have also been studied in the past to explore their electrochromic properties [4,5]. Both of these thin films exhibited very weak or no electrochromism. Antimony-doped tin oxide powders have been used as oxidation catalysts [6] or as electrically conductive pigments [7]. These powders, however, have not been investigated for their electrochromic properties.

We discovered that when dispersed onto inert inorganic supports such as titania, silica, or alumina nanocrystallites of tin oxide heavily doped with antimony exhibited surprisingly high levels of electrochromism [8]. The contrast ratio of printed reflective displays depends on the antimony doping level, the type of support, and the synthesis processes and the annealing temperature of the ATO precursor materials. The synthesis processes and the structural evolution of ATO nanocrystallites have been reported elsewhere [9]. In this paper, we will discuss the design strategy, the device performance, and the nanostructure of printed, flexible electrochromic displays using interdigitated electrodes.

2. Design strategy of printed display devices

The design objective is to print the display on flexible polymer films utilizing commercially viable conductive inks in an interdigitated electrode structure. Fig. 1a shows a schematic diagram illustrating the cross-sectional view of a display consisting of several layers of printed materials. An appropriate circuit can be designed and screen-printed on a thin polymer film with silver–carbon ink as working and counter electrodes. Then, a layer of carbon ink is printed, completely covering the silver–carbon layer to provide corrosion protection. Without this conforming carbon layer protection, the display can not maintain a long cycle life. Electromigration of silver microcrystals may occur under prolonged use of the display device. When silver microcrystals interact with other components the display device is degraded.

After printing the conforming carbon layer, the connecting circuits are then covered with an insulating material. The actual electrode surface is then printed with light-colored conductive metal oxide powders dispersed in a polymer binder. The electrochromic material can be mixed into, or printed on top of, the conductive metal oxide dispersion. A layer of an aqueous gel electrolyte is then put down before the whole system is sealed with a transparent polymer film. Fig. 1b shows a backscattered electron image of the cross-sectional view of a display device consisting of a Mylar support, Ag/C electrodes, and an ATO–TiO$_2$ electrochromic layer. The total thickness of the electrochromic layer and the conductive metal oxide dispersion layer is about 50 µm.

When an external voltage is applied between the working and the counter electrodes, electric current moves vertically through the conductive metal oxide dispersion to the interface between the electrochromic material and the gel electrolyte. Electrochromic color change takes place in this interfacial region. Ionic current flow through the electrolyte completes the electrical circuit. If the inter-electrode spacing is kept significantly larger than the thickness of the metal oxide coating layer, then the leakage current within the metal oxide dispersion layer can be minimized. This leakage current can be further reduced by printing a thin layer of insulator between the working and counter electrodes as illustrated in Fig. 1a.

For this ‘side-by-side’ display design to work, high conductivity of the electrolyte is required to maximize current flow through the desired path. Detailed discussions on circuit designs and the selection of materials for various printed layers have been previously reported [2]. Sophisticated patterns can be designed using commercially available graphic design programs. Desired patterns can be transformed into display devices by utilizing specialized screen printing technology with a high production rate and low cost. Fig. 2a shows a micrograph of a printed numerical display, revealing the uncovered Ag/C electrodes, covered connecting leads, and the insulator layer. Fig. 2b shows the same
area after printing a layer of ATO–TiO₂ electrochromic materials, covering the whole display device except the conducting leads for external connections.

3. Electrochromic ATO nanocrystallites

The electrochromic layer is the key element in determining the quality of electrochromic devices. Although various electrochromic materials can be formulated into printable ink, we discovered that tin oxide nanocrystallites heavily doped with antimony gave surprisingly good electrochromic properties with high contrast ratio and fast switching rate [8]. The detailed synthesis processes of ATO nanocrystallites and the structural evolution of these nanophase materials with annealing temperature and doping level have been reported elsewhere [8,9].

The electrochromic layer is composed of ATO nanocrystallites coated onto light-color supporting powders such as titania, silica, alumina, etc. Fig. 3a shows a schematic diagram illustrating ATO nanocrystallites highly dispersed on particulate titania. This design more effectively utilizes the ATO nanocrystallites and the ATO-support powders can be easily formulated into printable ink with appropriate polymer binders. Fig. 3b shows a backscattered electron image of a cross-sectional view of ATO–TiO₂ powders, revealing the coating of ATO nanocrystallites onto the TiO₂ particulate support.

Fig. 3c shows an atomic resolution transmission electron micrograph of an ATO–silica powder. Small ATO crystallites with an average size of about 4 nm were closely packed onto the silica support, forming a continuous coating layer with a thickness ranging from 10 to 100 nm. The ATO nanocrystallites encapsulated the particulate silica support. Because of the smaller size of the ATO crystallites, the total surface area of the ATO-support powders is very high (≈40 m² g⁻¹). Twins, dislocations, and other types of defects are present in individual ATO nanocrystallites. There is no preferential crystallographic orientation among the ATO nanocrystallites. A significant amount of disorder is present at the grain boundaries formed by these nanocrystallites. The average size of the ATO nanocrystallites changes with antimony doping levels and annealing temperatures of ATO precursor materials [9].

4. Device performance and discussion

The quality of an electrochromic device depends on many parameters including the contrast ratio, switching rate, and cycle life. High contrast ratio is preferred for all commercial display devices. Fig. 4 shows a word display printed with nanostructured ATO–silica electrochromic materials: in (a) and (b) the lettering is
Fig. 4. Word display using ATO–silica nanostructured electrochromic materials (±1.5 V).

polared cathodically and anodically, respectively, at 1.5 V. A high contrast ratio is clearly obtained.

The contrast ratio of nanostructured ATO displays depends on the ATO loading, the type of support, the doping level of antimony, the average size of the ATO nanocrystallites, the oxidation state of the antimony dopant, and the spatial distribution of antimony containing species [8,9].

Fig. 5b shows variations of the contrast ratio with the change of antimony doping level for a display device prepared with materials consisting of ATO nanocrystallites supported on TiO$_2$ powders. At low doping levels the contrast ratio rapidly increases with the antimony content. At higher doping levels the contrast ratio slowly increases to a maximum at about 43 mol.% antimony, and then slowly decreases with further increase of the antimony concentration.

Fig. 5a shows variations of the contrast ratio with the change of annealing temperature. This display device was prepared using ATO nanocrystallites (43 mol.% Sb) supported on alumina powders. The contrast ratio first increases with the increase of annealing temperature, reaches a maximum at about 600°C, and then decreases with further increase of annealing temperature. It is clear that the contrast ratio of the printed display device crucially depends on the doping level of antimony and the annealing temperature of the ATO precursor materials.

Although transition-metal oxides, especially thin films of tungsten trioxide, have been extensively and intensively studied, the fundamental mechanism of their electrochromism is still not well understood. The microstructure of these thin films may play a significant role in determining their electrochromic performance. Different models of the nanostructure of thin films have been proposed [10]. For example, depending on the preparation method, a tungsten trioxide film can be viewed as a nanocomposite rather than a truly amorphous material. The grain sizes or domains of the nanocomposite film can be a few nanometers or smaller. It is also suggested that columnar structures in thin films enhance the electrochromic properties of these films [10]. The intercolumnar regions may allow easy transport of ions across the films. The presence of nanoclusters or nanocrystallites in thin films may also modify the band structure of these materials.

The improved electrochromic properties of the ATO-support powder materials can be attributed to the formation of nanocrystallites with a large number of antimony-rich grain boundaries. At a nanoscopic level, these nanostructured materials provide a high-surface area that allows easy transport of mobile ions across the ATO nanocrystallites. The fast switching rate of the printed displays is attributable to the high surface area and large number of grain boundaries of nanostructured metal oxide powders because more ATO sites can

![Fig. 5. (a) Contrast ratio versus annealing temperature for ATO (43% antimony) supported on alumina. (b) Contrast ratio versus antimony doping level for ATO supported on titania.](image-url)
be quickly accessed during the switching (charge injection and expulsion) process. Furthermore, the majority of the antimony dopant may be preferentially located at or near the grain boundaries. An increased level of electronic states at these grain boundaries may be responsible for the color formation and high contrast ratio observed in ATO electrochromic devices.

Electron microscopy results showed that variations of the contrast ratio with the change of antimony doping level and annealing temperature can be correlated to the average size of the ATO nanocrystallites and the intimate mixing of antimony with tin oxide [9]. Antimony not only acts as a dopant to modify the electronic structure of tin oxide but also inhibits the growth of tin oxide nanocrystallites at annealing temperatures \(< 700^\circ\text{C}\). At low dopant level or higher annealing temperatures, the average size of the ATO nanocrystallites increases significantly. Consequently, the total number of grain boundaries and the amount of antimony available to provide electron charge carriers are reduced. Thus, the contrast ratio of the display devices is reduced. Furthermore, at higher annealing temperatures or very high antimony doping levels, antimony can migrate out of tin oxide nanocrystallites to form separate phases. This will change the electronic structure as well as the conductivity of the ATO materials. The electrochromic properties of ATO nanostructured materials are optimized at an antimony-doping level of about 43% and an annealing temperature of about 600°C.

5. Summary

We have developed a commercially viable process for fabricating electrochromic display devices without using transparent electrodes. The simple interdigitated printing process can be easily scaled up for commercial production of flexible displays. The nanostructure of ATO-support powders determines the performance of this type of electrochromic devices. The enhanced electrochromic performance of ATO nanocrystallites is attributable to high-surface area, easily accessible sites through grain boundaries, and increased level of electronic states introduced by higher levels of antimony dopant.

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References