

3-1: Towards true paper-quality displays - The development and commercialisation of NanoChromics™

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Abstract

Electrochromic displays offer the possibility of providing high brightness in reflective mode due to the fact that no polarization of the incident or reflected light is required. The use of appropriately roughened reflective layers can enable the diffuse or Lambertian reflection of light, truly imitating the optical nature of paper as a reading medium. Furthermore, the use of an electrochromic system, essentially an electrochemical device, allows for the integration of charge storage layers, endowing such devices with an on-state memory and associated low power consumption. In this paper we describe the NanoChromics™ system and overview the several strategies employed towards the migration of this technology to flexible display formats.

1. Introduction

Technologies used to display information in reflective mode have evolved from the use of ink and paper, to chalk boards through to reflective flapper boards and on to a variety of electronic technologies such as reflective and transmissive Liquid Crystal Displays (LCD). Emissive technologies such as Cathode Ray Tubes (CRT), Plasma Display Panels (PDP) and Light Emitting Diodes (LED) have been used with limited success in providing readable solutions in some environments. The limitations of CRT, PDP and LED are due to the fact that they have varied relative brightness. For example CRT devices have a brightness of up to 600 Cd/m², PDP, up to 400 Cd/m², and LED up to 8000 Cd/m². On bright sunny days, when the level of illuminance may be 30,000 lux, even the brightness of the characters of LED displays compete inadequately with the amount of reflected ambient light for the display medium to be readable. Transmissive LCD offers some reflectivity and is a superior solution to the problem of these technologies but as they partially emit light via a backlight the contrast may change with level of illuminance.

In these bright environments, the flapper board technology provided the best readability but as an electromechanical device was prone to breakdown resulting in a high level of required maintenance. The solution to the problems experienced by the aforementioned technologies is to develop an electronic, diffusively reflective display that does not change in contrast ratio and readability whatever the level of ambient light. Moreover, the development of such a technology on flexible substrates gives rise to many commercial opportunities that use the advantages of flexible substrates, namely light weight, conformability, flexibility, continuous processing and display scalability.

Research and Development at NTERA Limited has focused on the near-term commercial opportunities for highly reflective, paper-white glass displays. However, flexible displays have been developed based on several strategies that will enable migration of

the technology to many flexible display applications. This paper provides an overview of the NanoChromics technology, followed by an overview of the strategies being employed towards the development of the flexible display platform.

2. NanoChromics Technology

Previous reports [1,2] have described the structure of an electrochromic device incorporating a transparent nanocrystalline, nanoporous film as the cathode onto which a monolayer of electrochromic viologen molecules such as those in Figure 1 are self-assembled. The viologen molecules are a family of dicationic bipyridinium salts that form the coloured cationic radical upon accepting an electron. The electrochromic effect is reversible and can be mediated in an electrochromic device in the presence of solution based electron donors or through effective capacitive films within the device that are capable of releasing electrons. The molecules exhibit striking stability with the ability to undergo this reversible colour change over several million cycles. In addition to the reversible electrochromic effect, the modification of the R substituent on the molecule allows for the engineering of colour in the system with blue, green and black colours achievable [3]. The anode electrode required in the device also consists of nanocrystallites arranged in a nanoporous, ceramic-like film. Each electrode in the device requires specific properties from the materials used.

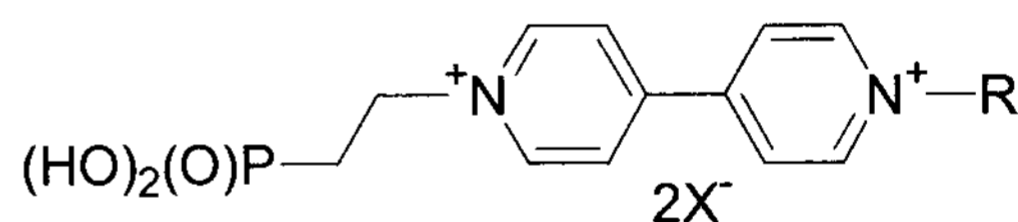


Figure 1 Generic Structure of Viologen Molecule Attached to Nanostructured Titania

The cathode materials require high transparency, appropriate electronic band energetics (to efficiently interact with the adsorbed molecule's redox properties), the capability of forming mechanically rugged high surface area, porous networks, good chemical and electrochemical stability and, possess a suitable chemistry to efficiently adsorb the electrochromic viologen molecules. Several wide-bandgap semiconductors such as titanium dioxide provide this range of properties.

The anode materials must provide efficient conductivity, the ability to release electrons, have a large surface area and porosity (providing a large enough electrochemical capacitance to match the cathode), are equally chemically and electrochemically as stable as the cathode and mechanically rugged. Degenerated semiconductors such as antimony doped tin oxide (ATO) have been found to have the best combination of these properties. Additional capacity in these electrodes may be introduced by the adsorption of electron donors such as modified ferrocenes and phenothiazines to the electrode [4].

The white reflector layer must be stable and inert chemically, possess mechanical ruggedness and be an efficient light scatterer. Titanium dioxide pigment passivated with other insulating metal oxides provides this reflective medium and is available inexpensively in commercial quantities. Figure 2 illustrates the construction of a display device. Pixellation in the display is achieved by directly printing the required seven-segment pattern, iconic characters or pixel arrays on to the ITO layer of the cathode. There usually is no requirement to pattern the anode. Applying a DC voltage of up to 1.0 Volts to the cell operates the display. The potential places charge on the TiO_2 :Viologen electrode, supplied by the ATO anode. Charge is balanced on both electrodes by the presence of alkali salts in the electrolyte medium between the two electrodes.

Display devices with this construction reflect light incident on the device diffusively from the white reflector. With pixels switched on the device reflects the characteristic blue colour of a viologen contrasted against the white reflector. The display device thus operates such that in environments of high brightness, the contrast ratio and readability are not adversely affected.

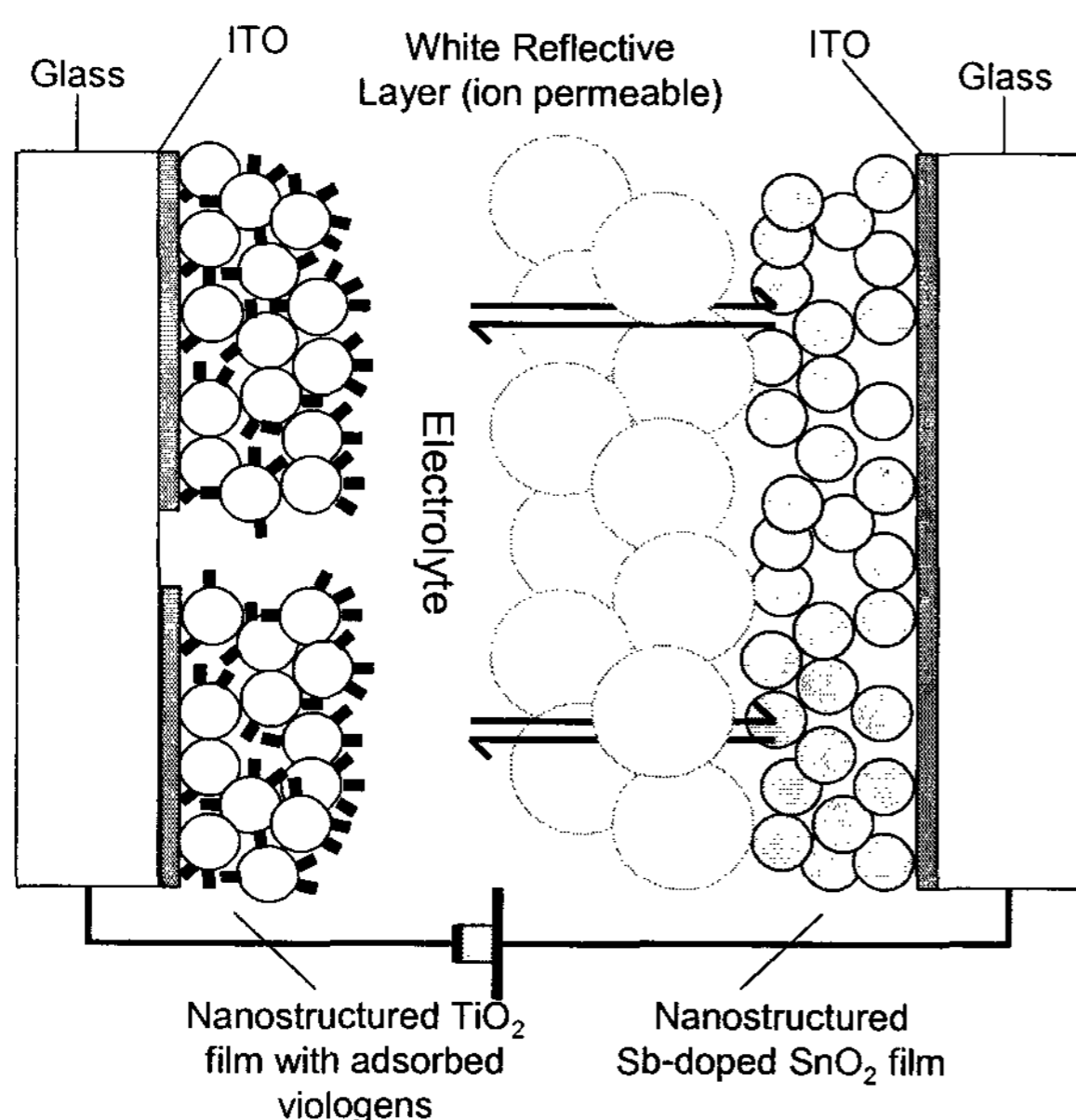


Figure 2 Device cross section of the display device showing segmentation of the cathode into individual pixels.

The process involved in preparing the nanocrystalline, nanoporous films involves the use of temperatures higher ($400\text{ }^{\circ}\text{C}+$) than the glass transition temperatures of many of the substrates utilized in the fabrication of flexible displays. This high temperature provides energy to support the combustion of organic materials in the printing inks and to sinter the particles together to an intermediate stage with retention of porosity. It was thought that the high temperature required to sinter the nanocrystallites endowed the film with sufficient ohmic contact between nanoparticles for efficient charge percolation throughout the film. Sintering to an intermediate stage provides an open, porous network of nanocrystallites to make available an extremely high surface area for the adsorption of viologens such that a high contrast ratio in a display is achieved.

With the materials requirements as stated, several problems needed to be resolved. The removal of temperature in the

formation of the nanostructured film, the retention of the high surface area required for viologen adsorption whilst providing a film capable of percolating charge efficiently enough to enable a fast reversible switching characteristic in the display, the development of a solid, freestanding gel electrolyte and aspects of engineering in encapsulating the device were identified as the key issues to resolve.

The function of the high temperature is to combust organic materials as well as to sinter the particles. To assess the absolute need to sinter the particles, the temperature in the process has been reduced to $300\text{ }^{\circ}\text{C}$. At this temperature combustion of the organic materials has occurred efficiently and devices have been fabricated with equivalent performance to the higher temperature processed display devices on glass. However, the temperature is still too high to be compatible with commonly used substrates for flexible displays.

3. Flexible Display Preparation

Two strategies for the preparation of films were employed that do not require sintering and thus are applicable to displays based on polymer substrates. The first strategy involves the coating of electrodes with printable nanomaterials/binder composite pastes in which the binder remains in the film after casting. In the second strategy the Titania particles are modified in the precursor colloidal dispersion of nanoparticles and formulated as in the first strategy for low temperature processing. Each strategy is described in more detail below.

3.1 Nanomaterial/binder Composite Films

Several internally developed formulations were prepared varying the level of binder in the ink such that the resultant film, once dried, had sufficient capacity to uptake viologen molecules in the quantity required for effective display assembly.

Initially, cathode films were cast on rigid, glass substrates and coupled with conventionally printed and sintered anode/white reflector electrodes in test devices in order to isolate the performance of the cathode from the other known issues. Figure 3 is a micrograph wherein the binder can be clearly seen linking the nanoparticulate material in the film.

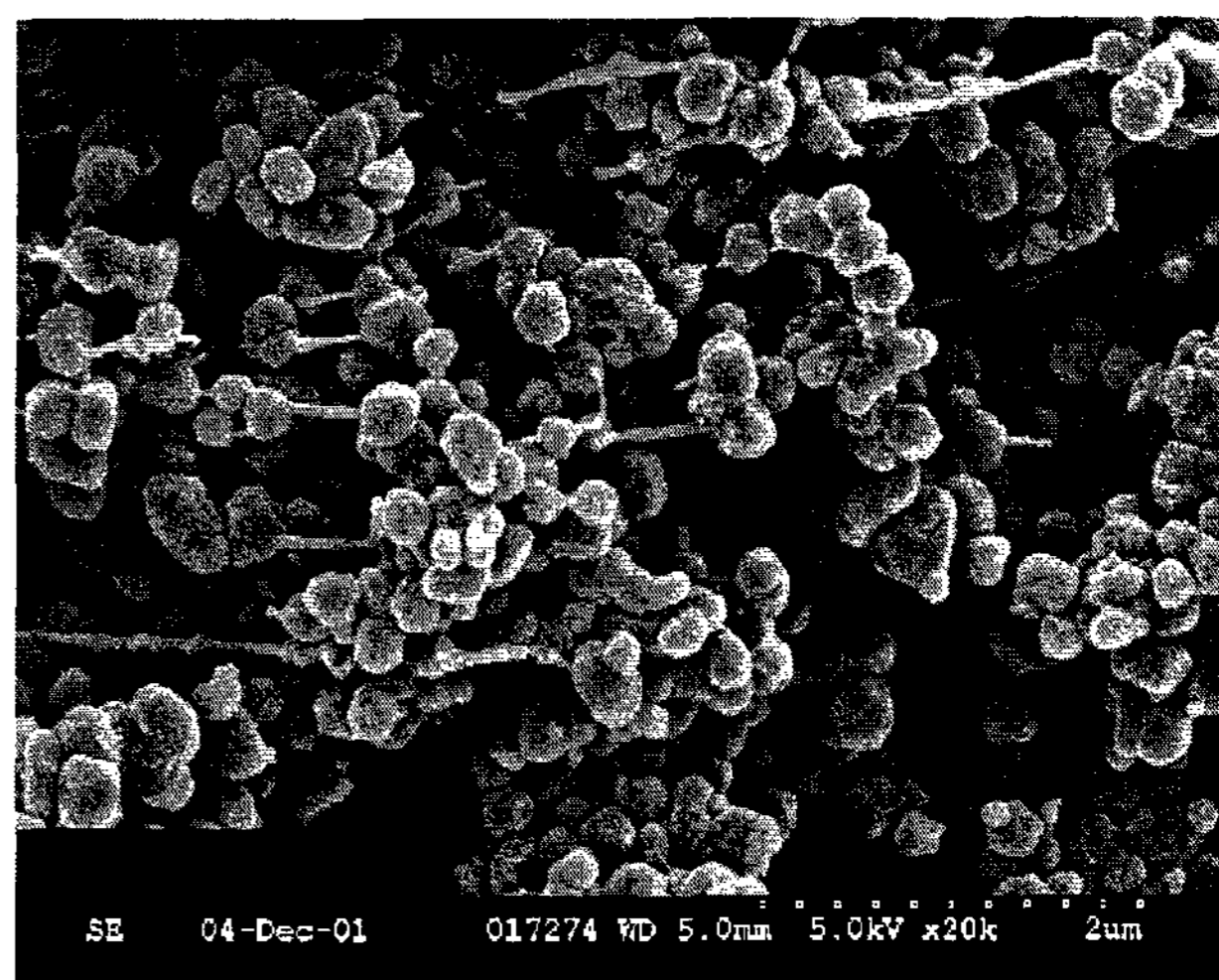


Figure 3 Nanomaterial/binder composite film

The device geometry was a 5 cm x 5 cm square of Fluorine doped

tin oxide coated glass with a 2 cm x 2 cm square of the composite titania film applied in the center of the glass. The counter electrode had a similar geometry with the white reflector layer printed on top of the antimony tin oxide layer. The electrolyte used in this device was Lithium perchlorate (0.2M) in gamma-butyrolactone. The performance was compared with conventional, high temperature processed devices and the results of this comparison are in Table 1 below. The contrast ratio (quotient of the higher and lower diffuse reflectances) of the devices was slightly lower than that of the comparison, presumably due to the amount of viologen adsorbed in this film. The switching speed is also affected, perhaps by the insulating nature of the binder in the nanomaterial/binder composite film.

Devices were prepared with similarly optimized anode formulations and both cathodes and anodes were deposited on ITO/PET substrates and assembled using pressure sensitive adhesive as the encapsulant. Again, a liquid based electrolyte (Lithium perchlorate (0.2M) in gamma-butyrolactone) was used to provide proof-of-principle. The performance of test devices is also compared with that of a conventional device in Table 1. Surprisingly, the optical performance of this device was better than that of the hybrid low temperature cathode/high temperature anode device in that the contrast ratio was higher and a marked improvement in the switching speed was observed. It is unclear how the performance improvement may be due to the better matching of capacitance in the cells by the inclusion of two equivalently formulated electrode materials.

| Device | Contrast Ratio | Switching Speed (On) (s) | Switching Speed (Off) (s) |
|---------------|----------------|--------------------------|---------------------------|
| HT Electrodes | 7.4 | 0.9 | 0.8 |
| LT Cathode | 5.1 | 1.5 | 1.1 |
| LT Electrodes | 6.2 | 0.3 | 0.3 |

Table 1 Comparison of Optical Performance of Test Devices with combinations of Low Temperature (LT) and high Temperature (HT) Nanostructured films

The paste formulations used in the ITO/PET constructed devices above were printed in a static display pattern and assembled into a flexible display. Figure 4 shows such a display operated under flexing. It is clear to see the paper-white nature of the display and the angular independence associated with the absence of polarizing materials.



Figure 4 Flexible static display device operating under flexing and "Memory" condition

3.2 Pre-modified Nanoparticle Colloids

For this architecture, nanoparticulate TiO_2 was modified with viologen by mixing the colloidal dispersion in a solution of viologen. The modified titania nanoparticles were recovered by centrifugation. Following rinsing to remove excess viologen, the material was incorporated into a printing paste and deposited onto an ITO-glass coated substrate and devices prepared using the Low-Temperature processed counter-electrode materials described above. Typical device performance was as is shown in Table 2 below.

| Device | Contrast Ratio | Switching Speed (On) (s) | Switching Speed (Off) (s) |
|------------------------|----------------|--------------------------|---------------------------|
| Modified Nanoparticles | 7.9 | 3.2 | 1.8 |

Table 2 Optical Performance of a test devices with pre-modified titania nanostructured films.

Although the device showed good contrast ratio, poor switching was observed. It was thought that the pre-modification of the titania nanocrystallites hindered the charge percolation throughout the film. An advantage of this device architecture is that, owing to the high degree of aggregation in the pre-modified titania, the cathode is itself white. This has the potential to eliminate the need for a separate reflector and the high degree of light scattering within the film leads to a high overall absorption efficiency by the adsorbed viologen.

4. Engineering Issues Specific to Flexible Displays

As mentioned in section 2, several key issues needed to be resolved in preparing flexible NanoChromics display devices. The preceding sections elaborate on the progress made at NTERA in solving the central, basic research issues of formulation and temperature removal from the process. The remaining issues were considered engineering issues and are

largely related to the nature of a flexible electrochromic displays.

The use of a self-supporting ion-permeable gel electrolyte in place of a liquid electrolyte improves the durability of a flexible device by reducing the hydrostatic pressure on the seal between the electrodes when the device is flexed. Several suitable electrolytes are known in the literature and in developing for such an electrolyte the methods of Mustarelli and co-workers [5] were modified and used. In addition to providing the self-supporting electrolyte, the white reflector was incorporated into the gel.

The reflective electrolyte developed at NTERA, involved the reflector pigment particles being suspended in a solution of the binder similar to that used in the cathode paste and a film of this paste was deposited. A solvent exchange process results in the formation of a composite film of swollen polymer-electrolyte with uniformly distributed reflector pigment particles. This reflective gel electrolyte further simplifies the construction of the device by replacing separate electrolyte, reflector and spacer elements with a single space filling reflective electrolyte.

Since an electrochromic display is essentially an electrochemical cell, incorporating a redox-active viologen molecule, it is necessary to isolate it effectively from redox-active species in its environment in order to maintain stable switching characteristics. In the case of rigid devices, this is effectively done by the glass substrate. Flexible devices, being made on inherently more permeable polymeric substrates, offer greater challenges to the maintenance of chemical homeostasis in the cell and work is continuing on optimising the choice of both substrate and seal materials.

5. Conclusion

At NTERA significant research has been carried out towards the realization of flexible variants of NanoChromics. This work illustrates that it is possible to build functional devices on plastic substrates. The issues to be resolved largely depend on complementary technologies such as substrate development and appropriate sealing materials and methodology. As it is possible to assemble these displays on flexible substrates, a significant opportunity exists to supply a range of markets with truly "paper-white" high quality, readable displays that are cost effective when compared with competitive technologies.

6. References

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