Ultrafast Electrochromic Windows Based on Redox-Chromophore Modified Nanostructured Semiconducting and Conducting Films

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Described is the construction of an ultrafast electrochromic window. One electrode of this window is based on a transparent nanostructured TiO₂ (anatase) film (4.0 μ m thick) supported on conducting glass (F-doped tin oxide, 10 Ω cm⁻², 0.5 μ m thick) and modified by chemisorption of a monolayer of the redox chromophore bis(2-phosphonoethyl)-4,4'-bipyridinium dichloride. The other electrode is based on a transparent nanostructured SnO₂ film (3.0 μ m thick) supported on conducting glass (F-doped tin oxide, 10 Ω cm⁻², 0.5 μ m thick) and modified by chemisorption of a monolayer of the redox chromophore [β -(10-phenothiazyl)propoxy]phosphonic acid. The electrolyte used is LiClO₄ (0.2 mol dm⁻³) in γ -butyrolactone. The excellent performance of a 2.5 cm \times 2.5 cm window over 10 000 electrochromic test cycles—switching times (coloring and bleaching) of less than 250 ms, coloration efficiency of 270 cm² C⁻¹, steady-state currents (colored and bleached) of less than 6 μ A cm⁻², and memory of greater than 600 s (time required for low end transmittance to increase by 5%)—suggest a practical technology.

Introduction

Electrochromic (EC) materials, i.e., materials that change in color on application of a potential, are the subjects of an increasing number of reports in the literature and a growing number of patent applications.¹ This increased activity is due, generally, to a growing awareness of the commercial potential of EC materials and, specifically, to the fact that a number of leading manufacturers have now demonstrated the commercial viability of products incorporating EC materials.

It is still the case, however, that only a few of the commercial applications foreseen for EC materials, namely rear-view EC mirrors and large segment static displays, have been brought to the market. Other potential applications, including large-area privacy/architectural glazing and high contrast angle-independent dynamic displays have yet to reach the market. Failure to commercialize these applications reflects the limitations of existing EC materials, which may be divided in two classes as outlined below.

First, there are devices that change color upon intercalation of small ions into a thin metal oxide film. Examples of metal oxides used include WO₃, V₂O₅ and TiO₂; examples of ions used include Li⁺ and Na⁺. These materials are usually deposited as amorphous or polycrystalline thin films onto conducting glass substrates and the ions present in the electrolyte intercalated under an applied potential. To obtain sufficient optical absorption, ion-intercalation must extend into the bulk of the metal oxide film. The rates of coloring and bleaching are, therefore, limited by the rate of ion transport in to and out of the metal oxide film. As a consequence, the switching times of such devices are typically of the order of tens of seconds even for relatively small area devices. Second, there are devices that change color upon reduction or oxidation of a redox chromophore. The redox chromophore is either dissolved in a solution or incorporated in a polymeric film deposited on a transparent conducting substrate. In the case of the viologens, a well-known class of redox chromophore, their reduction leads to a deep blue or green color. The rates of coloring and bleaching are, therefore, limited by the rate of diffusion of the chromophore to the conducting substrates, or the rate of migration of electrons within the polymeric film. As a consequence, the switching times of such devices are typically of the order of tens of seconds even for relatively small area devices. While a rapidly switching device may be constructed by adsorbing a monolayer of a redox chromophore at the surface of a conducting substrate, the extent to which the device colors is not sufficient for practical applications.

Transparent nanoporous-nanocrystalline TiO₂ films on conducting glass referred to as nanostructured TiO₂ films, have been used as photoanodes in efficient dye-sensitized photoelectrochemical solar cells.² This has led to a great deal of activity in the area of nanostructured semiconductor materials in general and nanostructured TiO₂ electrodes in particular. A characteristic feature of nanostructured TiO₂ electrodes is that they typically have a porosity of 50% and an internal surface area that greatly exceeds their geometric area. When used in an electrochemical system, application of a negative potential leads to a rapid accumulation of electrons in the nanostructured TiO₂ electrode as charge may be readily compensated by ions adsorbed or intercalated at or near the electrode–electrolyte interface.

The rapid accumulation of charge in nanostructured TiO_2 electrodes, compensated in an aprotic electrolyte by intercalation of small ions, leads to formation of blue color centers. The extent of coloration of a nanostructured TiO_2 electrode is, however,

not sufficient for many practical applications.³ To overcome this limitation, nanostructured TiO₂ electrodes have been modified by chemisorption of a monolayer of a viologen, which colors blue when reduced by an accumulated electron. This approach combines the advantages of EC devices based on metal oxide films with those based on redox chromophores in solution or within a polymer film.^{4–6}

Here we describe the construction of a novel electrochromic window based on modified nanostructured metal oxide films. which exhibits unprecedentedly fast switching times.^{7,8} One electrode of this window is based on a transparent nanostructured TiO₂ film (anatase, 4.0 μ m thick) supported on conducting glass (F-doped tin oxide, 15 Ω cm⁻², 0.5 μ m thick) and modified by chemisorption of a monolayer of the redox chromophore bis-(2-phosphonoethyl)-4,4'-bipyridinium dichloride. The other electrode is based on a transparent nanostructured SnO2:Sb film $(3.0 \,\mu\text{m} \text{ thick})$ supported on conducting glass (F-doped tin oxide, 15 Ω cm⁻², 0.5 μ m thick) and modified by chemisorption of a monolayer of the redox chromophore [β -(10- phenothiazyl)propoxy]phosphonic acid. The electrolyte used is 0.2 M LiClO₄ in γ -butyrolactone. The excellent performance of a 2.5 cm \times 2.5 cm window over 10 000 electrochromic test cyclesswitching times (coloring and bleaching) of less than 250 ms, coloration efficiency of 270 cm² C⁻¹, steady-state currents (colored and bleached) of less than 6 μ A cm⁻², and memory of greater than 600 s (time required for low end transmittance to increase by 5%)—suggest a practical technology.

Experimental Section

Preparation of Transparent Nanostructured TiO₂ Electrodes. Transparent nanostructured TiO₂ films were deposited on F-doped tin oxide glass substrates (15 Ω cm⁻², 0.5 μ m thick, TEC 15 supplied by Libby-Owen-Ford) as described in detail elsewhere.^{2,5} Briefly, a colloidal TiO₂ dispersion was prepared by hydrolysis of titanium tetraisopropoxide and autoclaved at 200 °C for 12 h to yield a dispersion of 10 nm diameter nanocrystals. Concentrating this dispersion (160 g L⁻¹) and addition of Carbowax 20000 (40 wt % equivalent of TiO₂) yields a white viscous paste. This paste was spread using a glass rod on the conducting glass substrate masked by Scotch tape. Following drying in air for 1 h the film was fired, also in air, at 450 °C for 2 h. The resulting transparent nanostructured electrodes are 4 μ m thick and possess a surface roughness of about 1000.

Preparation of Transparent Nanostructured SnO₂ Electrodes. Transparent nanostructured SnO2:Sb films were deposited on F-doped tin oxide glass substrates (10 Ω cm⁻², 0.5 μ m thick, TEC 15 supplied by Libby-Owen-Ford) as described in detail elsewhere.⁹ Briefly, 20 drops of acetic acid (2.0 mol dm⁻³) were added with stirring to an aqueous dispersion (50 g) of 5 nm diameter Sb-doped SnO₂ nanocrystals (15% by wt. SnO₂: Sb, supplied by Alfa). The gel, which formed immediately, was diluted by addition of water (15 mL) and autoclaved at 200 °C for 12 h. Addition of Carbowax 20000 (3.75 g) with stirring for 8 h yields an amber viscous paste, which was diluted with water (15 mL) to make it suitable for spreading. This paste was spread using a glass rod on the conducting glass substrate masked by Scotch tape. Following drying in air for 1 h the film was fired, also in air, at 450 °C for 1 h. The resulting transparent nanostructured SnO₂:Sb electrodes are $3.0 \,\mu$ m thick and possess a surface roughness of about 1000.

Synthesis of Redox Chromophores. The modified viologen I was prepared as shown in Scheme 1. As phosphonic acid moieties are chemisorbed at a metal oxide surface it is possible

SCHEME 1: Reagents and Conditions for Synthesis of Bis(2-phosphonylethyl)-4,4'-bipyridinium Dichloride (I)^{*a*}



^a (a) Reflux, water, 72 h. (b) 50% HCl, reflux 24 h.

to link this redox chromophore to the surface of the nanostructured TiO₂ electrode prepared as described above^{10,11} 4,4'bipyridine (4.4 g) and diethyl-2-bromoethyl phosphonate (15.0 g) were added to water (75 mL). The reaction mixture was refluxed for 72 h and allowed to cool. Following addition of concentrated hydrochloric acid (50%, 75 mL) the reaction mixture was refluxed for a further 24 h. To recover the product, the reaction mixture was concentrated (to 50 mL), 2-propanol (200 mL) added dropwise, stirred on ice for an hour and filtered. The white crystalline product was washed with cold 2-propanol and air-dried to give the pure redox chromophore bis(2phosphonoethyl)-4,4'-bipyridinium dichloride (I) (12.72 g, 84.24% yield).

Calculated for **I** ($C_{14}H_{20}N_2Cl_2O_6P_2$): C, 37.77; H, 4.53; N, 6.29. Found: C, 35.09; H, 4.49; N, 6.09. ¹H NMR (water- d_2): δ 2.31–2.43 (m, 4H); δ 4.68–4.80 (m, 4H); δ 8.33 (d, unresolved meta-coupling, 4H); δ 8.94 (d, unresolved meta-coupling, 4H).

The modified phenothiazine **VIII** was prepared as shown in Scheme 2. As phosphonic acid moieties are chemisorbed at a metal oxide surface, it is possible to link this redox chromophore to the surface of the nanostructured SnO_2 :Sb film described above.^{10,11}

III: β -(10-Phenothiazyl)propionitrile. Triton B (0.6 mL of a 40% aq soln) was added dropwise to a solution of phenothiazine (**II**, 50 g) in acrylonitrile (45 mL) on ice resulting in a vigorous reaction. The reaction mixture was refluxed for 1 h and allowed to cool. The resulting crude product was recrystallized from a 30:70 mixture of hot ethanol and acetone to yield orange crystals of **III** (31.27 g, and 49.6%).

¹H NMR (acetone- d_6): δ 2.22–2.62 (t, 2H, J = 6.0 Hz); δ 3.82–4.04 (t, 2H, J = 6.0 Hz); δ 6.4–7.00 (m, 8H).

IV: β -(*10-Phenothiazyl*)*propionic Acid.* Compound **III** (31.27 g) was added to a mixed solvent (350 mL methanol, 105 mL water) NaOH (35 g) solution, refluxed for 15 h and allowed to cool. The crude product was poured on ice water and acidified by the addition of dil. sulfuric acid until a white precipitate formed. The crude product was recrystallized to yield **IV** (17.0 g, 52.26%).

¹H NMR (acetone- d_6): δ 2.56–2.80 (t, 2H, J = 7.2 Hz); δ 4.04–4.28 (t, 2H, J = 7.2 Hz); δ 6.88–7.20 (m, 8H).

V: β -(10-Phenothiazyl)propionate Ester. Compound **IV** (17 g) was dissolved in 1:2 by volume mixture of ethanol and toluene (700 mL) acidified by addition of concentrated sulfuric





^{*a*} (a) Acrylonitrile, Triton B (40% aq solution), 0 °C. (b) Reflux 1 h. (c) Methanolic sodium hydroxide, reflux 15 h. (d) Ethanol-toluene, concentrated H_2SO_4 , reflux 12 h. (e) Diethyl ether (dry), LiAlH₄. (f) Pyridine-chloroform (dry), phosphorus oxychloride, stir, -15 °C, 2 h. (g) Stir, RT, 1.5 h. (h) Water, stir, RT, 12 h.

acid (4 mL) and refluxed overnight. The solution was concentrated (to approximately 50 mL) and diluted by addition of water (500 mL). The crude product was extracted into ethyl acetate (4 \times 200 mL), washed with water, dried over MgSO₄, filtered and the solvent removed under reduced pressure. White crystals of **V** precipitated from the solution on cooling (11.85 g, 63.9%).

¹H NMR (chloroform-*d*): δ 1.34–1.61 (t, 3H, J = 7.1 Hz); δ 2.97–3.21 (t, 2H, J = 7.4 Hz); δ 4.28–4.65 (m, 4H); δ 7.08–7.62 (m, 8H).

VI: β -(*10-Phenothiazyl*)*propanol.* A solution of the compound V (11.85 g) in dry diethyl ether (33 mL) was added dropwise to a suspension of LiAlH₄ (4.74 g) in dry diethyl ether (70 mL) and stirred overnight at room temperature. Excess LiAlH₄ was decomposed by the dropwise addition of water and filtered. Removal of the solvent under reduced pressure gave the green solid VI (5.57 g, 54.7%).

¹H NMR (chloroform-*d*): δ 2.00–2.05 (m, 2H); δ 3.72–3.76 (t, 2H, J = 6.4 Hz); δ 4.00–4.05 (t, 2H, J = 5.9 Hz); δ 6.92–7.21 (m, 8H).

VII: [β -(10-Phenothiazyl)propoxy]phosphonic Acid Dichloride. A solution of **VI** (1.0 g) and pyridine (1.0 mL) in dry chloroform (60 mL) was cooled to -15 °C. A solution of phosphorus oxychloride (4.73 mL) and pyridine (1.0 mL) and dry chloroform (40 mL) was added dropwise over 0.5 h. The reaction mixture was stirred at -15 °C for 2 h and the resulting homogeneous solution allowed to reach ambient temperature over 1.5 h. The chloroform was removed under reduced pressure and the crude product washed with toluene (3 × 50 mL) to remove any unreacted phosphorus oxychloride affording a green oil **VII** (0.9 g, 65.2%).

¹H NMR (chloroform-*d*): δ 2.11–2.27 (m, 2H); δ 3.56–3.59 (m, 2H); δ 3.98–4.01 (m, 2H); δ 6.86–7.13 (m, 8H).

VIII: [β -(10- Phenothiazyl)propoxy]phosphonic Acid. A solution of **VII** (0.9 g) in deionized water (60 mL) was stirred overnight. The crude product was extracted in ethyl acetate (4 × 50 mL), washed with water, and dried over sodium sulfate. The white crystals that formed were removed by filtration and the filtrate recrystallized a further three times to yield the impure product **VIII** (0.30 g, 40%). The impurity, also a white crystalline solid, was determined by ¹H NMR, ³¹P NMR, mass spectrometry and elemental analysis to be β -(10-phenothiazyl)-propyl chloride, **IX**. It is noted that following recrystallization, the product still contained significant quantities of **IX** as an impurity (approximately 80% by mass). It is also noted, since this impurity does not incorporate phosphonic acid groups it is not adsorbed at the surface of a nanostructured SnO₂:Sb electrode.

Calculated for **VIII** (C₁₅H₁₆O₄NSP): C, 53.43; H, 4.76; N, 4.15; P, 9.19. Found: C, 63.58; H, 5.42; N, 4.77; P, 1.86. ¹H NMR (CDCl₃): δ 2.24–2.28 (t, 2H, J = 6.3 Hz); δ 3.67–3.70 (t, 2H, J = 6.2 Hz); δ 4.09–4.12 (t, 2H, J = 6.5 Hz); δ 6.91–7.19 (m, 8H). ³¹P NMR (CDCl₃): δ 1.69–1.89 (H₃PO₄); δ –11.96

Calculated for **IX** (C₁₅H₁₄NSCl): C, 65.00; H, 5.10; N, 5.10; S, 11.63; Cl, 12.70. Found: C, 64.78; H, 5.07; N, 4.99; S, 12.31; Cl, 12.12. ¹H NMR (CDCl₃): δ 2.25–2.28 (t, 2H, J = 6.3 Hz), δ 3.66–3.70 (t, 2H, J = 6.0 Hz); δ 4.07–4.12 (t, 2H, J = 6.0 Hz); δ 6.898–7.21 (m, 8H).

All elemental analysis was performed at the Chemical Services Unit, Department of Chemistry, University College

SCHEME 3: Construction of Electrochromic Window



Dublin. ¹H NMR spectra were recorded using a JEOL GPX 270 MHz spectrometer at the Chemical Services Unit, Department of Chemistry, University College Dublin. ³¹P NMR were measured using a Brucker 400 MHz spectrometer at the NMR Center, Department of Chemistry, Trinity College Dublin.

Preparation and Characterization of Modified Nanostructured Electrodes. A 2.5 cm × 2.5 cm transparent nanostructured film of TiO₂ or SnO₂:Sb was deposited on a 3.9 cm × 3.9 cm conducting glass substrate as described above. The TiO₂ film was modified by chemisorption of the viologen I from an aqueous solution (0.02 mol dm⁻³) during 24 h, washed with distilled 2-propanol, dried in air and stored in a darkened vacuum desiccator for 24 h prior to use. The SnO₂:Sb film was modified by chemisorption of the phenothiazine **VIII** from a chloroformic solution (0.02 mol dm⁻³) during 6 h, washed with distilled chloroform, dried in air and stored in a darkened vacuum desiccator prior to use.

Electrochemical and spectroelectrochemical characterization of the modified electrode employed the following: A glass single-compartment 3-electrode cell with a modified nanostructured TiO₂ or SnO₂:Sb electrode (geometric surface area 1 cm²) as the working electrode, a platinum sheet counter electrode, and a Ag/AgCl/1 M KCl (aq) reference electrode. The electrolyte was thoroughly deaerated by bubbling with Ar for 30 min prior to experiments. The cell was incorporated in the sample compartment of a Hewlett-Packard 8452A diode array spectrophotometer and connected to a Solartron SI 1287 potentiostat.

Construction of Electrochromic Window. A 2.5 cm \times 2.5 cm transparent nanostructured film of TiO₂ or SnO₂:Sb was deposited on a 3.9 cm \times 3.9 cm conducting glass substrate. The TiO₂ electrode was modified by chemisorption of the viologen I from an aqueous solution (0.02 mol dm⁻³) during 24 h, washed with distilled 2-propanol, dried in air and stored in a darkened vacuum desiccator for 24 h prior to use. The SnO₂:

Sb electrode was modified by chemisorption of the phenothiazine **VIII** from a chloroformic solution (0.02 mol dm⁻³) during 6 h, washed with distilled chloroform, dried in air and stored in a darkened vacuum desiccator for 24 h prior to use.

A cell, with an internal spacing of about 400 μ m, was constructed from a modified nanostructured TiO₂ electrode mounted on a modified nanostructured SnO₂:Sb electrode, as shown in Scheme 3, and sealed using a thermoplastic gasket (IPBOND 2025, supplied by Industria Plastica Monregalese). The above gasket had an opening at one corner. The sandwich structure was evacuated in a modified vacuum desiccator, the opening dipped in electrolyte solution, and filled by admitting Ar into the vacuum desiccator. The electrolyte solution consisted of LiClO₄ (0.2 mol dm⁻³) in γ -butyrolactone. It should be noted that both the LiClO₄ and γ -butyrolactone were carefully purified, rigorously dried and degassed by bubbling with Ar for 30 min prior to use. Finally, the cell was sealed using a UV-curable epoxy resin.

Findings are also reported for EC windows with the following nominal areas: $0.5 \text{ cm} \times 0.5 \text{ cm}$, $1.0 \text{ cm} \times 1.0 \text{ cm}$, $3.0 \text{ cm} \times 3.0 \text{ cm} \times 10 \text{ cm}$. These windows were all assembled as described above and as shown in Scheme 3.

Testing of Electrochromic Window. A National Instruments DAQ board in a Macintosh Power PC was used for electrochromic cycling. One cycle consisted of applying a voltage of 1.2 V which biases the viologen modified nanostructured TiO₂ electrode negative of the phenothiazine modified SnO₂:Sb electrode for 15 s, and a voltage of 0.0 V for 15 s. Optical absorption spectra were recorded using a Hewlett-Packard 8452A diode array spectrophotometer. A Solartron SI 1287 potentiostat was used to record potential–current characteristics. All reported testing was done at room temperature.



Figure 1. Optical absorption spectra of the electrochromic window in Scheme 3 prior to (bleached) and following application of a voltage of 1.20 V (colored) which biases the viologen modified nanostructured TiO_2 electrode negative of the phenothiazine modified nanostructured SnO_2 :Sb electrode.



Figure 2. Optical absorption spectra measured at the indicated point of the electrochromic window in Scheme 4 following application of a voltage of 1.20 V (colored) which biases the viologen modified nanostructured TiO₂ electrode negative of the phenothiazine modified nanostructured SnO₂:Sb electrode.

Results

Optical Absorption Spectra of EC Window. Shown in Figure 1 are the optical absorption spectra of a 2.5 cm \times 2.5 cm EC window assembled as shown in Scheme 3. In the bleached state the EC window has a slight yellow color due to the phenothiazine derivative adsorbed at the surface of the nanostructured SnO₂:Sb film. The relatively high absorbance in the bleached state is due to reflection losses in the multilayer assembly, which have not been corrected for. Application of a voltage of 1.2 V, which biases the viologen modified nanostructured TiO₂ electrode negative of the phenothiazine modified SnO₂:Sb electrode, causes the EC window to color blue-red.

Shown in Figure 2 are the optical absorption spectra of the EC window assembled as shown in Scheme 4. These spectra were measured at the indicated positions at an applied voltage of 1.2 V which biased the viologen modified nanostructured TiO_2 electrode negative of the phenothiazine modified SnO₂: Sb electrode.

Clearly under the reported conditions the viologen modified nanostructured TiO_2 electrode colors blue (Position A), while the phenothiazine-modified nanostructured SnO_2 :Sb electrode colors red (Position B). Consistent with these observations is the further observation that, as in Figure 1, the region where these electrodes overlap (Position C) the EC window colors blue-red.

To permit a complete assignment of the optical absorption spectrum of the EC window in the colored state, cyclic voltammograms (CVs) were measured for both the viologen modified nanostructured TiO_2 electrode and the phenothiazine modified nanostructured SnO_2 :Sb electrode, see Figure 3. The optical absorption spectra of the same electrodes were measured simultaneously at the indicated applied potentials.

As may be seen from the CV in Figure 3a, all the viologen molecules chemisorbed at the surface of the nanostructured TiO_2 electrode are all singly reduced at applied potentials more negative than -0.9 V. As may be seen from the corresponding optical absorption spectra in Figure 3b, due to formation of the radical cation of the viologen, this electrode colors blue.¹² At applied potentials more negative than -1.0 V all the viologen molecules chemisorbed at the surface of the nanostructured TiO₂ electrode are doubly reduced and the electrode colors a faint yellow-green.^{12,13}

The nanostructured TiO₂ electrode used to prepare the EC window shown in Scheme 3 is 4 μ m thick and has a surface roughness of about 1000 [2]. The concentration of surface Ti⁴⁺ sites is approximately 2 × 10¹³ cm⁻² implying; assuming each viologen is chemisorbed through one phosphonate group, a surface concentration of 2 × 10¹³ cm⁻² viologens.¹⁴ Taking into account the surface roughness (1000) and the extinction coefficient of the reduced form of this viologen at 608 nm (14 000 mol⁻¹ dm³ cm⁻¹),¹² this implies an upper limit for absorbance at this wavelength in the colored state of about 0.5. Having singly reduced all the viologen molecules chemisorbed at the surface of the nanostructured TiO₂ film in Figure 3b, the absorbance at 608 nm is increased by 0.5.

As may be seen from the CV in Figure 3c, all the phenothiazine molecules chemisorbed at the surface of the nanostructured SnO_2 :Sb electrode are singly oxidized at applied potentials more positive than +0.9 V. As may be seen from the corresponding optical absorption spectra in Figure 3d, due to formation of the radical cation form of the phenothiazine, this electrode colors red. At an applied potential of +1.1 V all the phenothiazine molecules chemisorbed at the surface of the nanostructured SnO_2 :Sb electrode are doubly oxidized and the electrode is a faint yellow-green in appearance.

The nanostructured SnO₂:Sb electrode used to prepare the EC window in Figure 1 is 3 μ m thick and has a surface roughness of about 1000.⁹ The concentration of surface Sn⁴⁺ sites is assumed to be 2 × 10¹³ cm⁻² implying a surface concentration of 2 × 10¹³ cm⁻² phenothiazine. Taking into account the surface roughness (1000) and the extinction coefficient of the oxidized form of this phenothiazine at 515 nm (8000 mol⁻¹ dm³ cm⁻¹),¹⁵ this implies an upper limit for absorbance at this wavelength in the colored state of about 0.3. Having reduced all the phenothiazine molecules adsorbed at the surface of the nanostructured SnO₂:Sb film in Figure 3d, the absorbance at 515 nm is increased by 0.3.

On the basis of the CVs and spectra, shown in Figure 3, it is possible to conclude the following: First, that the viologen molecules chemisorbed at the nanostructured TiO_2 electrode undergo a one electron reduction to form the corresponding radical cation and color blue; and second, that the phenothiazine molecules chemisorbed at the nanostructured SnO_2 :Sb electrode undergo a one electron oxidation to form the corresponding

SCHEME 4: Construction of Test Electrochromic Window



radical cation and color red. Together, these observations account for the blue-red, or essentially neutral, color of the EC window.

Switching Times of EC Window. The rate of coloration of a 2.5 cm \times 2.5 cm EC window assembled as shown in Scheme 3 was measured following application of a voltage of 1.2 V which biased the viologen modified nanostructured TiO₂ film negative of the phenothiazine modified SnO₂:Sb film. As may be seen from Figure 4a the coloration time, defined as the time taken for the transmittance to decrease by two-thirds of the difference between the steady-state transmittances in the bleached and colored states, is about 250 ms. The rate of bleaching of the same EC window was measured by applying a voltage of 0.0 V to a previously colored device. As may also be seen from Figure 4a the bleaching time, defined as the average time taken for the transmittance to increase by twothirds of the difference between the steady-state transmittances in the colored and bleached states, is about 105 ms.

Also shown in Figure 4a are the transmittance transients measured on coloring and bleaching a 0.8 cm \times 0.8 cm and a 8.7 cm \times 8.7 cm device. The former show coloring and bleaching times of 80 and 35 ms, respectively. The latter shows coloring and bleaching times of 1450 and 530 ms, respectively. Interestingly, the measured switching times are proportional to the area of the EC window.

Because of the above windows being assembled by hand,



Figure 3. (a) Cyclic voltammogram of viologen modified nanostructured TiO₂ electrode versus Ag/AgCl (1.0 mol dm⁻³ KCl) in an electrolyte consisting LiClO₄ (0.2 mol dm⁻³) in γ -butyrolactone. (b) Potential dependent optical absorption spectra of viologen modified nanostructured TiO₂ electrode versus Ag/AgCl (1.0 mol dm⁻³ KCl) in an electrolyte consisting LiClO₄ (0.2 mol dm⁻³) in γ -butyrolactone. (c) As in (a) for phenothiazine modified nanostructured SnO₂:Sb electrode.



Figure 4. (a) Transient optical transmission at 608 nm of electrochromic windows similar to that shown in Scheme 3 versus area following application of a voltage of 1.20 V which biases the viologen modified nanostructured TiO_2 electrode negative of the phenothiazine modified nanostructured SnO_2 :Sb electrode. (b) Coloring times obtained from transients in (a) and similar data. (c) Bleaching times as in (b).

there is significant variability in these values. It is expected that much of this variability will be eliminated by automation of key assembly steps. Nevertheless, the coloring and bleaching times of a number of different EC windows, whose nominal active areas were $0.5 \text{ cm} \times 0.5 \text{ cm}$, $1.0 \text{ cm} \times 1.0 \text{ cm}$, $2.5 \text{ cm} \times 2.5 \text{ cm}$, $3.0 \text{ cm} \times 3.0$ and $9.0 \text{ cm} \times 9.0 \text{ cm}$, have been measured. These times, with the exception of those measured for the 9.0 cm $\times 9.0$ cm devices, are plotted versus the active area of the EC window in Figures 4b and 4c. A linear regression of the above data yields parameters (slope and intercept) that may be used to predict the average coloring and bleaching times of any EC window whose active area is known. The average



Figure 5. (a) Transient optical absorbance at 608 nm and current consumption by the electrochromic window in Scheme 3 following application of a voltage of 1.20 V which biases the viologen modified nanostructured TiO_2 electrode negative of the phenothiazine modified nanostructured SnO_2 :Sb electrode or application of a voltage of 0.00 V. (b) Absorbance versus accumulated charge calculated from data in (a). (c) The persistence of the optical absorbance in (a) under opencircuit conditions.

coloring and bleaching times measured for 9.0 cm \times 9.0 cm EC windows are 3.0 and 0.7 s, respectively. The measured coloring and bleaching times are, as far as the authors are aware, the fastest switching times reported for EC windows of their respective areas.

Coloration Efficiency of EC Window. The peak and steadystate currents of a 2.5 cm \times 2.5 cm EC window, assembled as shown in Scheme 3, have been measured during coloring and bleaching and are shown in Figure 5a.

The peak and steady-state currents measured on coloring are 6.5 mA cm⁻² and 5 μ A cm⁻², respectively. The peak and steady-



Figure 6. Transient optical absorption at 608 nm by the electrochromic window in Scheme 3 during electrochromic cycling (application of a voltage of 1.20 V which biases the viologen modified nanostructured TiO_2 electrode negative of the phenothiazine modified nanostructured SnO_2 :Sb electrode for 15 s, followed by application of a voltage of 0.0 V for 15 s after 1 and 10, 000 cycles.

state currents measured on bleaching the same EC window are also 6.5 mA and 5 μ A cm⁻², respectively.

The coloration efficiency $CE(\lambda)$ at 608 nm, defined by eq 1, was determined from the slope of the plot of the increase in absorbance $\Delta A(\lambda)$ versus the charge accumulated in the device ΔQ , see Figure 5b. The measured CE (608 nm) is 270 C⁻¹ cm².

$$CE(\lambda) = \frac{\Delta A(\lambda)}{\Delta Q}$$
(1)

Both the above peak and steady-state currents are very low and suggest that the power consumption of the EC window will be low and that it should have a long-term memory.

Concerning power consumption, a 2.5 cm \times 2.5 cm EC window will have an associated steady-state current of 31 μ A in the colored state. This implies that the rate of charge consumption is 3.1 \times 10⁻⁵ C s⁻¹ or 5.0 \times 10¹⁴ electrons s⁻¹.

Concerning the long-term memory, if a voltage of 1.2 V is applied to the EC window for 60 s and the circuit opened the EC window first colors and then bleaches on the time scale of hours. More quantitatively, and as may be seen from Figure 5c, the absorbance of the EC window measured at 608 nm takes about 3 h to return to the initially measured value, while the time required for the minimum transmittance in the colored state to increase by 5% is 600 s.

Stability of EC Window. The stability of a 2.5 cm \times 2.5 cm EC window, assembled as shown in Scheme 3, was tested under ambient conditions by subjecting it to 10 000 electrochromic cycles. Each electrochromic cycle consisted of applying a potential of 1.2 V, which biases the viologen modified nanostructured TiO₂ electrode negative of the phenothiazine modified nanostructured SnO₂:Sb electrode, for 15 s and applying a voltage of 0.0 V for 15 s, see Figure 6a. The parameters used to characterize cell performance were measured after 1, 10, 100, 1000 and 10 000 electrochromic cycles and are summarized in Table 1.

Generally, the findings summarized in Table 1 establish that a 2.5 cm \times 2.5 cm EC window, assembled as shown in Scheme 3, is relatively stable under ambient laboratory conditions is relatively stable over 10 000 cycles.

Discussion

Existing nanomaterials based EC window technologies are discussed in outline. The novel nanomaterials based EC window

 TABLE 1: Stability of Window under Electrochromic Cycling^a

number of electrochromic cycles ^b	1	10	100	1000	10000
transmittance in bleached state (%)	64	61	67	57	64
transmittance in colored state (%)	13	12	17	14	23
coloring time (ms)	460	443	605	448	422
bleaching time (ms)	245	270	215	265	212
peak coloring current (mA cm ⁻²)	10	12	7	12	9
peak bleaching current (mA cm ⁻²)	16	17	17	12	11
steady-state colored current (μ A cm ⁻²)	33	28	17	13	15
steady-state bleached current ($\mu A \text{ cm}^{-2}$)	1	2	1	2	1

^{*a*} This test was performed under ambient conditions on a 2.5 cm \times 2.5 cm device assembled as shown in Scheme 3. ^{*b*} Each electrochromic cycle involved applying a voltage of 1.2 V which biased the viologen modified nanostructured electrode negative of the phenothiazine modified electrode for 15 s and then applying a voltage of 0.0 V for 15 s.

technology for which results have been reported above is discussed in detail.

Existing Nanomaterials Based EC Window Technologies. The electrochromic properties of nanostructured TiO_2 electrodes were first reported by Marguerettaz et al.⁴ These authors described the spectroelectrochemical properties of a nanostructured TiO_2 electrode modified by chemisorption of a monolayer of viologen molecules in a protic electrolyte. At negative applied potentials electrons were accumulated in the nanostructured TiO_2 electrode, the chemisorbed viologen molecules were reduced, and the electrode colored a deep blue.

EC window devices based on a nanostructured TiO₂ film were first reported by Cinnsealach et al.^{5,6} These authors described an EC window assembled, as shown in Scheme 5, from one electrode consisting of a viologen modified nanostructured TiO₂ film supported on conducting glass, a second electrode consisting of conducting glass, and a liquid electrolyte consisting of LiClO₄ and ferrocene in γ -butyrolactone. On application of a voltage which biased the nanostructured TiO₂ electrode negative of the conducting glass electrode, the viologen molecules (redox chromophores) chemisorbed at the surface of the nanostructured TiO₂ electrode were reduced. At the same time a fraction of the ferrocene molecules (redox promoters) present in the electrolyte were oxidized at the conducting glass electrode.

In the EC window described above, the redox chromophore is chemisorbed at the surface of a nanostructured TiO₂ film.^{5,6} As a consequence, the rate of reduction of the redox chromophore is not limited by the rate of diffusion of this molecule to the electrode. This is generally the rate-limiting step in commercial EC windows based on the reduction of solution phase redox chromophores. Furthermore, the charge accumulated in the nanostructured electrode is readily compensated by ions adsorbed at the surface of the constituent nanocrystals of the nanostructured film.¹⁶ As a consequence, the rate of reduction of the redox chromophore is not limited by the rate of ion intercalation in the bulk electrode material. This is generally the rate-limiting step in commercial EC windows based on ion intercalation in a compact metal oxide film. It is assumed that the rate-limiting step in the EC window in Scheme 5 is diffusion of the redox promoter to the anode. The fact that the oxidized redox promoter can diffuse to the modified nanostructured electrode and accept electrons from the reduced redox chromophore accounts for the fact that the above EC window exhibits a significant leakage current and is selferasing.^{5,6} The fact that the redox chromophores are in effect stacked, the surface roughness of the nanostructured TiO₂ film being about 1000,² accounts for the fact that the electrode colors a deep blue upon application of a suitable voltage. In short, SCHEME 5: Electrochromic Window Designed by Cinnsealach et al.^{5,6} Based on Viologen Modified Nanostructured TiO₂ and Conducting Glass Electrodes



SCHEME 6: Electrochromic Window Designed by Campus et al.¹⁸ Based on Viologen Modified Nanostructured TiO₂ and Prussian Blue (Electrodeposited on Conducting Glass or on Nanostructured TiO₂ on Conducting Glass) Electrodes



this self-erasing EC window is characterized by relatively fast switching times and low transmissivity in the colored state.

In a subsequent development of this technology, Cinnsealach et al. described differently colored (blue and green) EC windows based on a series of modified viologens which could be chemisorbed at the surface of a nanostructured TiO_2 film.^{5,6} Boehlen et al. also described a modified viologen, which could be chemisorbed at the surface of a nanostructured TiO_2 film and which colored (pink) on being reduced.¹⁷

In a further development of this emerging technology Campus et al. described an EC window assembled, as shown in Scheme 6, from an electrode consisting of a viologen modified nanostructured TiO₂ film supported on a conducting glass, a second electrode consisting of either a thin-film of Prussian Blue electrodeposited on conducting glass or a very thin-film of Prussian Blue electrodeposited on a nanostructured TiO₂ film, and a liquid electrolyte consisting of LiN(SO₂CF₃)₂ in glutaronitrile.^{18,19} On application of a voltage which biased the viologen modified nanostructured TiO₂ electrode negative of the Prussian Blue modified conducting glass or nanostructured TiO₂ electrode, the viologen molecules (redox chromophores) were reduced. At the same time the Prussian Blue molecules (redox chromophores) electrodeposited at the surface of the second nanostructured TiO₂ electrode were oxidized.

In the above EC window one redox chromophore, namely the viologen, is chemisorbed at the surface of a nanostructured TiO_2 film.¹⁸ As a consequence, the rate of reduction of the redox chromophore is not limited by the rate of diffusion of this molecule to the electrode. Furthermore, the charge accumulated in the nanostructured electrode is compensated by ions adsorbed at the surface of the constituent nanocrystals of the nanostructured film.¹⁶ As a consequence, the rate of reduction of this redox chromophore is not limited by the rate of diffusion of ions in the bulk electrode material. The second redox chromophore, namely the Prussian Blue, is electrodeposited as a film on a conducting glass substrate. As a consequence the rate of oxidation of the Prussian Blue molecules is limited by the rate of hole diffusion in the bulk film. Alternatively, the Prussian Blue is electrodeposited as a thin film on the surface of a nanostructured TiO₂ electrode. While this might be expected to increase the rate of oxidation of this molecule, the absence of a population of acceptor states isoenergetic with the donor states of the redox chromophore inhibit electron transfer and, in fact, results in a device with slower switching speeds.¹⁸ The fact that neither of the redox chromophores, either viologen or Prussian Blue, are present in solution ensures that the colored states persist and that this EC window has a long-lived memory. In short, this nonself-erasing EC window is characterized by relatively slow switching times and very low transmissivity in the colored state.

New Nanomaterials Based EC Window Technology. In an attempt to combine the best features of the EC windows described above the 2.5 cm \times 2.5 cm EC window shown in Scheme 3 has been assembled.^{7,8} This EC window consists of a nanostructured TiO₂ electrode modified by chemisorption of a viologen. The above electrode consists of a network of interconnected anatase nanocrystals supported on a conducting glass substrate.⁴ As there are Ti atoms, which require additional oxygen atoms to complete their coordination shell at the surface of these nanocrystals, oxygen-containing ligands that act as Lewis bases are strongly chemisorbed.^{10,11} As a consequence, the viologen **I** is strongly chemisorbed at the surface of the nanostructured TiO₂ electrode.

The EC window in Scheme 3 also consists of a nanostructured SnO_2 :Sb electrode modified by chemisorption of a phenothiazine. This electrode consists of a network of interconnected

SCHEME 7: Energy Level Diagram of Electrochromic Window in Scheme 7



nanocrystals supported on a conducting glass substrate.⁹ As there are undoubtedly Sn atoms which require additional oxygen atoms to complete their coordination shell at the surface of these nanocrystals, oxygen containing ligands that act as Lewis bases are strongly chemisorbed. As a consequence, the phenothiazine **VIII** is strongly chemisorbed at the surface of the nanostructured SnO₂:Sb electrode.

The electrolyte used in the present device is γ -butyrolatone containing added LiClO₄ (0.2 mol dm⁻³). This electrolyte has the advantages of a low freezing-high boiling solvent that is stable to photodecomposition at the surface of nanostructured metal oxide electrodes. This is not the case for solvents more typically employed in EC windows such as ethylene carbonate and propylene carbonate.²⁰ The requirement for a redox promoter in the electrolyte is eliminated by adsorbing redox chromophores at the surface of the nanostructured TiO₂ and SnO₂:Sb electrodes, which are reduced and oxidized, respectively. This ensures, in turn, that this EC window is characterized by low power consumption and an extended memory.

As may be seen from Figure 1, application of a voltage of 1.2 V which biases the viologen modified nanostructured TiO_2 electrode negative of the phenothiazine modified nanostructured SnO_2 :Sb electrode causes the EC window in Scheme 3 to develop a blue-red color. As may be seen from Figure 2, this effect has its origin in the fact that under these conditions the viologen modified nanostructured TiO_2 electrode colors blue, while the phenothiazine modified nanostructured SnO_2 :Sb electrode colors red. The mechanism of operation of the EC window outlined above is described in more detail below. These findings are summarized in Scheme 7.

The redox potential of the conduction band edge of the nanostructured TiO₂ film at the semiconductor-liquid electrolyte interface is -0.9 V in an electrolyte consisting of γ -butyrolactone containing added LiClO₄ (0.2 mol dm⁻³). This value is determined from measurements of the onset of the absorption assigned to electrons accumulated in the conduction band of the nanostructured TiO₂ film (not shown), and is consistent with values obtained for similar electrodes in electrolytes consisting of an aprotic solvent containing added LiClO₄.²¹ The reduction potential of viologen I adsorbed at the surface of a nanostructured TiO₂ film has been measured in solution (-0.61 V).²² As may be seen from Figure 3, viologen reduction is observed at potentials close to that of the conduction band edge and, therefore, at potentials more negative than that of the reduction potential of the viologen. Clearly, viologen reduction is mediated



by the conduction band states of the nanostructured TiO_2 electrode at which these molecules are adsorbed.

The highly doped nature of the SnO₂:Sb electrode means that there is a sufficiently high density of states present in the intraband region to ensure this material is highly conducting.⁹ The oxidation potential of the phenothiazine **VIII** adsorbed at the surface of the nanostructured SnO₂:Sb film has been measured in solution (+0.81 V).²² As may also be seen from Figure 3, phenothiazine oxidation is observed at potentials close to that of the oxidation potential of the molecule in solution. Clearly, phenothiazine oxidation is mediated by the intraband band states of the nanostructured SnO₂:Sb electrode at which these molecules are adsorbed.

As stated, on applying a voltage which biases the viologen modified nanostructured TiO_2 electrode 1.2 V negative of the phenothiazine modified nanostructured SnO_2 :Sb electrode the viologen is reduced to the corresponding radical cation, while the phenothiazine is oxidized to the corresponding radical cation. Since reduction of the viologen is efficiently mediated by the conduction band states of the nanostructured TiO_2 film, and since oxidation of the phenothiazine is efficiently mediated by the intraband states of the Sb doped SnO_2 nanostructured film, the coloring (and bleaching) times of the EC window in Scheme 3 are very rapid as may be seen from Figure 4. It is clear, therefore, that doped metal oxide nanostructured films will be important in constructing ultrafast EC window and display technologies.

As the viologen and phenothiazine molecules are chemisorbed at the surface of nanostructured TiO_2 and SnO_2 :Sb films, the principal source of the leakage current in the device shown in Scheme 4, namely diffusion of the oxidized redox promoter to the reduced redox chromophore, is eliminated. Consequently, as may be seen in Figure 5, the steady-state current measured in the colored and bleached states are very low and endows the device with a memory.

Finally, as may be seen from Figure 6, the EC window in Scheme 3 is relatively stable, both under electrochromic cycling and under prolonged coloration.

Conclusions

Using a viologen modified semiconducting nanostructured metal oxide film as one electrode, and a phenothiazine modified conducting nanostructured metal oxide electrode it has proved possible to construct an ultrafast electrochromic window. Ultrafast Electrochromic Windows

The ultrafast nature of this window is a direct consequence of combining a semiconducting nanostructured metal oxide electrode modified by a redox chromophore which colors upon being reduced with a conducting nanostructured metal oxide electrode modified by a redox chromophore which colors upon being oxidized.

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