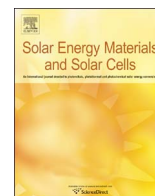




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Consecutive anchoring of symmetric viologens: Electrochromic devices providing colorless to neutral-color switching

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ABSTRACT

In this study, colorless to neutral-grayish color ECDs based on the consecutive anchoring of alkyl-substituted and aryl substituted symmetric viologens (blue and green switching viologens respectively) are reported.

The strong binding affinity towards nanostructured TiO₂ layer of both viologens equally provided with phosphonate anchoring group, allows the employment of a single nanostructured layer wherein both viologens were adsorbed (glass/TCO/viologens-modified-TiO₂/TCO/glass), while showing very rapid anchoring times (≤ 15 min).

The effect of the TiO₂ layer thickness and grafting conditions on the ECD performance have also been investigated, reaching switching times ≤ 6 s and good performance up to 2 000 cycles for the optimized ECDs. Additionally, the influence of the electrolyte on the observed coloration has also been explored. The use of water-based gel polyelectrolyte has allowed significant enhancement of the neutral-grayish EC behavior (α^* and $b^* \leq |10|$). The beneficial impact of water-based gel polyelectrolyte and potential in color-tailored electrochromics is emphasized.

1. Introduction

In the growing technological field of electrochromics and emerging multicolor systems [1–3], neutral-tones such as gray can be excellent candidates for effective light filtering since they absorb wide range of the visible spectrum, while being best suited to any chromaticity surroundings easing therefore their implementation in diverse applications. However, electrochromic devices (ECDs) that provide more neutral and grayish colorations in their colored states whilst ensuring a colorless-off-state remain a field to be improved [4]. Most EC materials, exhibit a lack of neutral colorations by itself whereas the ones proved to show gray-black colored state, exhibited very slow switching responses (which may even reach minutes) [5], or were not colorless in the bleached state [6–18]. Some reported strategies to overcome these limitations comprise complex device architectures such as bilayered electrodes [19] and the use of two working electrodes (WEs) and two counter electrodes (CEs) [20] or EC formulations consisting of the mixture of 3 viologens [21].

Some advantages of the viologens over other EC materials are that they may exhibit a colorless off state and competitive switching performances. The color exhibited upon applying a suitable cathodic

potential depends on the chemical structure of the chains bonded to the nitrogen atoms. Hence, 1,1'-alkyl substituted viologens provide blue/violet color [22], whereas 1,1'-aryl substituted viologens usually exhibit green color in the first reduced form [22,23]. The viologens have been integrated in different device architectures, either mixed with the electrolyte or deposited over an electrode. The former corresponds to the simplest configuration of any ECD and can provide high optical contrast since the chromophores are distributed all over the electrolytic layer, but the switching times are usually poorer as the pace of diffusion of the viologen towards the electrode limits its rate of reduction. Conversely, the latter approach habitually consisting of nanostructured metal oxide films (i. e., nanocrystalline TiO₂ [24–26]) deposited on the electrode in which the viologens are adsorbed, has been proven to overcome this limitation as a result of rapid electron transfer between the nanoparticles and the viologen molecules [27].

In this regard, double-layered TiO₂-based working electrodes in which blue and green viologens were successively immobilized in the bottom and top layers of the stacked electrode, have been proven to provide neutral-color (black) electrochromism [28]. However, the processing of the double-layered electrodes results in additional steps in the device fabrication. Furthermore, the processing of the second

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TiO₂ film must be done under particular conditions and may limit the final device performance. Therefore, the controlled co-anchoring of different viologens in the same TiO₂ layer appears to be an appealing approach.

The present study reports on colorless-to-neutral color ECDs based on the sequential anchoring of a fast grafting blue-switching viologen and an aryl-substituted green-switching viologen on the same nanostructured TiO₂ layer (glass/TCO/Viologens-modified-TiO₂/electrolyte/TCO/glass). We demonstrate herein that this approach provide more neutral-character ECDs than the single-viologen-modified ones, while maintaining satisfactory colorless bleached state and transmittance changes. The effect of the TiO₂ layer thickness and grafting conditions on the device performances have also been investigated. Additionally, with the aim of enhancing the neutral-character of the optimized ECDs, the effect of the solvent in the observed coloration has also been evaluated.

2. Material and methods

2.1. Materials

4,4'-dipyridyl (98%), triethyl phosphite (98%), α,α' -dichloro-p-xylene (98%), 2,4-dinitrochlorobenzene (98%), Poly(vinyl alcohol) (PVA, Mw 61 000), sodium tetraborate (borax, 99.5%), potassium ferrocyanide (98.5%) potassium ferricyanide (99%), lithium perchlorate trihydrate and hydroquinone (HQ) ($\geq 99\%$) were provided by Aldrich, whereas diethyl 4-aminobenzylphosphonate (98%), γ -butyrolactone and ultra-pure silica gel (40–60 μm , 60 A) were supplied by Acros Organics. Hydrochloric acid (37%) and required organic solvents such as toluene, hexane, chloroform, 2-propanol, acetone, ethanol were purchased from Scharlab. Titanium dioxide dispersion (Ti-Nanoxide T) was supplied by Solaronix. All these reagents were used without further purification except for γ -butyrolactone which was degassed for 15 min with N₂ before being used.

Fluorine-doped tin oxide (FTO) coated glass substrates provided by Solems (Rs 6–8 $\Omega \text{ sq}^{-1}$) were washed with heated acetone before being used. Transparent silicone (Loctite 595) was provided by R.S. Amidata.

2.1.1. Synthesis

1,1'-Bis(phosphonomethyl-4-benzyl)-4,4'-bipyridilium dichloride [*BnV*²⁺] was obtained according to previously reported procedure [29]. (94% yield). ¹H NMR (D₂O, δ , ppm): 9.14 (d, 4H, $J = 6.87$ Hz), 8.50 (d, 4H, $J = 6.84$ Hz), 7.45 (m, 8H, 2C₆H₄), 5.90 (s, 4H, 2CH₂N) and 3.06 (ds, 4H, 2CH₂P, $J = 20.8$ Hz). ¹³C NMR (D₂O, δ , ppm): 152.96, 148.04, 140.45, 133.33, 132.51, 132.17, 129.64, 67.33, 38.98 and 37.98. ³¹P NMR (D₂O, δ , ppm): 19.31. IR (bulk ATR): ν (cm⁻¹) = 3040 (C-H), 2800–2603 (PO-H st), 2263–2200 (PO-H comb), 1631, 1558 (C=C, C=N), 1207, 1150 (P=O st), 913 (P-OH st) and 830 (*o*-phenylene H).

1,1'-Bis(phosphonomethyl-4-phenyl)-4,4'-bipyridilium dichloride [*PhV*²⁺] was synthesized as previously reported [24]. (79% yield). ¹H NMR (D₂O, δ , ppm): 9.42 (unresolved dd, 4H, $J = 6.83$ Hz), 8.79 (unresolved dd, 4H, $J = 6.85$ Hz), 7.66 (dd, 4H, $J = 8.54$, Hz) 2C₆H₄, 7.77 (unresolved dd, 4H, $J = 8.33$ Hz) and 3.18 (ds, 4H, 2CH₂P, $J = 20.9$ Hz). ¹³C NMR (D₂O, δ , ppm): 153.11, 148.14, 143.31, 142.21, 134.27, 129.76, 126.75, 38.63 and 37.62. ³¹P NMR (D₂O, δ , ppm): 18.4. IR (bulk ATR): ν (cm⁻¹) = 3028 (C-H), 2800–2413 (PO-H st), 2340–2250 (PO-H comb), 1631, 1596 (C=C, C=N), 1207, 1169 (P=O st), 1050–969, 928 (P-OH st) and 827 (*o*-phenylene H).

2.1.2. Electrolytes

Anhydrous electrolytes were fabricated by varying concentrations of redox mediator hydroquinone from 0.0075 to 2.0 mmol L⁻¹ while keeping the concentration of LiClO₄ at a constant value of 0.2 mol L⁻¹, in γ -butyrolactone.

Gel electrolyte comprising 2 mmol L⁻¹ of potassium ferrocyanide

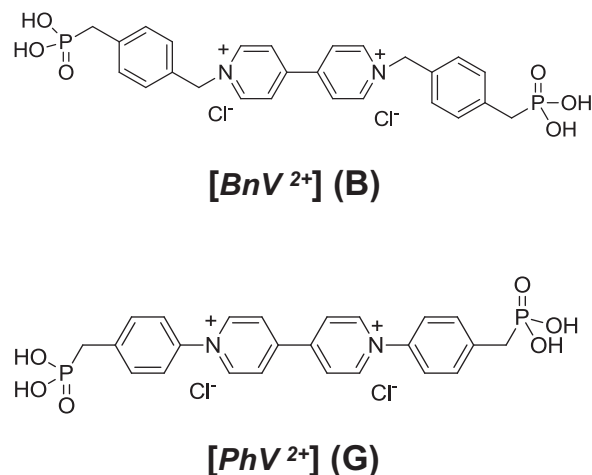


Fig. 1. Chemical structures of the viologens.

and ferricyanide was fabricated according to previously reported procedure [30]. Briefly, 1:1 M ratio of ferro/ferricyanide potassium pair was added to 4% solution of PVA. Following stirring until a complete homogenization, 4% sodium tetraborate solution was poured to the mixture in a 1:4 volumetric ratio. The gel obtained after stirring with spatula was allowed to settle overnight.

2.2. Methods

Nanostructured TiO₂ films were obtained by doctor-blade technique using 1137 equipment from Sheen provided with wire wound rods and quadrangular applicators of different groove depths (from 12 to 100 μm).

The thermal treatments were carried out in a Carbolite CWF 11/23 chamber furnace.

The thicknesses of the nanostructured films were examined in cross-sectional view using a ULTRA plus ZEISS field emission scanning electron microscope (FESEM).

Powder X-ray diffraction measurements were performed in a 2 θ range from 10 to 7 using a Bruker D8 advance diffractometer with CuK α radiation ($\lambda = 1.5406$ Å). The crystalline phases of TiO₂ were identified by using the NIST M & A collection code A 50867 ST1243 (pattern 03-065-5714).

UV–vis transmittance responses were registered using a Jasco V-570 spectrophotometer. A detailed information related to the measuring procedure can be found in our previous report [29].

Color of the ECDs was evaluated through L*a*b*(1976) and xyY (1931) color coordinates obtained by spectrophotometric method developed by R. J. Mortimer and T. S. Varley [31,32]. CIE 1976 color space represents the relation between green (- a*) and red (+ a*), and between blue (- b*) and yellow (+ b*). In the case of xyY (1931) color space, x and y axis correspond to the relation between blue and red and blue and green respectively. L*a*b* color coordinates were represented in color swatches using a color converter software to ease their interpretation.

The ECDs were lit with fluorescent light source (Phillips TL-D 80 18W/840) during the acquisition of the photographs (Canon IXUS 105) without the employment of flash, using a focal distance of 5 mm, maximum opening of 3 and exposition time between 30 and 50 s⁻¹.

The chronoamperometric and cyclic voltammetric (30 mV/s) studies were carried out using Biologic MPG potentiostat-galvanostat.

Fourier transform infrared (FT-IR) spectra registered with a 4100LE FTIR from Jasco, were carried out by Attenuated Total Reflectance (ATR) technique.

¹H, ¹³C and ³¹P NMR spectra were acquired using a Bruker

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