A new approach for design of organic electrochromic devices with inter-digitated electrode structure ☆

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ABSTRACT

We present a new approach for design of organic electrochromic devices (ECD) with inter-digitated electrode (IDE) structure and three-electrode dynamic operation. The advantages of the IDE design include the ability to produce fast and homogenous color change over large areas. In addition, it enables fabrication of multi-color devices. Our method involves photolithographic etching of ITO followed by electrophoretic deposition (EPD) and mechanical compression of porous titania to produce finely patterned electrodes with high surface area. The titania layer is chemically modified by new stable and reversible electrochromic viologen derivatives involving phenylphosphonic acid anchoring moiety. The new device demonstrates reversible and strong color change from colorless to deep blue and yellow.

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1. Introduction

Recent development of new display technology is attracting considerable attention and significant amount of funding. Moreover, many research groups concentrate on fabrication of flexible displays. Electrochromic devices (ECDs) are expected to enter this niche and fulfill the requirements from such devices [1–8]. High contrast ratio and short response time are among their properties and they are also available in various colors [9–11]. In addition, ECD power consumption is low compared to conventional displays, which makes them attractive for light weight applications such as cellular phones and electronic paper. The flexible ECDs are expected to be light and in addition will be less fragile compared to rigid devices. All together, ECDs and flexible ECDs in particular are very attractive for a variety of applications [12–16].

Previous reports on organic electrochromic devices described a multilayer structure with the electrochromic material either bonded to the substrate [9,10,15–18] or dissolved in the sandwiched solution [19].

Our technique aims to improve the existing technologies and it seems to be promising in manufacturing flexible ECDs. The concept of our method is fabrication of organic ECD in an inter-digitated structure and three-electrode dynamic operation. In IDE the distance between anode and cathode is minimized and thus the voltage drop problem is reduced and the electric field is homogenously distributed over all the electrode area. Therefore, the advantages of the inter-digitated design include the ability to produce homogenous color changes over large areas, fast response time and possibility to fabricate multi-electrode or multi-color devices [20]. To prepare the inter-digitated pattern in fine structure and high quality on glass or PET we used lithographic etching. On top of the ITO we deposit a nanoporous layer of titania to increase the surface area of the working electrode (WE) by several orders of magnitude. This affords higher electrochromic material concentration on the electrode surface and, therefore, improves the contrast ratio and color intensity of the device.

The conventional method to prepare porous titania electrodes is based on a viscous titania paste that is spread on the substrate. This method is not suitable for preparation of patterned electrodes with a fine structure (electrode finger widths of 1–2 mm). For this reason we used EPD to make the nanoporous TiO_2 layer [21,22]. EPD is suitable for deposition of porous materials on conductive electrodes with widths that are fractions of a millimeter. Further, the EPD technique enables selective

deposition on only one of the two electrodes sharing the same substrate even when electrode widths are less than 1 mm. Other advantages of EPD are: shorter preparation time compared to other techniques, low cost and simple setup. This method allows formation of very stable and uniform layers with controlled thickness and homogenous microstructure. EPD can be used for low-temperature nanoporous layer preparation when the high temperature processing is impossible, for example: for plastic substrates. EPD involves charged particles in a stable suspension that move toward a conductive substrate when a dc electric field is applied. The charged particles are accumulated on the surface of the substrate. Particle charging provides coulombic repulsion for the formation of a stable suspension and charging that allows particle movement to the oppositely charged electrode. No deposition occurs when the particles are not charged. The deposition time, dc electric field and the suspension concentration determine the thickness of the resulting titania layer. Titania nanoparticles are commercially available in powders. The P-25 powder (Evonik-Degussa) contains about 70% nanocrystals of anatase and 30% rutile. The average diameter of particles is 25 nm. The titania layer produced using this powder is opaque. More transparent titania layer can be produced with P-90 powder (Evonik-Degussa, average of 14 nm particle diameter), which consist of 95% anatase and 5% rutile. If moderate transparency is desired, a mixture of the two powders can be used. A mechanical compression was applied for preparation of more transparent, more mechanically stable titania layers with an improved adhesion to conductive substrates. Details about our compression procedure are reported elsewhere [22].

Electrochromic compounds of the viologen family [23] are adsorbed onto the surface of the titania layer. Viologen chromophores have been one of the most strongly favored candidate-compounds for electrochromic display devices to substitute LEDs and LCDs, due to their electrochemical fast reversible behavior and the marked color change between the two oxidation states [24]. The limitations of the known viologen derivatives are: poor adhesion to substrates and the tendency for aggregation. To improve adhesion, viologen derivatives involving the phosphoric acid residue, $P(O)(OH)_2$, were synthesized. The phosphoric acids are known to interact strongly with the TiO_2 nanoparticle surface [25]. We prepared two viologen derivatives with phosphoric acid groups: a symmetric derivative with two phosphoric acid groups, and an asymmetric derivative with only one phosphoric acid group. The symmetric derivative with two anchoring groups is expected to interact strongly with the surface being bonded by the two ends. Using the smaller, asymmetric viologen, which is bound to the surface by one side only, may result in higher dye concentration on the surface [14]. In addition, two benzyl groups are attached to the N atoms of the bi-pyridine moiety. The benzyl substituents are expected to prevent aggregation of the viologen rings owing to their bulkiness. In the absence of steric hindrance, the planar π-systems tend to interact in a plane-to-plane manner and form π-dimers and oligomers. In such dimers, the spin is coupled and a multi-centered bond of sigma-type forms. However, in most systems some steric hindrance is present so that the two planes cannot approach each other closely enough and full spin coupling does not occur. In such cases, π-oligomers form to provide the maximal degree of coupling. In the case of ion radicals, dimerization is hindered also by coulomb repulsion. Thus, the cation radical of the simplest viologen N,N-dimethyl derivative in solution exists in equilibrium with the respective oligomers, which diminishes the intensity of the color. In molecules involving the relatively bulky benzyl groups, there are five single bonds capable of free rotation. At room temperature, such molecules can adopt various conformations that prevent aggregation. The combination of the phosphoric acid residue and the benzyl groups in the viologen molecule allows achieving higher concentration of the electrochromic material and improves its binding to the surface while avoiding oligomerization. Using the new stable and reversible electrochromic viologen derivatives, we succeeded to achieve high chromophore concentration on the substrate surface.

Finally, the sealed cell device can be operated by a small portable potentiostat. Here we present the new cell, which demonstrates distinguishable color change and shows promise for future devices.

2. Experimental

2.1. Chemicals and substrates

Glass slides with ITO coating (8–12 Ω/sq resistivities) were purchased from SPI. Flexible substrates ITO/PET (indium oxide doped by tin conductive layer on polyethylene terephthalate plastic) with resistivity of 50 Ω/sq were purchased from Bekaert Specialty Films (USA). P-25 titania nanopowder was purchased from Evonik-Degussa (Germany). All chemicals were reagent grade and used as received. Photoresist SPR220 and the developer 319MIF from Microchem were used as purchased.

2.2. Preparation of electrochromic compounds

We prepared two viologen derivatives with phosphoric acid groups. One derivative is symmetric with two phosphoric acid groups, Fig. 1(a), and the second is asymmetric with only one phosphoric acid group, Fig. 1(b). The viologen 1,1-bis(4-phosphonobenzyl)-4,4′-bipyridinium and the asymmetric analog were synthesized from 4,4′-bipyridine and diethyl [4-(bromomethyl)phenyl]phosphonate and subsequent hydrolysis of the product by aqueous HBr. The full synthetic details will be published elsewhere.

2.3. Preparation of patterned electrodes in fine structures

Photolithographic etching was used to fabricate the patterned electrodes. This method enables creating patterns in high precision and in various designs. The lithographic etching process was done in a clean room of class 100.

Prior to photolithography, we prepared a mask with the desired electrode design. The mask quality was checked under a microscope. We used methanol, acetone and isopropanol to clean the glass slides and the masks. A thin layer of photoresist (SPR220) was deposited on the ITO slide using a spinner (DELTA
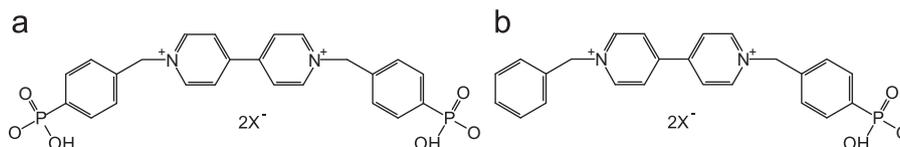
Fig. 1. Two derivatives of 1,1-bis(4-phosphonobenzyl)-4,4′-bipyridinium were used as the electrochromic compound: (a) symmetric and (b) asymmetric. The anion, X⁻, can easily be exchanged to any desired anion (bromide, chloride, nitrate, perchlorate, sulphate, etc.).

82) at high speed. After the photoresist was dried in the oven, we placed the positive mask on it and exposed it to UV light (UV lamp 20 mW/cm^2) for 50 s. The photoresist was developed using 319MIF for 2 min and then washed with distilled water. To remove the bare ITO, we used concentrated hydrochloric acid (37%). Then we removed the photoresist using acetone and cleaned the slide with solvents. After completion of the process, the electrode conductivity was tested with a digital multimeter to assure the quality of the connections. In this work we present two types of electrodes: the first is a slide of 1.5×3 cm^2 divided to two, Fig. 2(a). This structure is referred hereafter as the divided electrode. The second is an inter-digitated electrode (IDE) where two sets of electrode fingers are laid side by side, Fig. 2(b). The size of the IDE was 3×3 cm^2, and the finger widths range between 1 and 2 mm.

ITO electrodes on PET were produced using dry-film photo-lithography, which is a low-cost process commonly used for printed circuit boards (PCB) manufacturing. For this process we used Laminar 5038 (Shipley Company LLC) dry-film photoresist, 38 μm thick. The film was exposed to UV light and developed with sodium carbonate/potassium carbonate solution.

2.4. Selective coating of patterned electrodes with porous titania

To coat the electrodes with porous titania, we used the electrophoretic deposition technique [21,22] on conductive glass and plastic substrates. The process included deposition of the titania nanoparticles P-25 (Evonik-Degussa) followed by compression and thermal treatment.
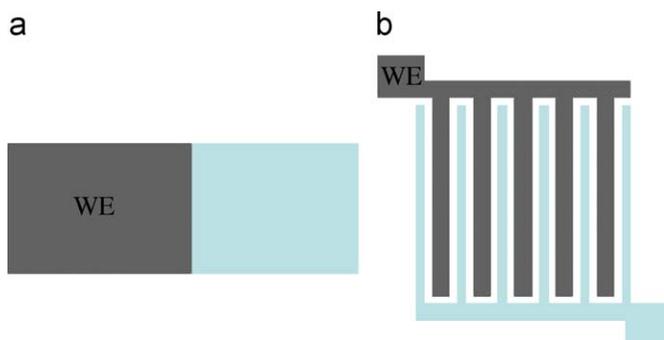

Fig. 2. Structure of the divided electrode (a) and IDE (b). The grey area represents the modified ITO with porous titania layer and chromophore; WE = working electrode. The light blue area represents the unmodified ITO.

We started with samples modeling the IDE structure: ITO films on glass or PET divided by an insulating line into two parts to form two electrodes on one surface, the divided electrode. Only one part (one electrode) was covered with titania nanoparticles, and the second part was used as the counter or reference electrode. A series of experiments was performed to establish the optimal parameters for selective deposition on the model electrodes.

We first cleaned the substrates with ethanol and mild soap, and then washed them with water and distilled water. The suspension for EPD was prepared by the following procedure: 0.65 g of TiO$_2$ P-25 nanoparticles were mixed with 150 ml of ethanol and a small amount of acetylacetone (0.6 ml). The suspension was stirred with a magnetic stirrer for 24–72 h in a closed vessel (herein "TiO$_2$ suspension"). Small amounts of iodine (27 mg), acetone (4 ml) and water (2 ml) were added to 100 ml of ethanol and stirred with a magnetic stirrer or sonicated with cooling the solution in an ice bath until the iodine was dissolved (herein "charging solution"). Just prior to EPD, TiO$_2$ suspension was added to the charging solution and mixed. This was followed by the sonication for 15–20 min using an ultrasound processor VCX-750 (Sonics and Materials, Inc.) to homogenize the mixture with cooling the suspension in an ice bath. The obtained suspension was used for EPD. The electrophoretic cell contained two electrodes of ITO conductive glass; one electrode was a cathodic substrate and the other electrode served as a counter electrode. The electrodes were placed vertically and immersed into the suspension of 250 ml in a glass beaker. The distance between electrodes was 54 mm. A schematic description of the EPD setup is shown in Fig. 3(a). The EPD process was performed using constant current mode at room temperature. A Keithley 2400 Source Meter was used as a power supply. The duration of deposition with the current density and the suspension composition determines the thickness of the nanoporous layer. To create a single layer of about 5 μm on FTO-glass and ITO/PET plastic substrates we used current density of 0.4 mA/cm^2 by multilayer approach 22. A final nanoporous layer was obtained by repeated deposition steps. Each layer was dried separately followed by multilayer compression and thermal treatment. In the present work we deposited three layers. The duration of each deposition step was 20 s, followed by drying first at room temperature and then at 70–100 °C. Before the compression, titania films prepared by EPD were dried at 150 °C for 30 min. After cooling the samples to room temperature, and immediately before compression, n-hexane was uniformly dropped on the titania film surface. The wet layer was covered with polyethylene foil (20 μm) with no delay. A pressure of 2500 kg/cm^2 was then applied. The sintering was performed only for the glass-based
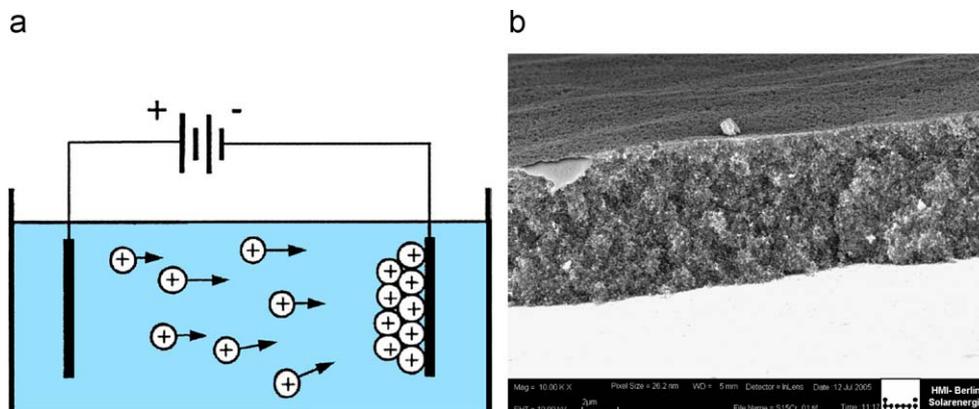

Fig. 3. (a) Scheme of the EPD setup. Two electrodes are immersed in a charged solution while connected via a potentiostat. When potential is applied, the charged particles deposit on the working electrode, on the right. (b) HRSEM picture of the cross section of 8 μm P-25 titania layer prepared by EPD and compression.

samples: at 500 °C for 30 min. Plastic substrates cannot withstand temperatures higher than 150 °C. Therefore, in the case of plastic electrodes we used 150 °C for 40 min. An example of uniform 8-μm-thick P-25 titania layer obtained by EPD and compression is shown in Fig. 3(b). The EPD procedure and mechanical compression were identical for the divided electrode and the IDE.

2.5. Dye adsorption

Patterned electrodes coated with porous titania on glass or PET were immersed in the aqueous solution of the dye molecule (approximately 0.2 M) for about 48 h. After immersion the electrodes were washed with distilled water and then dried under N_2 flow.

2.6. Electrolyte composition

The electrolyte choice is a major issue in electrochromic devices. Common electrolytes are lithium or proton based. During the first stage of the research we selected a well-known efficient electrolyte, $LiClO_4$. The electrolyte solution in most samples consisted of 0.1 M $LiClO_4$ (purum, >98% of Fluka) in Propylene Carbonate (PC, anhydrous 99.7% from Aldrich). In some cases, as noted in the text, we used the electrolyte solution of dimethyl-sulfoxide (DMSO, anhydrous 99.9% from Aldrich) with 0.05 M tetra-butyl ammonium perchlorate (Bu_4NClO_4, puriss $\geq$98.5%, electrochemical grade of Fluka). In the future we plan to replace the electrolyte solution with gel electrolyte.

2.7. Device assembly

The electrochromic cell was designed in a multilayer structure, often called 'sandwich', in which two electrodes on different slides are facing each other and separated by a spacer. The first electrode is the patterned ITO with the electrochromic compound. A rubber frame cut from a silicone plate (2 mm thick) was placed on top of this electrode. The second ITO glass slide (without a pattern) was placed on the top of the frame. The inner void was filled with the electrolyte solution, injected through the rubber frame with a small syringe (needle 27 G). Finally, 'fix all' silicone glue was used to seal the cell. The glue was left to dry at room temperature overnight. Adhesive copper tapes (3 M) were used to connect the cell electrodes to the output wires of the potentiostat.

2.8. Electrochemical and spectral measurements

A three-electrode system was used to characterize the new electrochromic cell. The WE was the patterned ITO with the electrochromic material and the counter electrode (CE) was the ITO with no dye, Fig. 2. The second ITO glass, placed on the top of the rubber frame was used as the reference electrode (RE).

Voltammetric measurements were performed with an Autolab model PGSTAT30 (Ecochemie). Cyclic voltammograms of the ECDs were measured in the range of $\pm$2.0 V, and adjusted for each sample separately. All measurements were performed using the step size of 0.00198 V and scan rate of 0.1 V/s. For demonstrations outside the lab we used a portable potentiostat: Palmsens, manufactured by Ecochemie. Palmsens is a hand-held battery powered potentiostat/galvanostat for use with electrochemical cells in the range of $\pm$2.0 V and up to 100 mA.

For spectroscopic measurements we used a tungsten–hydrogen lamp with wide range in the visible wavelengths (LS-1, Ocean Optics). The light beam from the lamp was transferred with an optical fiber and focused using a focusing lens onto a second optical fiber. The sample was placed between the two fibers behind the lens and an additional iris. Spectra were obtained using an optical spectrometer (QE65000, Ocean Optics). Optical absorption spectra in the range 350–1000 nm were recorded at different potentials. The potential of interest was determined using the Autolab potentiostat.

3. Results

Viologens exist in three oxidation states. The first reduction step of the di-cation $V^{2+}\rightarrow$ radical-cation $V^{1+\bullet}$, is reversible and involves the color change from colorless to blue. During the second reduction step the radical-cation $V^{1+\bullet}$ is transformed into the neutral form V^0. This process is poorly reversible and involves the color change from blue to yellow. The three viologen color states are presented in Fig. 4 for TiO_2/ITO glass immersed in solution at three different potentials; colorless at 0.0 V (a), blue at $-$0.7 V (b), and pale yellow at $-$1.5 V (c). The potential at which the color change occurs depends on the chemical structure of the viologen, the coupled anions, the content of the electrolyte solution, the experimental parameters, and the type of counter and reference electrodes. In a simple experimental setup we tested the new symmetrical viologen with the chloride anion adsorbed to the porous titania layer on ITO. The electrode changed color to blue at $-$0.7 V vs. Ag wire as the RE, in DMSO solution containing 0.05 M of Bu_4NClO_4. When the potential decreased to $-$1.5 V (vs. Ag wire) the electrode turned yellow. To return the electrode to its colorless state a positive potential was applied, in the range 0.5–1.5 V. A similar behavior was observed for a flexible electrode, Fig. 5.

The divided electrode with the asymmetrical new viologen was tested in a closed cell with 0.1 M $LiClO_4$ in PC. In this setup, the CE and the RE were the ITO slides, Fig. 6. The coloring efficiency on the electrode surface depends on the electric field. With the divided electrodes, we tried various electrode positions in order to
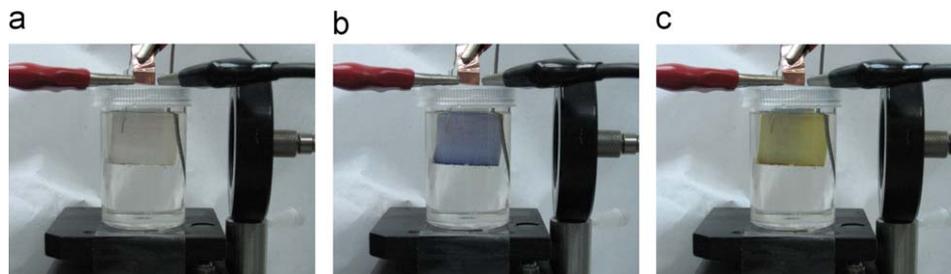

Fig. 4. Color change of the new symmetrical viologen dichloride adsorbed on a glass electrode with titania layer. Pictures were taken during a CV measurement, in the range $\pm$2 V, with Pt wire as the counter electrode (shown on the right) and Ag wire as the reference electrode (shown on the left). All three electrodes were submerged in DMSO with 0.05 M Bu_4NClO_4. The electrode changed color from colorless at 0.0 V (a) to blue at $-$0.7 V (b) and pale yellow at $-$1.5 V (c).

achieve fast and homogenous color changes. The best performance was observed when the WE and RE were the divided electrodes and the CE was on the top (shown in Fig. 6). The color change from transparent to blue occurred at −1.0 V, Fig. 6(b). To turn the electrode 'off' (return to colorless) a positive potential between 0.2 and 1.0 V was applied, Fig. 6(a). The cyclic voltammogram of this cell is shown in Fig. 6(c). The total of 58 cycles in the range −1.0 to 0.2 V reproduced the same line shape indicating that the process is reversible without noticeable

degradation for at least 50 cycles. After sufficient time the current of the cell decreased suggesting that some irreversible processes occurred. We believe that it is the result of imperfect sealing and the presence of impurities in the electrolyte. Drying the cell components (electrodes and electrolyte) and vacuum sealing may considerably improve the reversibility and, therefore, extend the lifetime of the cell.

The absorption spectrum of the electrode at −1.0 V is shown in Fig. 7 (blue line). It is centered at 580 nm and is about 150 nm
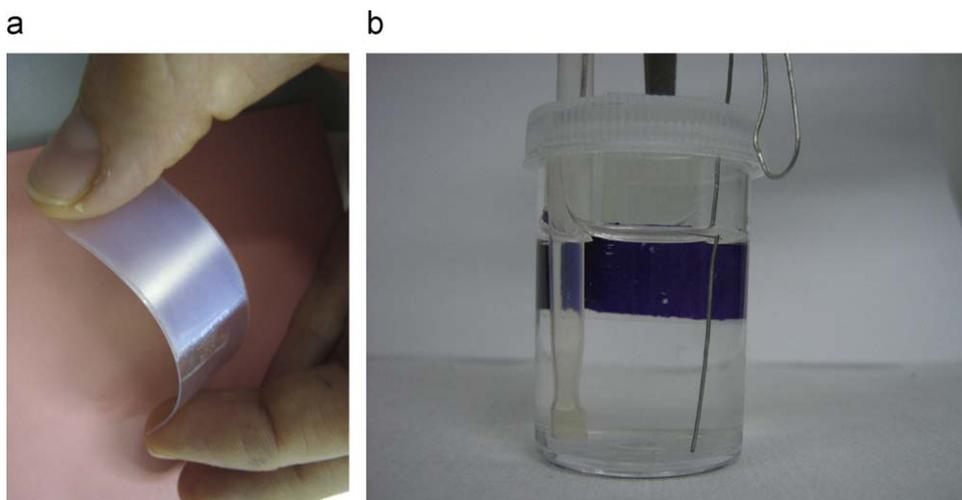

Fig. 5. Flexible electrochromic electrode made with PET/ITO substrate. (a) Nanoporous titania layer on the PET/ITO withstands bending. (b) The asymmetrical viologen adsorbed to the porous layer creates a strong color effect when potential is supplied.
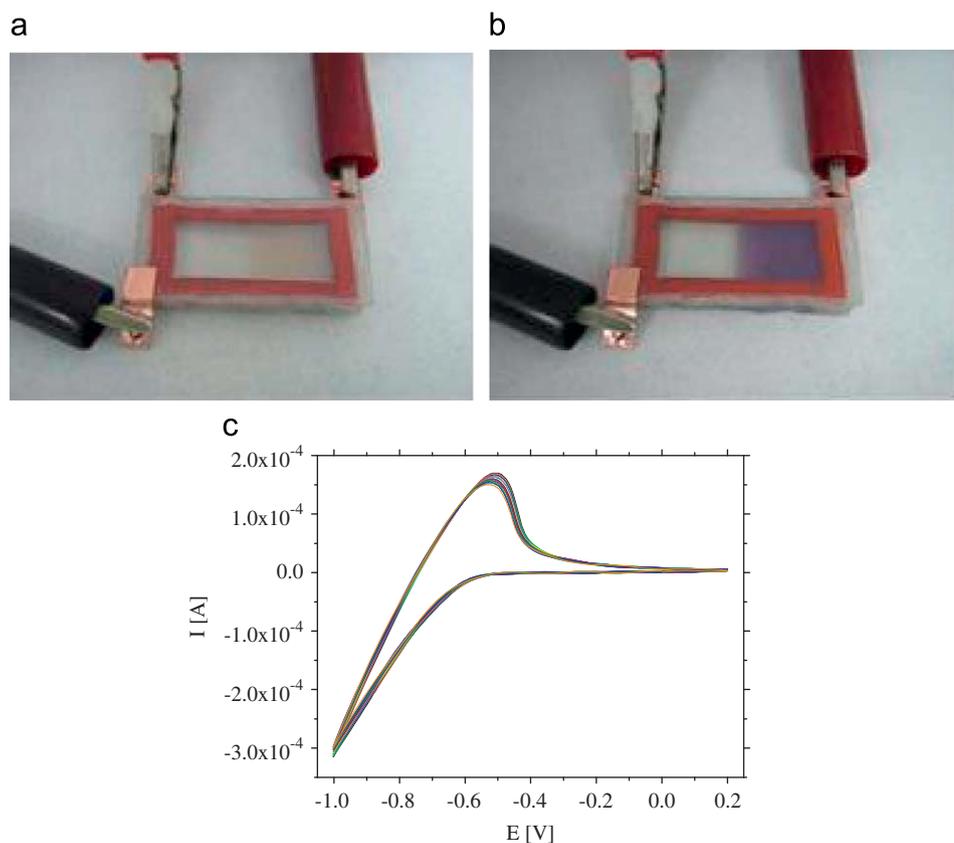
Fig. 6. Divided electrode on ITO with the asymmetrical viologen dibromide adsorbed to a 5 μm layer of porous titania (P-25). LiClO$_4$ in PC serves as the electrolyte solution. Upper glass is coated with ITO (8–12 Ω/sq) and sealed with transparent fix-all silicone glue. The electrode shows no color when voltage is zero (a). At −1.0 V the electrode turns blue (b). The electrode can be set back to its original colorless stage with a positive potential in the range 0.5–1.0 V (not shown). (c) 58 cyclic voltammetry scans of the cell were measured with step size of 0.00198 V and scan rate 0.1 V/s. Shown are scan 1 and scans 36–58.

wide. This peak disappears when −1.5 V is applied to the cell (yellow line). The calculated contrast ratio between the blue and yellow states is 3.6.
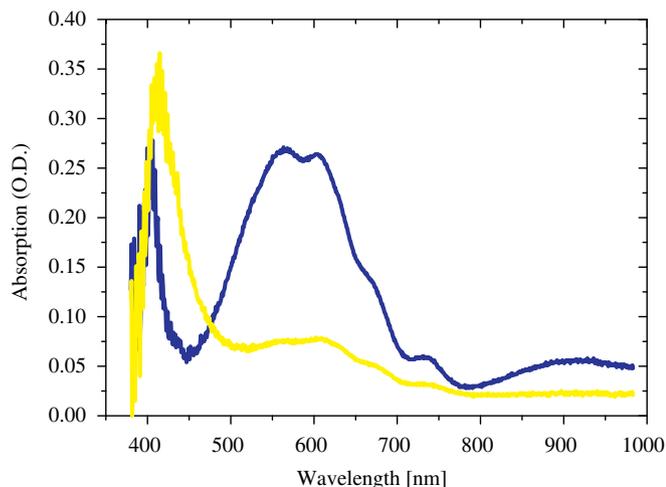

Fig. 7. Absorption spectra of the asymmetrical viologen dibromide adsorbed onto the porous titania layer on ITO (divided electrode). At −1.0 V the viologen changes color to blue with maximum absorption at ~600 nm (black line) and it turns yellow when −1.5 V is applied (gray line). In both spectra we made correction of the background by subtracting the absorption spectrum of the uncolored electrode (not shown).

In addition, we measured the transmission spectra of a similar electrode at different potentials in the range 0.2 and −1.0 V. The spectra are shown in Fig. 8. The electrochromic electrode changed gradually from colorless at 0.2 V to blue at −0.5 V with maximum absorption centered at ~600 nm. This absorption line disappears when the potential is changed to −1.0 V and absorption shifts to wavelengths below 500 nm. At this potential the electrode appears yellow. The isosbastic point at ~500 nm indicates that in this case there is equilibrium between two forms only. The rate of color change in this case depends on the rate of potential change. The sharp lines at 404, 434 and 545 nm come from the lamp which we used, see experimental.

As mentioned earlier the best coloring efficiency for the divided electrodes was found in the case when the WE and CE face each other. However, in IDE due to the short distance between the electrode fingers (cathode and anode) the electric field is straight [26] and therefore the color change is fast and homogenous. Fig. 9 presents the color change in a cell with IDE structure. The color change to blue of this electrode occurred at −1.0 V and the CV is similar to the one observed for the divided electrode, not shown. We noticed that the color of IDE after potential-pulse changed in less than 1 s for a 3 × 3 cm² electrode. A cell with no pattern of the same size changed its color only after few seconds and the color change was not homogenous over all the area of the electrode. This phenomenon can be seen in video movies, which we recorded during measurements. A more precise evaluation of response time for the IDE electrodes is still under investigation. Decoloration occurred at positive potentials.
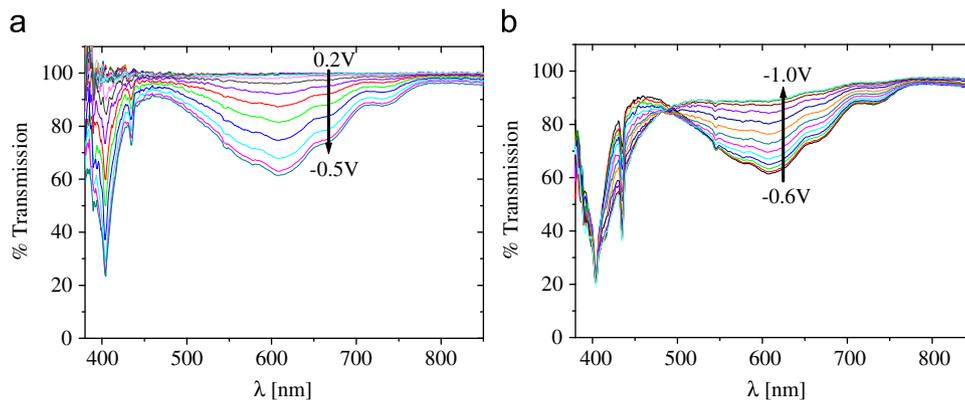
Fig. 8. Transmission spectra of the divided electrochromic electrode measured during a cyclic voltammetry scan. (a) The electrode is transparent at 0.2 V and changes color to blue when the potential was changed to −0.5 V in steps of 0.025 V. (b) As the potential applied was changed from −0.6 to −1.0 V using the same step size the electrode changed color to yellow. The absorption shifts to lower wavelengths.
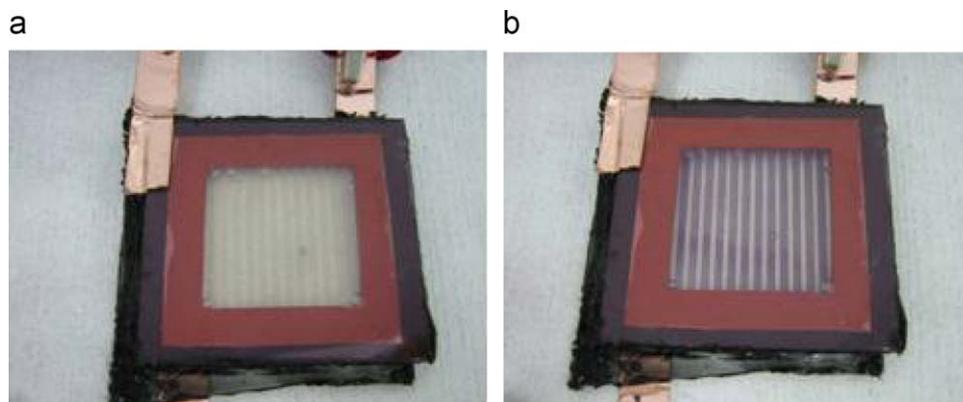
Fig. 9. IDE patterned electrode in a cell. A significant color change from transparent (a) to blue (b) is observed when −1.0 V is applied to the cell.

To complete the device with additional colors we may follow the suggestions of previously published data indicating that the red, blue and green colors can be achieved by variations of the substituent on the viologen [2]. However, the nature of these substituents had not been disclosed. In addition the effect of the counter anion, X^-, remains to be studied.

4. Conclusions

In this investigation we present a new approach for the design and preparation of organic electrochromic cells. Our method involves photolithographic etching of ITO on glass or PET to fabricate electrodes with fine details and high precision. This electrode preparation method enables preparing electrodes of any desired design with high precision suitable for a variety of practical applications. We succeeded to fabricate divided and inter-digitated electrodes with strong coloration effect. Our modified viologen achieves a high contrast ratio, which is comparable to previously reported contrast ratio for a similar system [27].

Our current goal is to increase the lifetime of the ECD. Such a goal may be achieved by transition to solid or semi-solid electrolytes, enhancing the conductivity of the electrodes and vacuum sealing the cell. New viologen derivatives capable of red and green coloration are under preparation, which will enable preparation of RGB devices.

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