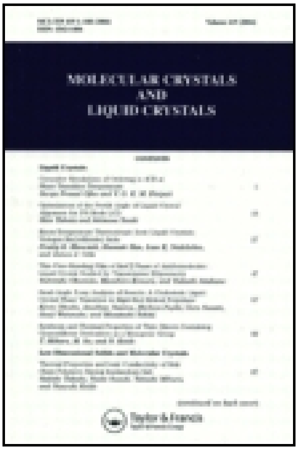

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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To cite this article: O. I. Aksimentyeva, D. O. Poliovyi, A. V. Fechan & O. M. Yevchuk (2008): Nanostructured Electrochromic Layers, Molecular Crystals and Liquid Crystals, 497:1, 30/[362]-37/[369]

To link to this article: http://dx.doi.org/10.1080/15421400802458225

Mol. Cryst. Liq. Cryst., Vol. 497, pp. 30/[362]–37/[369], 2008
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802458225

Nanostructured Electrochromic Layers

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We have proposed a new method to obtain the electrochromic materials by electrochemical polymerization of aminoarene monomer inside a TiO_2 *nanocrystalline layer on the ITO surface. It has been found that a conducting polymer integrated into the nanoporous titanium dioxide matrix causes a significant improvement in electrochemical and electrooptical properties of the hybrid layer and provides a higher contrast ratio in comparison with that for a polyaminoarene layer on the free ITO surface, as well as the widening of the angle of view for the known non-emissive display.*

Keywords: display; electrochromic layer; polyaniline; titanium dioxide

INTRODUCTION

Hybrid materials based on nanostructured TiO_2 and a conducting polymer recently attracted a great attention as suitable electrodes for solar cells [1,2], *p–n* heterojunction diodes [3], solid polymer electrolyte for dye-sensitized solar cells [4], gas sensors [5], corrosion protection [6], and electrochromic devices [7,8]. Titanium dioxide has a good stability, environment-friendliness, and the interesting properties as a semiconductor. With the advent of large surface-area of nanocrystalline TiO_2 electrodes, the conversion efficiencies in solar cells became high enough to elicit the general interest in this type of materials [2]. The ability of TiO_2 to reflect white light with high efficiency is useful for the fabrication of display materials [8]. At the

The work is supported by the State Foundation on Fundamental Studies at the Ministry of Education and Science of Ukraine, Project No. 25.4/116.

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present time, viologene – modified nanostructured TiO_2 – is an attractive material for non-emissive electrochromic displays [7,8]. However, the known method to fabricate a viologene-based nanostructured layer has a long duration, because the process of viologene adsorption into nanostructured TiO_2 layer proceeds more than 24 h. Moreover, the obtained layer exhibits only the monochromic color change (light blue – dark blue) and has a significant instability due to the desorption of electrochromic molecules from the TiO_2 matrix to the electrolyte solution [7]. On the other hand, electrically stimulated generations of color from conducting polymers and colored light emissions from these materials lead to the creation of organic-based electrochromic, electroluminescent, and lasing devices [8,9]. Conducting polymers, such as polyaniline (PANI) and its derivatives, may be considered as "smart" materials because of their ability to change optical characteristics and color under external factors. Polyaniline-type polymers have been successfully utilized in the preparation of various nanocomposites with inorganic oxides [4,8]. However the insolubility of PANI in most common solvents increases the difficulties to prepare PANI–TiO_2 nanocomposite thin films.

Recently, we offered novel multichromic electrooptical devices with a conducting polyaminoarene layer electrodeposited on the transparent electrodes which operate both on three- and two-electrode circuit bases, by serving as a model of organic display [9,10]. In order to increase the color contrast and the electrochemical stability of device, we developed, in the present paper, an alternative method for the nanostructured electrochromic layer formation by electrochemical polymerization of aminoarene precursor molecules into a nanoporous titanium-dioxide layer on the ITO surface.

EXPERIMENTAL

As a precursor to the formation of an electrochromic polymer into the TiO_2 matrix, aniline in the form of its sulphate salt was utilized. All solutions were prepared using 0.5 M aqueous sulphuric acid as a solvent. Chemicals of analytical grade and deionized water were employed. The colloidal solution of TiO_2 was prepared as described in [7,11]. A titanium (IV) isopropoxide (Aldrich, 99.9%) solution in 2-propanol was slowly dripped over 30 min into a stirred mixture of glacial acetic acid and deionized water at 0°C. The resulting solution was heated to 80°C for 8 h and to 230°C for 12 h and sonicated for 5 min. The formation of a nanostructured TiO_2 layer on the ITO electrode was carried out from a colloidal solution of nanocrystalline TiO_2 (particle size of 10–14 nm) spread over the cleaned conducting glass ITO surface and fired at 450°C during 30–40 min. The geometric areas of samples were 1 cm^2, and their average thickness was 4.5 μm. Electrochemical polymerization of a 0.1 M aniline solution in 0.5 M sulphuric acid was carried out in three-compartment cell under nitrogen at the potential sweeping between $E = -0.2 \ldots 1.5$ V (Ag/AgCl). As a working electrode, the ITO plate or ITO plates with a nanoporous TiO_2 layer were employed. A Pt wire was used as a counter electrode.

The display optical characteristics of the obtained electrochromic layer were measured using special equipment shown in Figure 1. As a base to the arrangement, a goniometer H5 was used with attached elements such as: the spherical reflecting surface, a lighting element to drive the intensity of a luminous flux (annular 22-W lamp LTE), a photodiode with high sensitivity in the visible spectral range, and a measuring device. For the contraction of the directivity diagram, a black protective element served simultaneously as a sample holder was employed.

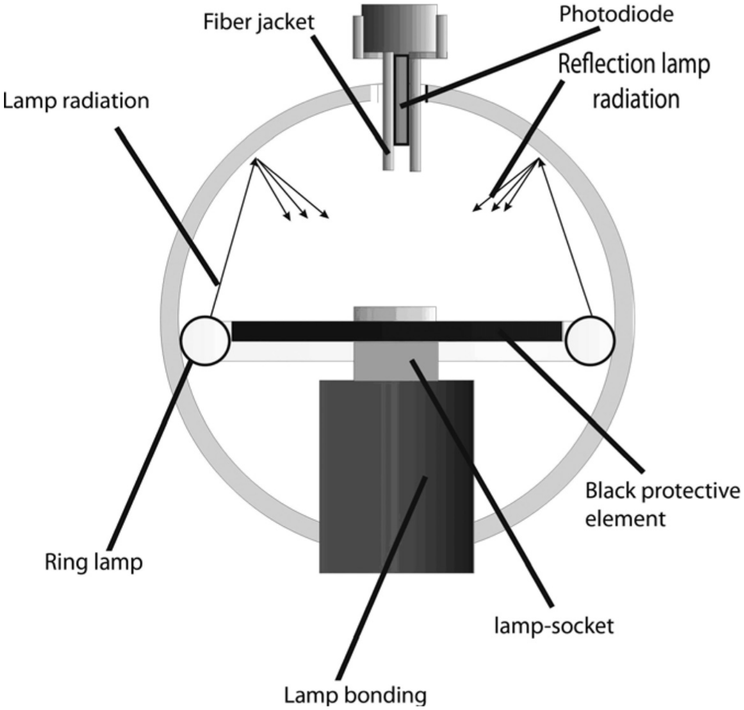


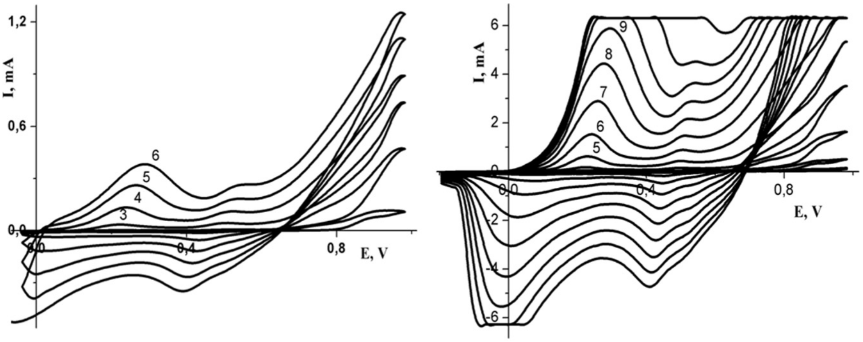
FIGURE 1 Equipment to measure the optical characteristics of a display.

We have measured the photodiode current caused by a luminous flux reflected from the investigated surface. The displacement of a photodiode on the spherical surface makes it possible to record the coefficient of light reflection depending on the angle of view. From the measured magnitude of the reflection coefficient for colored (F_{colored}) and bleached (F_{bleached}) states of the electrochromic device, the value of contract ratio (C, %) at the given angle of view can be calculated according to the formula

$$C(\%) = \frac{F_{\text{bleached}} - F_{\text{coloured}}}{F_{\text{bleached}}} \cdot 100\%.$$

Results and Discussion

The method of electrochemical polymerization with the cyclic sweeping of the potential was used to synthesize electrochromic substances both on the clean substrate and inside the nanostructured layer TiO_2. The method gives the possibility to control a quantity of electoactive electrochromic substances formed on the electrode surface by monitoring the anode or cathode peak current (I_p^a, I_p^c). As one can see from the cyclic current-voltage curves (CVC), the electrolysis of a monomer solution in the potential range $E = -0.2$–$1.2\,\text{V}$ (Ag/AgCl) leads to the formation of an electroactive polymer layer on the ITO surface (Fig. 2a,b). The peak current at the potentials $E = 0.25$–$0.30\,\text{V}$ increased in direct proportion to the cycle number (N). In the presence of a TiO_2 film on the electrode surface, a response of current increased



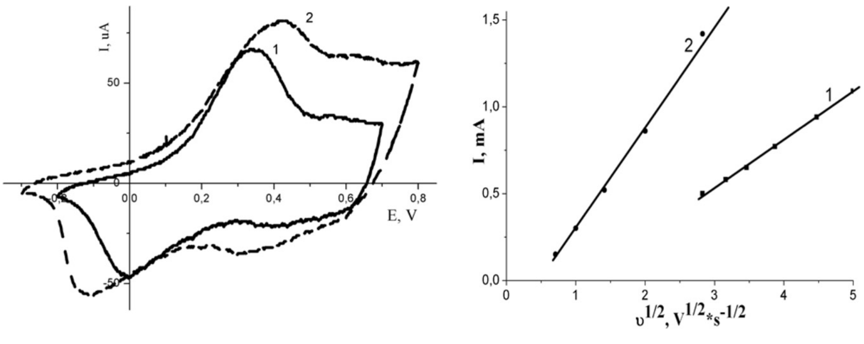
(a) (b)

FIGURE 2 CVC curves obtained during the PANI electrodeposition (a) on the ITO surface; (b) inside a TiO_2 layer on the ITO surface at the sweep rate $\nu = 100\,\text{mV/s}$. Figures correspond to the cycle number (N).

almost by two times (Fig. 2b) in comparison with that for a polyaniline film growth on the free ITO surface (Fig. 2a).

The significant catalytic effect of a nanostructured inorganic layer on the process of electropolymerization gives an evidence to suggest that the layer of colloid TiO_2 acts as a mediator of the electron transport between molecules of the organic precursor (aniline) absorbed by the nanoporous layer and the electrode surface. The molecules of the monomer, whose dimension does not exceed 0.5–0.7 nm, can penetrate into the nanostructured TiO_2 layer (the dimension of pores is near 14–20 nm). As a result of the electron transfer from a monomer molecule to the electrode surface, the cation-radical particles are formed. Oxidative coupling of such particles leads to a growth of polyaniline macrochains inside the pores. The synthesized substance is an emeraldine polymer salt with intensive green coloration. A high molecular mass of the polymer prevents its desorption from the TiO_2 layer to a solution and provides a strong immobilization of electrochromic substances inside the nanostructured layer.

The hybrid layer obtained has a compact uniform structure. Due to the conjugation of the electron density along the polyaminoarene chain, it easily transits from one redox state to another under a voltage change. According to the obtained CVC curves (Fig. 3a), the electrochemical activity of the hybrid layer is significantly higher as compared with that of a polyaniline film obtained under the same conditions. A film color changes reversibly from white and light yellow ($-0.2\ldots+0.1$ V) to green ($0.2\ldots0.4$ V) and, at a deep oxidation, to blue



(a) (b)

FIGURE 3 (a) CVC obtained for a PANI film on the ITO surface (1) and for a TiO_2-PANI hybrid layer (2) in 0.5 H_2SO_4 at the sweep rate $\nu = 20$ mV/s; (b) dependence of the anode peak current on the sweep rate for a PANI film (1) and for a nanostructured TiO_2-PANI layer (2) on the ITO surface.

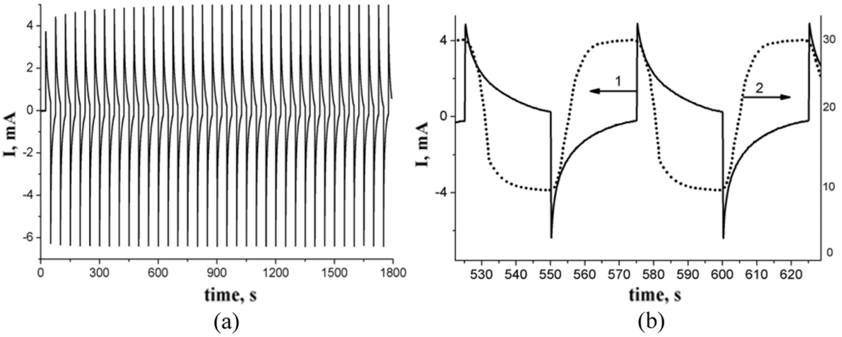
(0.6–0.7 V) and black (>0.8 V) and varies in the inverse sequence at the change of a polarity.

Higher electrochemical activity of a hybrid electrochromic layer can be demonstrated also by the dependence of the peak current on the potential sweep rate (Fig. 3b). The linear plots in the coordinates $I - \nu^{1/2}$ indicate that the coloration-discoloration processes in polyaniline and a hybrid layer follow to the law of semiinfinite diffusion [9].

A temporal stability of electrochromic characteristics for a nanostructured electrochromic layer is confirmed by the behavior of the electric current amplitude (Fig. 4a,b). In the zoom presentation (Fig. 4b), the electric current responses coupled with changes in the coefficient of reflection.

The obtained current – time dependences show the equality of the anode and cathode charge capacities (35.4 mC and 35.3 mC) required for the coloration and bleaching of the film. But the rates of these processes are different. The process of bleaching (reduction of the electrochromic substance) is running with a higher rate than that of the coloration process (oxidation of the electrochromic substance). The evidence of this is the more intensive cathode peak current $I_p^c = 6.38$ mA against the anode peak current $I_p^a = 4.74$ mA (Fig. 4a). These results are in good correlation with those of the study of the diffusion coefficient for a electrochromic PANI layer in coloration-discoloration processes [9,10].

With the obtained hybrid layers used in the construction of an electrochromic display, the contrast ratio of the electrochromic material is increased by a factor of 1.5–2.0 in comparison with that of free polyamonoarene films [12]. To compare the optical properties of the offered



(a) (b)

FIGURE 4 (a) Temporal dependences of the current response; (b) change of current (1) and the optical reflection coefficient (2) for a TiO_2-PANI layer under pulse variation of the electrode potential from 0 to 0.35 V.

electrochromic layer with commercial non-emission display materials, we have measured the dependence of the reflection coefficient on the angle of view in comparison with that of a reflecting monochromic electrophoretic display (EPD) Clear Vision from the E Ink Corp. At present, the EPD technology is most popular in the creation of reflecting displays and has a wide application for portable low-cost devices operating under conditions of a limited energy resource. This is similar to the potential application field of displays based on a nanostructured TiO_2-conducting polymer layer. On the basis of measurements of the contrast value and the angle of view (Fig. 5), we have found that optical elements based on TiO_2-PANI in comparison with EPD ClearVision have the following advantages.

- Magnitude of the angle of view for the proposed optical element achieves 35° at a constant reflection coefficient (k) which slowly decreases in the angle interval $35^\circ - 60^\circ$; whereas, for EPD, the coefficient rapidly drops to $k = 14\%$ after 35°. This feature is due to the use of both a dispersion TiO_2 layer with a high reflection coefficient in the preparation of the display material and PANI as the electrochromic substance with a wide interval of variation in the absorption coefficient.
- The contrast value of the proposed element of visualization is $C = 75.6\%$ which is a very high characteristics for displays of the reflection type and electrochromic displays [8,13]. On the contrary, EPD exhibits a contrast ratio $C = 58.1\%$ on a similar method of

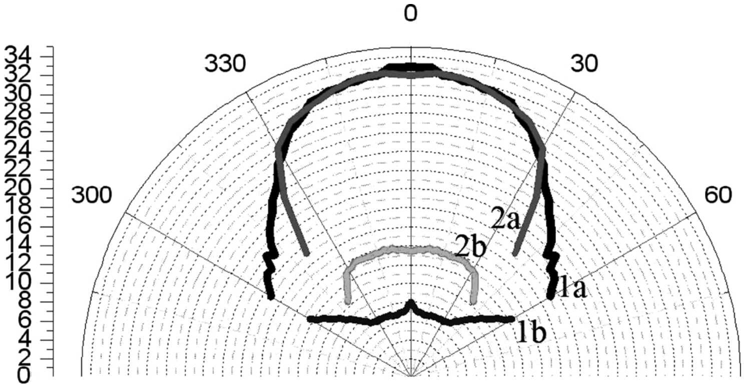


FIGURE 5 Diagram of the reflection coefficient of a display device: 1 – on the base of a nanostructured layer TiO_2-PANI; 2 – for the electrophoretic display (EPD) from the E Ink Corp.: (a) bleached; (b) colored state.

testing. This may be connected with the higher absorption ability of the electrochromic layer in a colored state in comparison with that of EPD.

CONCLUSION

This study provides a novel approach to fabricating the nanostructured electrochromic materials by the electrochemical polymerization of aminoarenes in a colloid dispersed TiO_2 layer formed on the transparent electrode surface [12]. A controlled synthesis of hybrid nanostructures based on a conducting polymer integrated into the porous semiconductor layer provides a higher electrochemical and electrooptical activities of the electrochromic material. Improving the characteristics of the obtained nanomaterials is caused by the formation of conducting polymer chains inside the pores of the semiconductor. As a result, the nano-sized structure of TiO_2 and electrochromic properties of the conducting polymer are reserved. The obtained results on the dependence of the reflection coefficient on the angle of view confirm the good display characteristics for a nanostructured layer, because an image is observed at the widened angle of view at a higher contrast ratio as compared with displays based on the e-ink screen material.

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