Molecular Crystals and Liquid Crystals

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

Multi-Color Electrochromic Device Based on Organic Electrochromic Materials

Jiyea Lee [a], Yuna Kim [a], Youngjung Kim [a], Jehoon Baek [a] & Eunkyoung Kim [a]

[a] Department of Chemical Engineering, Yonsei University, Sinchon-dong, Seodaemun-gu, Seoul, South Korea

Version of record first published: 22 Sep 2010

To cite this article: Jiyea Lee, Yuna Kim, Youngjung Kim, Jehoon Baek & Eunkyoung Kim (2008): Multi-Color Electrochromic Device Based on Organic Electrochromic Materials, Molecular Crystals and Liquid Crystals, 491:1, 74-79

To link to this article: http://dx.doi.org/10.1080/15421400802329178

Mol. Cryst. Liq. Cryst., Vol. 491, pp. 74–79, 2008

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802329178

Taylor & Francis
Taylor & Francis Group

Multi-Color Electrochromic Device Based on Organic Electrochromic Materials

Jiyea Lee, Yuna Kim, Youngjung Kim, Jehoon Baek, and Eunkyoung Kim
Department of Chemical Engineering, Yonsei University, Sinchon-dong, Seodaemun-gu, Seoul, South Korea

Multi-color electrochromic (EC) device was fabricated on a patterned ITO glass. Organic electrochromic dyes were encapsulated within nano-sized porous TiO_2 nanoparticles, and their relative electrochromic (EC) properties were determined using spectroelectrochemical method. Blue, green, and red colored organic dye doped TiO_2 nanoparticles were coated on a patterned ITO substrate to afford multi-colored EC electrode, which was coated with a photo-curable polymer electrolyte and then covered with a bare ITO glass as a counter electrode. Upon photo-curing of the electrolyte layer under UV light, an all-solid state multi-colored electrochromic device (ECD) was obtained. The resultant ECD showed reversible multi-color change within 8 sec and high optical contrast.

Keywords: electrochromic; multi-cell device; organic dye; TiO_2

INTRODUCTION

Electrochromic (EC) devices have attracted much attention due to their low power consumption, high stability, and easy processing [1]. Organic dye molecules have been widely studied for ECD application, for its low cost and simple redox electrochemistry accompanying color transition [2,3]. Organic dyes can be adsorbed into nano-sized porous nanoparticles, which can stabilize the dyes and improve EC properties due to increased surface area of the EC particles. For example, it has

We acknowledge the financial support of Ministry of Commerce, Industry and Energy of Korea (MOCIE), and the Ministry of Science and Technology (MOST) of Korea (No. R11-2007-050-01001-0).

Address correspondance to Eunkyoung Kim, Department of Chemical Engineering, Yonsei University, 134 Sinchon-dong, Seodaemun-gu, 120-749, Seoul, South Korea. E-mail: eunkim@yonsei.ac.kr

been reported that efficient charge movement and fast electron transfer were obtained from TiO_2 nanoparticles [4,5]. While most of the work have been reported for mono-colored nanoparticles, works on a multi-colored EC device based on nanoparticles are rare. Here in we report a reflective multi-color electrochromic device based on organic dye-adsorbed TiO_2 nanoparticles.

EXPERIMENTAL

Methoxy poly (ethylene glycol) 1000 monomethacrylate (MPEGM, 0.6 g), polyethyleneglycol dimethyether (PEGDMe, Mw = 550, 1.2 g), trially-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione (TATT, 0.144 g), 0.126 g of photoinitiator mixture and 0.01 ml of propylene carbonate were mixed for photocurable polymer electrolyte layer preparation. Lithium trifluoromethanesulfate ($LiCF_3SO_3$, 0.12 g) and 0.219 g of TiO_2 nanoparticle with well-controlled diameter distribution (average diameter, d = 15 nm) were purchased from Aldrich. They were dissolved to the above mixture and stirred for 2 h. 10 wt.% of Leucocrystal Violet (LCV), Crystal Violet Lactone (CVL), ODB2 (3-diethylamino-6-methyl-7-xylidinofluoran) and 1,1′-(1,4-butanediyl)bis-4,4′-bipyrinium (BDV) were mixed with polymer electrolyte and coated on an ITO glass, then UV irradiated. The samples with the same composition, but free of TiO_2 nanoparticles were also assembled to compare the effect of nanoparticles. Cyclic voltammetry was measured in two electrode device state without a reference electrode between -2 V and 2 V with scan rate of 0.1 V/sec. UV-VIS absorbance was measured at different voltage from -2 V to 2 V with 0.4 V interval and optical response was detected at maximum absorbance. The coloration efficiency, η (cm^2/C), C), was determined from the following Eq. (1) [6].

$$\eta = \Delta \mathrm{Abs}/Q_d \tag{1}$$

where, Q_d is the charge consumed for coloration process for the unit area, and ΔAbs is the absorbance difference between the bleached and colored state at a given λ. The coloration efficiency determines the optical density change induced as a function of the injected/ejected electronic charge, i.e., the amount of charge necessary to produce the optical change [7].

RESULTS AND DISCUSSIONS

Four different organic dyes having reversible color change under applied potential were introduced to all-solid-state ECDs. Electrochromic dyes

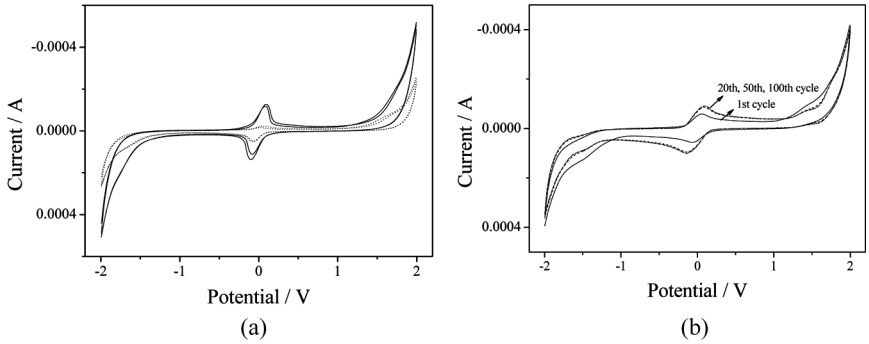

FIGURE 1 Cyclic voltammetry of BDV based ECDs; (a) assembled with TiO_2 adsorbed BDV (solid line) and without TiO_2 (dashed line), (b) multi cycle stability of TiO_2 adsorbed BDV based ECD.

were introduced to TiO_2 containing polymer electrolyte affording dye-attached TiO_2. Titanium atoms on the TiO_2 surface were proposed to act as active sites for anchoring the dye molecules. Dye attachment onto TiO_2 is well described in Refs. [7,8]. Cyclic voltammetry (CV) of the ECD was measured without reference electrode between -2 V and 2 V with a scan rate of 0.1 V/sec. It was noteworthy that the redox peaks were not much changed by the adsorption of dyes in TiO_2 nanoparticles. However, the CV of the device having an electrode of organic dye adsorbed TiO_2 nanoparticles showed higher current density compared to that without TiO_2 nanoparticles as shown in Fig. 1(a). The current density for BDV on TiO_2 nanoparticles was $\sim$400 mA higher than that of the TiO_2 free system, indicating that TiO_2 nanoparticles improved the redox process of organic dyes [9]. The stability of BDV based ECD was tested by cyclic voltammetry as shown in Fig. 1(b). CV on the sample of TiO_2 adsorbed BDV was stable after 10 redox cycles without showing redox peak potential shift. The peak current of the sample was slightly increased within 10 cycles but was not much changed even after hundreds cycles, indicating that the TiO_2 adsorbed system is redox stable.

All solid state EC devices showed different absorbance spectra depending on the applied potentials from 2 V to -2 V in a two-electrode cell structure. The UV-VIS absorbance changes of all cells were shown in Fig. 2. Maximum absorbance change was observed at -2 V and minimum at $+2$ V, indicating that the organic dye is cathodically coloring.

At negative potentials, all ECDs from CVL, LCV, ODB2 and BDV deeply colored showing a maximum absorption at 485 nm, 440 nm, 540 nm and 480 nm, respectively. Optical response was determined

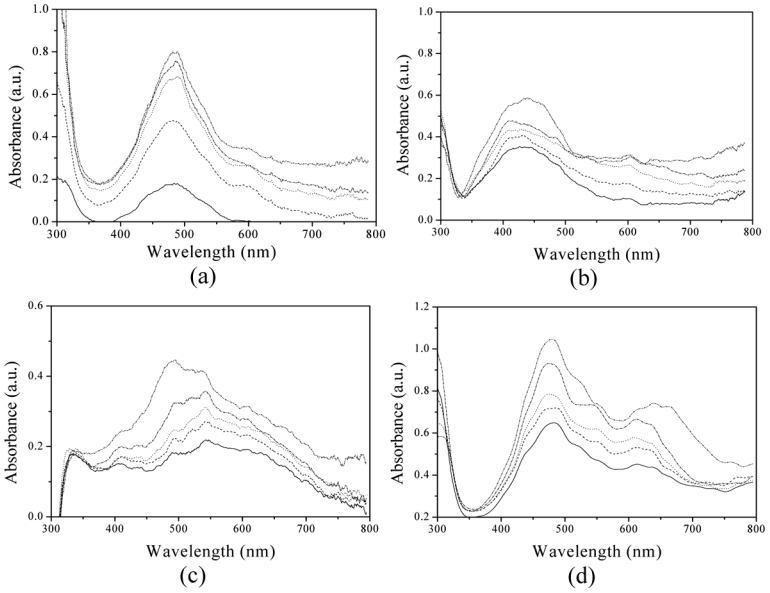

FIGURE 2 UV-VIS absorbance spectra; (a) CVL, (b) LCV, (c) ODB2 and (d) BDV based ECD according to the applied potential, from top to bottom; −2 V, −1.6 V, −1 V, 0 V, 2 V.

from the maximum absorbance with the potential step of −2 V and +2 V for 20 sec at each potential. Color contrast, response time and coloration efficiency of four devices are summarized in Table 1. The ECD from BDV adsorbed TiO_2 nanoparticles showed fastest switching within 8 sec with highest coloration efficiency of 73.4. The highest optical contrast (ΔAbs, a.u.) of 3.0 was obtained from the ECD prepared from CVL adsorbed TiO_2 nanoparticles. On the other hands, the ECDs assembled with organic dye only (without TiO_2 nanoparticles) showed much lower color contrast (ΔAbs <0.1) with poor

TABLE 1 Electrochromic Properties of Organic Dye-TiO_2 Based Electrochromic devices

Material	ΔAbs (a.u.)	Response time (s)	Coloration efficiency	Colored state
CVL	3.0	18	25.5	Green
LCV	0.4	9	45.1	Violet
ODB2	0.1	18	16.0	Dark grey
BDV	0.3	8	73.4	Blue

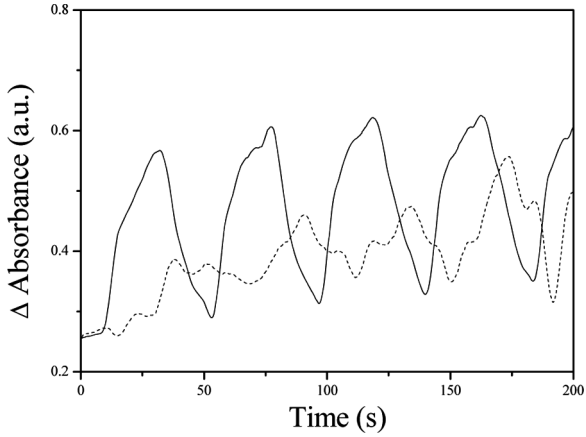

FIGURE 3 Optical response of BDV based ECDs; assembled with TiO_2 adsorbed BDV (solid line) and without TiO_2 (dashed line).

reversibility as compared in Figure 3. These results indicate that TiO_2 nanoparticles effectively encapsulate the organic dyes and provide better channel for the conduction required for the EC reaction due to the conductivity of TiO_2 nanoparticles [9].

Multi-color EC device was successfully fabricated with a patterned ITO glass electrode and organic dye-TiO_2 nanoparticles. Each section for different EC coloration was separated by a spacer and electrically isolated. Figure 4 shows photographs of EC response from the multi-colored cell. Each cell was operated independently according to the voltage application. Importantly the colored or bleached state upon application of $-2\,V$ and $+2\,V$, respectively, were remained even after voltage off, indicating that the cell pertain memory effect. Such a memory effect of ECD is crucial for energy saving color display.

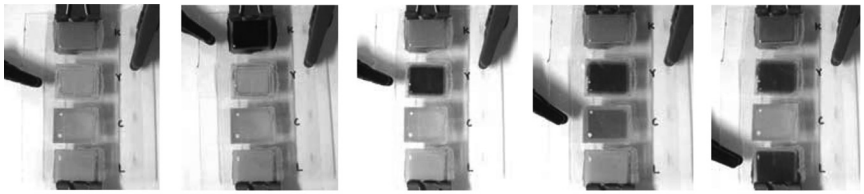

FIGURE 4 Operation of multi-color EC device; (a) bleached state, coloration of (b) BDV, (c) CVL, (d) LCV and (e) ODB2 at $-2\,V$.

CONCLUSION

Organic electrochromic dyes were adsorbed into porous TiO_2 nanoparticles to afford dye-adsorbed nanoparticles. A reflective type all-solid-state electrochromic device (ECD) was fabricated introducing organic dye encapsulated TiO_2 nanoparticles. The ECD prepared from the organic dye-TiO_2 nanoparticles showed much improved optical contrast and response time as compared to that of ECD without TiO_2 nanoparticles. A multi-color EC device was fabricated using four different colored organic dye-TiO_2 particles. It showed reversible EC properties with memory effect.

REFERENCES

[1] Kim, D. (1997). *J. Ind. Eng. Chem.*, *2*, 73.
[2] Kim, E., Lee, K., & Rhee, S. B. (1997). *J. Electrochem. Soc.*, *144*, 227.
[3] Kim, S. & Jung, E. (2005). *Chem. Mater.*, *17*, 6381.
[4] Cinnsealach, R., Boschloo, G., Nagaraja Rao, S., & Fitzmaurice, D. (1999). *Sol. Energ. Mater. Sol. Cell.*, *57*, 107.
[5] Edwards, M. O. M. (2005). *Appl. Phys. Lett.*, *86*, 073507.
[6] Artun, A. A., Aubert, P. H., Thompson, B. C., Schwendeman, I., Gaupp, C. L., Hwang, J., Pinto, N. J., Tanner, D. B., MacDiarmid, A. G., & Reynolds, J. R. (2004). *Chem. Mater.*, *16*, 4401.
[7] Sommez, G., Meng, H., & Wudl, F. (2004). *Chem. Mater.*, *16*, 574.
[8] Murakoshi, K., Kano, G., Wada, Y., Yanagid, S., Miyazaki, H., Matsumoto, M., & Murasaw, S. (1995). *J. Electroanal. Chem.*, *396*, 1.
[9] Gratzel, M. (2001). *Nature*, *409*, 575.