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journal homepage: www.elsevier.com/locate/solmatMulti-color electrochromic devices based on phenyl and heptyl viologens immobilized with UV-cured polymer electrolyte[☆]Ting-Hsiang Chang^a, Hsin-Che Lu^a, Min-Han Lee^a, Sheng-Yuan Kao^a, Kuo-Chuan Ho^{a,b,*}^a Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan^b Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan

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ABSTRACT

An UV-crosslinked ethoxylated trimethylolpropane triacrylate (ETPTA) polymer network and succinonitrile (SN) were employed to prepare a solid polymer composite electrolyte (PCE) matrix at room temperature, so as to immobilize heptyl viologen (HV) and phenyl viologen (PV) at the electrode surface in an electrochromic device (ECD). PV exhibits attractive electrochromic (EC) property, however, its aggregation occurs immediately in conventional liquid or gel electrolyte due to strong π - π stacking.

Herein, an all-solid-state ECD is proposed to tackle the said aggregation issue of PV. An all-solid-state ECD, consisting of HV, PV, and solid polymer electrolyte, is studied by changing the operating potential window to achieve multi-color characteristics. The proposed ECD shows transparent, green, marine, and gray color at the open-circuit potential, 0.6 V, 0.8 V, and 1.0 V, respectively. The first set of redox peaks is due to the redox reaction of PV, and the second set of the redox peaks is the overlap of the first reduced state of HV and the second reduced state of PV. The combination of two viologens in a simple cell configuration (glass/ITO/multicolor-EC + solid electrolyte/ITO/glass) not only offers the characteristics of di-reduced PV species but also opens up a new avenue for color-tuning.

1. Introduction

Electrochromism is a phenomenon in which the changes of coloring materials occur due to electrochemical reactions driven by the applied voltage bias [1–3]. The observed optical transmittance changes are based on redox reactions, that is, where one material is oxidized at an electrode's surface, the second material is reduced at the opposite electrode's surface. Due to the controllable optical properties of electrochromic (EC) materials, electrochromic devices (ECDs) have captured the interest of many research groups and industrial companies worldwide for the past few decades [4–6]. The EC products include smart windows for sunlight attenuation [7,8], EC displays [9,10], and anti-glare rearview mirrors *etc.* [11]. This anti-glare or energy-saving technology is attractive due to its relatively low driving voltage (usually no more than 3 V) [12–15], short switching time, and high coloration efficiency [16]. Comparing to other chromogenic technologies, such as liquid crystals [17,18], suspended particles [19,20], thermochromism [21], and photochromism [22], ECDs exhibit not only small operating potentials but also feature in users-controllable property upon applying

different potential bias. Several kinds of EC materials have been reported, such as conducting polymers [23,24], metal oxides [25], organic small molecules [26], metal complexes [27,28], and metallo-supramolecular polymers, *etc.* [29,30]. All of these EC materials have been subjected to intense investigation in the past few decades. Further challenge for the development on ECDs is to take advantage of multicolored properties of EC materials that are highly desirable from the viewpoint of practical energy-saving, especially for smart windows and displays [31]. Most of inorganic EC materials (*e.g.*, WO₃, NiO) offer only single color change [32,33], while conducting polymers exhibit slow response time and poor stability when exposed to heat and sunlight [34]. In contrast, organic small-molecules possess the advantage of high optical contrast, high coloration efficiency, and low cost. Since the lack of multicolor abilities is the intrinsic properties of most EC materials, one of the strategies to fabricate a multicolor ECD is through the incorporation of different EC materials [35,36].

Among various kinds of EC materials, viologens (also named as 1,1'-disubstituted-4,4'-bipyridinium salts) are promising organic EC materials that have three redox states, including the di-reduced state (V⁰),

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radical cation state (V^+), and dication (V^{2+}) states. The reversible reduction of viologens from dication (V^{2+} , bleached) states to radical cation state (V^+ , colored) shows remarkable color contrast that enables viologens suitable for many applications, as mentioned above. It was reported that the optical characteristics of viologens vary with different substituent groups on bipyridiniums [37]. However, the observed side reactions in viologen-based solution-type ECDs, including dimerization, comproportionation, aggregation, or even recrystallization, would damage the reversibility of viologens [38–40]. These side reactions occur easily especially in ECDs utilizing aqueous electrolyte or some viologens are easy to form agglomerates, (for examples, phenyl viologen and benzyl viologen), leading to the poor write–erase ability and poor cycling stability of the obtained ECDs. Despite the fact that 1,1'-diphenyl-4,4'-bipyridinium (phenyl viologen, PV) has been synthesized and studied for several decades [41], there are only few literatures reported this material for the use in the solution-type ECDs due to the nature of its poor cycling stability mentioned above.

In general, ECDs containing viologens in a liquid electrolyte suffer from not only the side reactions mentioned above but also the possibility of electrolyte leakage [42,43]. Most of the conventional liquid electrolytes are volatile, which cause safety concerns and poor long-term stability of the ECDs. To overcome this drawback, many strategies have been proposed for preparing viologen-based ECDs. For examples, thin-film type ECDs have been fabricated through electropolymerizing polyviologen thin film [13] or anchoring viologen on the titanium dioxide surface [44]. Several studies have revealed that the immobilization of viologens plays an important role in determining the switching times of viologen-based ECDs [44,45]. Nevertheless, these approaches usually suffer from their own natures of either small transmittance change or poor stability [45,46]. One of the approaches to prevent the leakage problem in a solution-type ECD is to use a solid-state electrolyte. There has been a continuous effort to find the gel or solid-state electrolytes possessing high ionic conductivity with suitable thermal, mechanical, and electrochemical stability for the use in ECDs. To address this challenge, our previous studies reported on incorporation of cross-linked polymer network in viologen-based ECDs, which were based on an all-in-one EC gel [45,47]. The polymer network can retard the aggregation of the viologen radical (V^+), thus obtaining better cycling stability of the ECDs. As for the solid-state electrolytes, succinonitrile-based electrolyte has been demonstrated as an ideal solid electrolyte to achieve high-performance ECDs [26,48]. Herein, the proposed multicolor ECDs contain two viologens in a simple symmetric device configuration, namely, glass/ITO/multicolor-EC+ solid electrolyte/ITO/glass. The prepared electrolytes encapsulated all redox active species in a homogeneous all-in-one EC gel, thus solving the possible leakage problem of viologen-based ECDs. This approach can effectively prevent leakage while enhancing the cycling stability by avoiding the formation of aggregation. With this method, it is possible to achieve variable colors, including transparent, green, marine, and gray, with a fast switching time, high coloration efficiency, and good reversibility. An ECD that enables control of multicolor states using only one type of EC material has rarely been reported. This work proposes a proof-of-concept system dealing with multicolor viologen-based ECDs and preventing the agglomeration of viologens on the electrode surface in ECDs.

2. Experimental section

2.1. Materials

Indium tin oxide (ITO) glasses were used as the substrates (Solaronix SA, $R_{sh} = 7 \Omega/\square$). The size of ITO was cut to $3.0 \times 4.0 \text{ cm}^2$ and the ITO glasses were cleaned as follows. The ITO glasses were ultrasonically cleaned in a neutral cleaner solution for 10 min, and then in deionized water for 5 min, finally in isopropanol for 5 min. Subsequently, the ITO glasses were dried under N_2 . Epoxy tape (3 M

Company, $60 \mu\text{m}$ thick) was used to control the active area of $2.0 \times 2.0 \text{ cm}^2$ on the ITO surface. Conducting copper tape (3 M Company, $3.0 \times 0.5 \text{ cm}^2$) was used as the bus bar at one side of the ITO glasses. Ferrocenemethanol (FcMeOH), ethoxylated trimethylolpropane triacrylate (ETPTA), 2-hydroxy-2-methyl-1-phenyl-1-propane (HMPP, photo-initiator), and tetrabutylammonium tetrafluoroborate (TBABF₄, > 95%) were all purchased from Sigma-Aldrich. Phenyl viologen dichloride (PVCl₂, > 99%), 1,1'-diheptyl-4,4'-bipyridiniumtetrafluoroborate (heptyl viologen; HV(BF₄)₂), and succinonitrile (SN, 99%) were purchased from Tokyo Chemical Industry (TCI). The chloride anions of PVCl₂ were substituted to tetrafluoroborate (BF₄⁻) anions by the approach reported in literature due to the poor solubility in organic solvent [49]. The UV-cured electrolytes in this study was prepared by adding 0.5 M TBABF₄ into SN melted at 60 °C. The reason to prepare such high concentration of electrolyte is due to the need to destruct the structure of crystalline succinonitrile [50]. Succinonitrile becomes liquid phase at room temperature after adding high concentration of TBABF₄ salt, which is easier for the subsequent experiments and application. Afterward, both ETPTA and HMPP were added to the electrolyte. The weight ratio of the polymer matrix/electrolyte was maintained at 15/85 (w/w) and the concentration of HMPP was fixed at 0.1 wt% of ETPTA.

2.2. Fabrication of electrochromic devices utilizing in-situ UV-curing method

Two small holes were drilled on the blank ITO glasses. Surlyn® (DuPont) film was used as sealant to fabricate an empty cell, and syringe was used to inject the all-in-one electrolyte solution into the cell. The cell gap of the ECD was fixed to be $60 \mu\text{m}$ using Surlyn®. Three types of UV-curable electrolytes were studied in this work: (1) Electrolytes without UV-curing. (2) Electrolytes with UV-curing but without applying potential bias. (3) Electrolytes with UV-curing and with applying potential bias, which is named as the *in-situ* UV-curing method in this study. The process involving *in-situ* UV-curing method is described in the next paragraph.

The ECD containing UV-curable electrolyte was subjected to a potential bias. After the completion of viologen reduction and reaching the equilibrium, which means that the viologen molecules were fully adsorbed on the ITO electrode, the ECD was exposed to UV-irradiation for 30 s. The *in-situ* UV-curing method was carried out using an Hg UV lamp (EXFO), with the irradiation intensity being fixed around 1000 mW cm^{-2} on the sample surface. After exposing to UV-irradiation and applying potential bias simultaneously, one obtains an all-solid-state ECD. The potential bias applied to the ECD during *in-situ* UV-curing was determined by the cyclic voltammetric measurement of the obtained UV-cured ECDs (Fig. S1). Since the measured current density can be considered as the amount of viologens reacted on the electrode, the smaller current density of the UV-cured ECD applied under 0.8 V during *in-situ* UV-curing method suggests the smaller amount of viologen radical species formed on the electrode surface. It is noticed that the other two ECDs, applied under both 1.0 V and 1.2 V during *in-situ* UV-curing, show the comparable current densities; this implies that the amount of viologen radical species formed on the electrode surface has reached its saturation. Therefore, we choose 1.2 V as the potential bias for the ECD during the *in-situ* UV-curing.

2.3. Measurements

A potentiostat/galvanostat (model PGSTAT 30, Autolab) was used for performing electrochemical experiments. An *in-situ* spectro-electrochemical measurement was carried out by using a spectrophotometer (model DH-2000-BAL, Ocean Optics) in combination with the above-mentioned potentiostat/galvanostat. Baseline of *in-situ* UV-vis measurement was done under air when measuring the spectra of the ECDs. The Nova NanoSEM scanning electron microscope was used for obtaining

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