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An electrochromic device based on all-in-one polymer gel through in-situ thermal polymerization[☆]

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ABSTRACT

A self-standing all-in-one electrochromic gel utilizing phenyl viologen (PV) and N,N,N′,N′-tetramethyl-1,4-phenylenediamine (TMPD) as the electrochromic materials is prepared by incorporating a thermo-cured cross-linked polymer matrix. The thermal-cured polymer matrix can prevent the agglomeration of PV happening on the electrode surface, resulting in the excellent write–erase ability of the obtained gelated ECD. Moreover, the cross-linker which possesses the long propoxylated arms leads to the easier diffusion for both PV and TMPD in the obtained polymer network. As a result, the obtained ECD exhibits a large transmittance change ($\Delta T > 67\%$ at 620 nm) within a short response time (< 3.5 s) under an extremely low driving voltage (0.5 V). Besides, this device remains over 55% of ΔT after 10,000 cycles of switching.

1. Introduction

Electrochromic devices (ECDs) change their color through the electrochemical manipulation of redox states of electrochromic (EC) materials [1–3]. Such devices have already been proposed in several potential applications such as electrochromic smart windows [4,5] anti-glare rearview mirrors [6], electrochromic helmet visors [7] and displays [8]. Since the smart window and display devices using suspended particles or liquid crystals often require a potential bias higher than 5 V to exhibit sufficient change in color, ECDs have attracted much attention due to their relatively low driving voltage (1–4 V) [4]. In addition to their low driving voltage, ECDs could be integrated with photovoltaic to fabricate the self-powered energy-saving electronic devices [9,10].

Among all electrochromic materials, viologens (1,1′-disubstituted-4,4′-bipyridiniums) have been considered as attractive candidates since they exhibit significant change in transmittance [11–13]. Besides, some viologen-based ECDs even possess driving voltage within 1 V [14], which makes this class of electrochromic materials even more attractive in terms of energy-saving. Nevertheless, most viologen-based ECDs possess poor long-term stability, which is attributed to the undesirable side reactions such as dimerization [15,16] and comproportionation [17] occurring during operation. Furthermore, it has been reported that the colored state of viologens has a lower solubility compared to the bleached state. As a result, high concentration of colored viologen tends to form agglomerates on the electrode surface [18]; such deposited agglomerates would begin to crystalize if the coloring process lasts longer [19]. The generated agglomerates hinder the bleaching reaction of viologens, leading to the poor write–erase ability and poor cycling stability of the obtained ECDs [20]. Moreover, most ECDs utilizing viologens are mostly solution-type [14]; such solution-type ECDs usually suffer from leakage of electrolyte, which also harms the stability and brings safety concerns [2].

The electrochromic process of 1,1′-diphenyl-4,4′-bipyridinium (phenyl viologen, PV) can be operated at an extremely low potential bias of about 0.5 V, with the help of N,N,N′,N′-tetramethyl-p-phenylenediamine (TMPD) as the redox couple on the counter electrode. The TMPD/TMPD^{+} redox couple can provide/extract electrons to and from PV^{2+}/PV$^{+\bullet}$ respectively during the operation of the device, therefore making the coloring/bleaching process easier under this narrow potential bias [14]. Although PV has been discovered and synthesized for several decades [21,22], there is not any reported study applied such material for practical ECDs due to the nature of its poor cycling stability mentioned

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above. Compared to other viologens such as coil-moiety bearing heptyl viologens, which have been widely utilized in ECDs [23], the rod-like linear molecules including PV are expected to form agglomerate on the electrode surface much easier [24–26]; this disadvantage thus limits the use of PV for ECDs.

Several strategies have been proposed to prevent the agglomeration of viologens on the electrode surface in ECDs. To effectively inhibit the intermolecular interaction between viologens, Monk et al. added electron mediators like ferrocyanide/ferricyanide [23,27] while Yasuda et al. included cyclodextrin with viologen to generate a complex that prevents deposition of viologen [28]. Wrighton et al. proposed a viologen-based polymer which was covalently anchored on the electrode surface [29], and Walder et al. anchored the viologen molecules onto a porous modified electrode [30]. All these strategies have successfully eliminated the agglomeration of viologens. However, the ECDs proposed in the above-mentioned literatures still used liquid electrolyte, which might cause the undesired leakage problem. For the first time, Chidichimo et al. [31] introduced substantial amount of poly(vinyl formal) into the viologen-based electrochromic system to obtain a thermal plastic laminable electrochromic gel. This electrochromic gel has successfully prevented the leakage problem. However, such ECDs possess much higher potential bias ($>$ 1.5 V) and longer response time to reveal significant color contrast. To date, very few viologen-based ECDs acquire all the merits such as low-driving voltage, good stability, and high transmittance change simultaneously.

Herein, the electrochromic polymer gel was incorporated into the viologen-based electrochromic system by utilizing a simple in-situ thermal curing method. PV and TMPD were served as the cathodic and anodic electrochromic materials, respectively. Methyl methacrylate (MMA) was used as a gelling agent while azobisisobutyronitrile (AIBN) was employed as a thermal curing initiator as suggested in literature [32]. Propoxylated trimethylolpropane triacrylate (PTPTA) was utilized as the cross-linker since it can provide a more robust network in the electrochromic gel than the two-acrylate cross-linker [33]. The PV and TMPD systems give the lowest driving voltage (0.5 V) for leakage-free, all-in-one, EC gel to date while exhibiting excellent cycling stability. The resulted thermal-cured polymer gel offers remarkably high transparency and superior ionic conductivity, making it an ideal polymer electrolyte for ECDs. A large transmittance change ($>$ 65%) was achieved; even the ECD was incorporated with the polymer network.

2. Experimental

2.1. Chemicals

Phenyl viologen dichloride ($PVCl_2$, $>$ 97%) was purchased from Tokyo Chemical Industry (TCI). Sodium tetrafluoroborate ($NaBF_4$, 98%), TMPD (99%), MMA (99%), propoxylated trimethylolpropane triacrylate (PTPTA), and tetra-n-butylammonium tetrafluoroborate ($TBABF_4$, 99%) were purchased from Sigma-Aldrich. Propylene carbonate (PC, 99%) was purchased from Alfa Aesar while AIBN (99.7%) was purchased from UniRegion. Deionized water (DIW) with the resistance of 18.2 MΩ was utilized throughout the experiment. Except PC which was dehydrated by 4 Å molecular sieve (Acros) for at least overnight, all other chemicals were used as received without further purification. Indium tin oxide coated conducting glass (ITO, Solaronix SA, $R_{sh}=7\ \Omega/\square$) was used as the conducting substrate throughout this work. Since $PVCl_2$ shows poor solubility in PC, the chloride anions were substituted to tetrafluoroborate (BF_4^-) anions by the approach reported in literatures [14,34]. Briefly, 0.3 g $PVCl_2$ was dissolved in minimal amount of 90 °C DIW. This solution was immediately mixed with 3.75 ml of 9.4 mM $NaBF_4$ aqueous solution under vigorously stirring. The resulted yellowish $PV(BF_4)_2$ precipitant was then washed thoroughly with ethanol/DIW solution. After drying, the obtained $PV(BF_4)_2$ powder exhibits nice solubility in organic solvents such as PC.

2.2. Preparation of the electrochromic gel

To obtain the all-in-one electrochromic gel, MMA was utilized as the monomer for polymer electrolyte and PTPTA was employed as a cross-linker. 5% (v/v) of MMA and 5% (v/v) of PTPTA were mixed homogeneously with equimolar electrochromic materials (0.05 M $PV(BF_4)_2$ and 0.05 M TMPD) and 0.5 M $TBABF_4$ along with the plasticizer PC to form an all-in-one electrochromic gel precursor. After blending, trace amount (8.2 mg) of the thermal cross-linking initiator (AIBN) was dissolved into the precursor. This precursor was then stored in vials or injected in sealed devices (illustrated in Section 2.3). Thereafter, the electrochromic gel precursor was heated at 90 °C for ca. 40 min for thermal curing.

2.3. Fabrication of ECDs

In this study, two types of ECDs are fabricated, namely, the gelated ECD (g-ECD) and the conventional ECD (c-ECD). The g-ECD was assembled by two ITO substrates with the equal size of $3.0\times4.0\ cm^2$ that acted as the working and counter electrodes. Prior to use, the ITO substrates were cleaned by isopropyl alcohol and then subjected to ozone treatment for 20 min. One of the ITO glasses was drilled with two holes for precursor injection. The cell gap was controlled by one layer of DuPont 60 μm Surlyn® (Solaronix S.A., Aubonne, Switzerland). The Surlyn® ionomer resin was first cut into $2.0\times2.0\ cm^2$ frame and cleaned by ethanol before laminated between the two ITO substrates. The laminated Surlyn® resin was then heated and pressed for sealing the device. After sealing the device, the obtained precursor mentioned in Section 2.2 was injected into the ECD through the drilled holes. The g-ECD was then obtained through subjected to 90 °C heating for 40 min to cure the electrolyte. For comparison, the c-ECD without using polymer electrolyte was also fabricated by injecting the electrolyte containing 0.05 M $PV(BF_4)_2$, 0.05 M TMPD and 0.5 M $TBABF_4$. Finally, the holes on all ECDs were further sealed by epoxy.

2.4. Measurements

Electrochemical data was obtained by using a potentiostat/galvanostat (Autolab, model PGSTAT30). Spectro-electrochemical data was acquired by in-situ electrochemical and optical measurements, which were conducted on a potentiostat/galvanostat in conjunction with a spectrophotometer (Ocean Optics, DH-2000-BAL). Electrochemical quartz crystal microbalance (EQCM) was done by utilizing a potentiostat/galvanostat connected with a quartz crystal microbalance oscillator (Seiko EG&G, QCA917). In this setup, 8.88-MHz AT-cut quartz crystal (QA-AM9-PT) with a Pt electrode (with an active surface area of $0.196\ cm^2$) served as the working electrode while homemade Ag/Ag^+ and Pt foil ($1\times4\ cm^2$) served as the reference and counter electrodes, respectively.

3. Results and discussion

3.1. Properties of the all-in-one EC gel

The cyclic voltammetric (CV) measurements of $PV^{2+}/PV^{+\bullet}$ and $TMPD^+/TMPD^0$ are presented in Fig. 1(a) and (b) respectively. When applying the negative potential sweep in Fig. 1(a), green color appears near the working electrode, indicating the formation