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Electrochromic property of nano-composite Prussian Blue based thin film

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Abstract

In this paper, we present fabrication of a nano-composite Prussian Blue (NPB) film to synchronously improve the contrast and switching time of regular Prussian Blue (PB) film by applying the concept of nano-technology. The NPB consists of indium tin oxide (ITO) nano-particles ($3.0 \pm 1.0\,\Omega$, 40 ± 5 nm) as a medium layer for PB to gain larger operative reaction surface area in Li^+ based electrolyte (1 M $LiClO_4$/PC) system. The procedures for preparation of NPB are: first, a well-dispersed ITO nano-particle solution is sprayed onto ITO glass (30 Ω/sq) at 200 °C; the PB film is then electroplated onto the pre-sprayed ITO nano-particles. Since ITO nano-particles can be well covered with PB, the NPB film forms a nano-porous electrochromic layer. The switching speed and contrast of NPB exhibit much better performances than traditional PB thin films. The structure, morphology, and electrochromic properties were characterized by scanning electron microscopy (SEM), cyclic voltammograms (CV), and UV–vis spectroscopy.

Keywords: Prussian Blue; Electrochromic; Nano-composite; Nano-particles; Li^+ based electrolyte; Nano-technology

1. Introduction

Electrochromism has become more and more important because it possesses low power consumption feature and has the potential to be applied to e-paper [1]. However, slow response time is always the vital drawback of this technology, and other performances, like contrast, also influence the extent of application. Our present work is to synchronously improve the contrast and the switching time of Prussian Blue (PB) by applying the concept of nano-technology.

PB has been widely used in electrochromic devices (ECDs) as a sole electrochrome [2,3] or an auxiliary electrode, especially in complementary tungsten oxide (WO_3)-PB ECD [4–8]. Usually WO_3 film uses H^+ or Li^+ based electrolyte [9,10], whose ion radius and mobility is the smallest and fastest, but WO_3 film may fail rapidly owing to dissolution in H^+ solution [9]. The K^+ based hydrated electrolytes are expected to have better electrochromic performances than Li^+ based ones because the radius of hydrated K^+ is smaller than that of hydrated Li^+ [11]. This is the reason why K^+ based electrolytes were utilized by almost published papers of PB. To combine WO_3 with PB, a polymer electrolyte prepared from polyvinyl alcohol (PVA) doped with H_3PO_4 and KH_2PO_4 was introduced into WO_3-PB ECD system by Habib et al. [4]. The polymer electrolyte contains both H^+ and K^+ ions; the former and latter intercalate or de-intercalate with WO_3 and PB, respectively. Li^+ based WO_3-PB ECD system has been published [8,12,13], however improvements on electrochromic performances of PB in Li^+ based electrolyte system was not yet reported.

Recently, nano-technology has been widely applied to ECD. Organic EC materials, Viologn coated on TiO_2 nano-particles [14] and poly(3,4-ethylenedioxythiophene) (PEDOT) nano-tubes [15], have been proposed for fabricating ECD. Inorganic EC materials, WO_3 and V_2O_5 nano-wires, were successfully prepared by thermal evaporation to improve electrochromic performances [16,17]. Delongchamp and Hammond [18–20] proposed that they combined conductive polymer (polycation linear poly(ethylene imine) (LPEI) or polycation poly(aniline) (PANI)) with PB nano-particles by layer-by-layer (LBL) method. These approaches to ECD all used the advantage of large surface area provided by nano-materials to overcome the drawback of long switching time.

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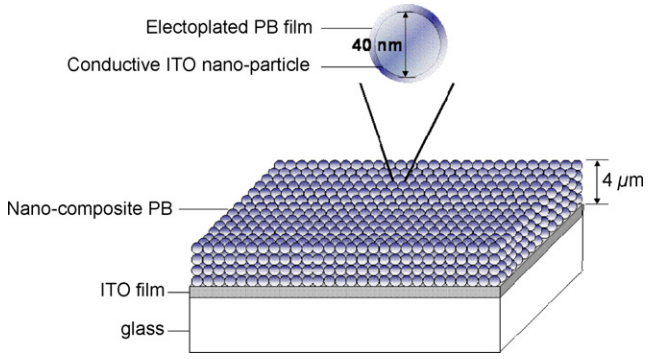

Fig. 1. Conceptual structure of nano-composite PB (NPB) film. After PB is electro-deposited, every ITO nano-particle can be well covered by PB and form a NPB structure.

In this paper, we explore elctrochromatic properties of a nano-composite PB (NPB) including cyclic voltammetry (CV), deposition efficiency, switching time, and transmittance contrast. In the present work, PB was electroplated on a pre-sprayed ITO nano-particles layer within a Li^+ based electrolyte system ($LiClO_4$/PC). It is desired that PB completely covers the surface of ITO nano-particles as shown in a conceptual diagram Fig. 1. The ITO nano-particles as a medium layer actually form a nano-porous structure shown in a later SEM analysis. It is envisaged that the operative reaction area of NPB is larger than that of the regular PB thin film, and therefore NPB is expected that the performances of switching time and transmittance contrast can be improved. The effects of pre-sprayed ITO nano-particles on the optical and electrochromic properties of PB in Li^+ based electrolyte were studied and discussed in detail.

2. Experiment

To prepare a NPB film, ITO nano-particles (LIHOCHEM Inc., 99.99%, 40 ± 5 nm, $3.0 \pm 1\,\Omega$) were first put into ethyl alcohol (99.5%) and dispersed in an ultrasonic tank. The well-dispersed ITO nano-particle solution was sprayed onto a heated ITO glass (30 Ω/sq, active area: 2 cm × 3 cm) at 200 °C by an airbrush with pressure set around 15 psi.

PB film was then electrodeposited onto the ITO nano-particle film/ITO glass by using galvanostatic electrodeposition (GED) method [11]. It is desired that PB film will cover on the ITO nano-particles to form NPB film, referred as sample 2. Another sample, PB film electrodeposited onto regular ITO glass, is prepared as sample 1 for a comparison in the morphology and electrochromatic performance with those of sample 2. The composition of the plating solution was an equi-volume mixture of 10 mM $K_3Fe(CN)_6$, 10 mM $FeCl_3$, and 1N KCl aqueous solution with dilute HCl to adjust to pH 1.25, and the electroplating conditions were 30 $\mu A/cm^2$, 500 s. Finally, both samples were washed in de-ionized water before further experiment.

The surface morphology and electrochromatic properties of sample 1 and sample 2 were characterized and analyzed by scanning electron microscopy (SEM, JEOL JSM-6330F/EDX),

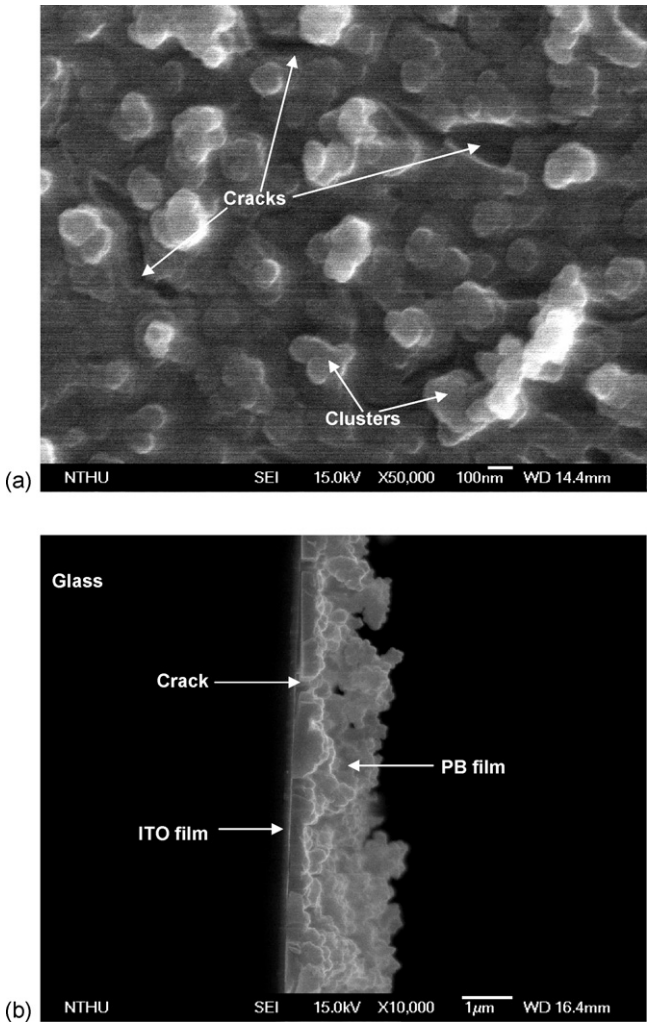

Fig. 2. SEM images of PB film on regular ITO glass substrate (sample 1) (a) top view at 50,000× and (b) cross-sectional view at 10,000×.

cyclic voltammetry (Autolab model PGSTAT12) and transmittance spectrum (Jasco V-570: UV/VIS/NIR double beam spectrophotometer). The CV was performed at voltage between −1 and +1.25 V relative to Ag/AgCl at a scanning rate of 10 mV s^{-1}. The electrolyte was 1 M $LiClO_4$/propylene carbonate (PC) and the counter electrode was Pt. The chronoamperometry was carried out with switching potential between +0.5 and −0.5 V relative to Ag/AgCl for every 30 s step, and 1 M $LiClO_4$/PC and Pt were also used here. The transmittance spectra of the prepared PB films were measured in a spectral range from 350 to 850 nm.

3. Results and discussion

3.1. Surface morphology analysis

Fig. 2(a) (magnification 50,000×) shows the surface morphology of the as electrodeposited PB film of sample 1, which has cracks between particle-like clusters. The SEM cross-sectional image in Fig. 2(b) also reveals that these clusters make the PB film rough and jaggy in surface. The diameters of these clusters range from several hundreds nanometers to