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Multicolor electrochromic thin films and devices based on the Prussian blue family nanoparticles

Tzu-Chieh Liao, Wei-Han Chen, Hung-Yun Liao, Lin-Chi Chen*

Department of Bio-Industrial Mechatronic Engineering, National Taiwan University, Taipei 10617, Taiwan

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ABSTRACT

Here we report a color palette of electrochromic (EC) nanoparticles (NPs) based on the Prussian blue (PB) family and present its promising multicolor thin film and device applications. We synthesized PB, cobalt-PB analogue (Co-PBA), nickel (Ni)-PBA, and copper (Cu)-PBA NPs and prepared the corresponding aqueous NP inks with or without 10 vol% PEDOT:PSS additive. Uniform EC films with high visual contrast were coated onto ITO electrodes by repeated spin-coating of the NP inks. The EC films were characterized with SEM, cyclic voltammetry, Li^+ diffusion speed, and *in situ* spectroelectrochemical methods. The EC colors of PB, Co-PBA, Ni-PBA, and Cu-PBA were achieved with these NP films. In particular, the PB NP film showed reversible green and yellow electrochromism that were not possible for an electrodeposited PB film, and Co-PBA, Ni-PBA and Cu-PBA films with sufficient thickness to exhibit visualized EC colors were also difficult to attain by electrodeposition. We also proved that a multicolor EC film could be prepared by a simple layer-by-layer interchanged coating of two different PBA NPs (*e.g.*, PB and Ni-PBA). Finally, we assembled a new, multicolor, and full-PBA EC window prototype based on a PB/Ni-PBA working electrode and a Cu-PBA counterelectrode.

1. Introduction

Electrochromic (EC) materials display visualized color changes when applied with potentials [1,2]. The spectral modulation capabilities and reversible redox properties of EC materials have led to the applications of visualized-transducers [3], windows [4,5], switchable mirrors [6], displays [7,8], and energy-saving buildings [9,10]. As far as solar-attenuation smart windows are concerned, a variety of inorganic [11,12] and organic [13,14] materials have been investigated and processed as thin films for device assembly to date. For instance, WO_3 is the most widely researched EC material for the smart window application owing to its capacity of large-area coating, high on-off cycle life, and broad-band spectral modulation (especially the IR range). There are already several commercial systems based on WO_3 accordingly. Several conducting polymers like polyaniline have also caught the attention due to their high color contrast, multicolor states, and low driving voltages. However, there is still plenty of room in exploring new promising EC materials, thin films and devices for smart window applications. It is because that conducting polymers seem to show less reversibility and stability when exposed to heat and sunlight [15]. Also, we can imagine that low abundance of tungsten (1.25 mg/kg in earth's crust) will inevitably limit the future development of WO_3-based windows owing to a potential cost raise in the raw material with an expanded WO_3 market.

Prussian blue (PB, $KFe^{III}Fe^{II}(CN)_6$) is basically made of iron element, and the electrochromism of such iron-based material was firstly reported by Neff's work [16]. Iron has a relatively high abundance (5.63×10^4 mg/kg in earth's crust) and is thus easier to access with a much lower cost as compared to tungsten. And this mixed-valence compound has been familiar with versatile niches in not only electrochromics but also secondary batteries [17,18], sensors [19,20], electrocatalysis [21,22], and radioelement removal [23,24]. Moreover, replacing the coordinate iron in the PB framework with other transition metals results in a distinct Prussian blue analogue (PBA) showing a different color [25]. For instance, cobalt-based PBA (Co-PBA, $K_2Co^{II}[Fe^{II}(CN)_6]$) is with pale green-to-reddish-brown electrochromism [26,27], and copper-based PBA (Cu-PBA, $K_2Cu^{II}[Fe^{II}(CN)_6]$) shows a pale yellow-to-red color change [28,29]. Nickel-based PBA (Ni-PBA, $K_2Ni^{II}[Fe^{II}(CN)_6]$) also reported showing transparent to yellow electorchromism [30]. Ruthenium hexacyanoferrate (Ru-PBA) changes its color from transparent to purple [31]. Thus, PB and PBAs are still catching many researchers' attentions, despite classical. Furthermore, by controlling the ratio of the valence metal ions, PBAs will further show different optical performance (*e.g.* Co–Fe ratio of Co–Fe PBA [32]), rendering various choices for EC application. In this work, we aim at fabrication of a full PBA-based EC window (*i.e.*, both

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* Corresponding author. Tel.: +886 2 3366 5343; fax: +886 2 2362 7620.
E-mail address: chenlinchi@ntu.edu.tw (L.-C. Chen).

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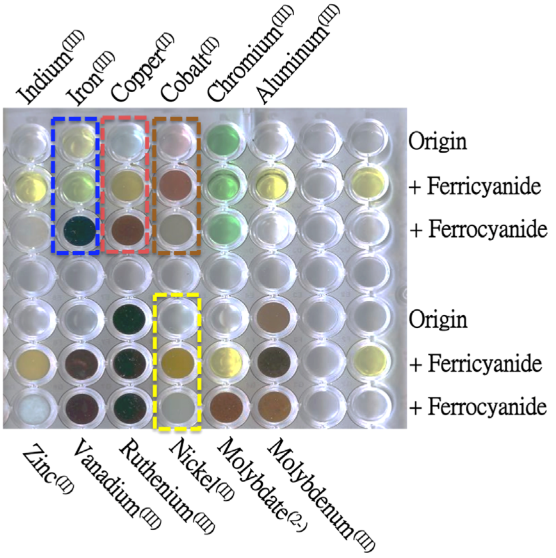

Fig. 1. A color palette of the PB family precipitates obtained by simply mixing metal ions with ferricyanide or ferrocyanide. This indicates that the PB family is of great potential in multicolor EC applications, wherein the Origin raw shows the aqueous transition metal solution that are not reacted with ferrocyanide or ferricyanide. (For interpretation of the reference to color in this figure legend, the reader is reffered to the web version of this article.)

working and counterelectrodes are PBAs) to reduce the dependence on WO_3 systems and to provide multicolor EC windows for custom choice.

As shown in Fig. 1, a micro-titer plate is used to exhibit and compare the colors of the PBA precipitates of different transition metal ions reacting with ferricyanide ($Fe^{III}(CN)_6^{3-}$, oxidized state) and ferrocyanide ($Fe^{II}(CN)_6^{4-}$, reduced state), wherein, the resources of Ru, Cu, Mo, Al, V, Fe, MoO_3, Cr, Zn, In, Ni and Co metal ions are $RuCl \cdot xH_2O$, $CuCl_2$, $MoCl_3$, $AlCl_3 \cdot 6H_2O$, VCl_3, $FeCl_3 \cdot 6H_2O$, $K_{0.30}MoO_3$, $CrCl_3 \cdot 6H_2O$, $ZnCl_2$, $InCl_3$, $NiCl_2$, $CoCl_2 \cdot 6H_2O$ respectively. This simple test indicates the promising potential of the PBA materials in multicolor EC applications. In addition to displaying multiple colors, a high visual contrast is also a desirable feature for smart windows. Hence, the thickness of a PBA thin film is a crucial factor to achieve our goal. However, conventional electrodeposited PBA films are hard to be grown to a sufficient thickness to display a high-contrast EC effect owing to unstable plating solutions (in general, PBAs have very small solubility product K_{sp} [25]. For example, the K_{sp} of PB is about 10^{-40}). By contrast, Gotoh et al. reported a method to prepare water-soluble PBA NP inks by ferrocyanide modification [33], and the method provided a basis for wet-coated PBA film fabrication. In our previous study, we used transparent PEDOT:PSS conducting polymer as a binder additive for spin coating of Zn-PBA (zinc hexaycyanoferrate) NPs to improve the ink viscosity, the NP suspension homogeneity, and the charge-transfer conductivity between the coated NPs [34], and the size issue of Zn-PBA particles to electrochemical properties is also discussed. Similarly, Lee et al. also built a full-PBA based ECD with PB and Zn-PBA, and the research further indicated that the redox reaction of the ECD could be accelerated by downsizing the Zn-PBA particles [35]. Thus, wet coating of PBA NPs can also be done using PEDOT:PSS matrix without making PBA NPs highly water soluble. Moreover, wet coating is good for doping to alter the optical performance [36] and to improve the durability [37] of an EC film. For example, Delongchamp et al. synthesized PB nanoparticles at first, and then employed layer-by-layer strategy to increase the PB electrode thickness steadily with linear poly (ethylene imine) (LPEI) to accelerate electrochromic switching speed [38]. Miao et al. also disclosed a hybrid Pt/PB nano-particle colloid, and the Pt-modified PB particles can be immobilized on Au electrode by metal–sulfur reactions [39]. Hence, another aim of our work is to engineer a simple, robust wet-coating strategy to prepare a PBA NP thin film.

In this work, four PB family NPs (PB, Co-PBA, Ni-PBA, and Cu-PBA) are synthesized and are processed as EC films with high visual contrasts by layer-by-layer spin coating. The surface morphology, redox features, spectral features, kinetic aspects, and optical responses of the PBA EC films are well characterized. We also demonstrate that a multicolor composite film can be attained by interchanged coating of two different PBAs, which proves the advantage of PBA NPs as a color palette to tune a customized multicolor EC film. Finally, we assemble a new, colorful EC window prototype based on two PBA electrodes. These will be described, presented, and discussed below.

2. Experimental

2.1. Materials

All chemicals used were reagent grades and were used as received without further purification. Iron chloride anhydrous, cobalt chloride hexahydrate, nickel chloride, and cooper sulfate pentahydrate were used to provide the transition metal ions for PBA synthesis. Potassium ferrocyanide trihydrate and potassium ferricyanide were used to react with the metal ions and form PBA NPs. A commercial PEDOT:PSS ink was used as an additive for PBA spin-coating. Indium tin oxide (ITO) glass ($R_{sh}=7\ \Omega/\square$) was used as the substrate for EC film coating. The working area was confined to be $2.0 \times 2.0\ cm^2$ with polyester tapes and a Cu tape contact. The organic electrolyte to sustain the EC reactions of PBAs was composed of sodium perchlorate or lithium perchlorate and propylene carbonate (PC).

2.2. Synthesis of PBA NPs

The PBA NPs were synthesized by mixing the transition metal ions with ferrocyanide or ferricyanide ions similar to the method reported in our earlier papers [25,34]. In the beginning, PBA precipitates were formed by drop-wise addition of a potassium ferrocyanide or ferricyanide solution into a transition metal ion solution (under stirring) with an equal molar ratio. The transition metal ions, Fe, Co, Ni, and Cu, were provided by $FeCl_3$, $CoCl_2 \cdot 6H_2O$, $NiCl_2$, and $CuSO_4 \cdot 5H_2O$ respectively. After 1 h stirring, the precipitates were centrifuged and washed with DI water to remove access reactants. The as-synthesized Co-PBA and Cu-PBA NPs could be dispersed in water solution easily. By contrast, PB and Ni-PBA NPs would tend to aggregate and could not disperse well in water. Thus, a particle modification process [33,40] was used to improve the dispersion of PB and Ni-PBA NPs in water.

2.3. Layer-by-layer spin coating of PBA NPs and thin-film characterization

Layer-by-layer spin coating was used to prepare a PBA film on ITO. The water-soluble PB, Co-PBA, Ni-PBA, and Cu-PBA NPs were prepared as aqueous inks for coating with or without 10 vol% PEDOT:PSS additive. For each film coating, the NP ink was spin-coated onto an ITO glass substrate at 600 rpm for 5 s and then at 1500 rpm for another 30 s. Afterward, the coated film was cured at 120 °C for 10 min to accomplish the coating of one PBA layer. A multi-layer film could be prepared by repeated or interchanged layer-by-layer spin coating accordingly. The PBA films were then characterized with SEM, three-electrode cyclic voltammetry (a platinum sheet as the counterelectrode and a silver bar as the