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A WO₃–poly(butyl viologen) layer-by-layer film/ruthenium purple film based electrochromic device switching by 1 volt application



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ABSTRACT

A layer-by-layer (LbL) assembly of poly(butyl viologen) (PBV) and poly(peroxotungstate) was used for preparing a cathodically coloring dual electrochrome WO₃–PBV film. A new formulation containing ferrocenecarboxaldehyde and potassium hexacyanoruthenate(II) was employed for the first time and anodically coloring ruthenium purple (RP) thin films were electrodeposited. X-ray photoelectron spectroscopy and Fourier transform infrared analyses confirmed the RP film structure to be an inorganic coordination polymer: K_xFe_x^{III}[Ru^{II}(CN)₆]_y, wherein Fe³⁺ and Ru²⁺ color centers are flanked by CN[−] ligands. Nanoscale electrical conductivities determined by conducting atomic force microscopy were deduced to be 1.03 and 147.4 mS cm^{−1}, for the RP and WO₃–PBV LbL films respectively, which confirmed their ability to function as mixed conductors, attributes pertinent during optical switching. Reversible bias induced transition between purple and colorless hues was attained in the RP film and between deep blue and colorless states was achieved for the WO₃–PBV LbL film with coloration efficiencies of 188 and 380 cm² C^{−1} respectively. A complementarily coloring electrochromic device of WO₃–PBV/RP was fabricated with an environmentally benign, inexpensive aqueous electrolyte, which switched between blue, purple, and colorless states. The device exhibited an electrochromic efficiency of 476 cm² C^{−1} at 580 nm, an outstanding transmission modulation of 49%, and short switching times (~1 s); all under remarkably low operating voltages of ±1 V. The WO₃–PBV/RP device can deliver high optical contrast under low operating bias, and is highly scalable and durable, which demonstrates it to be ideal for practical optical switching devices like fast changing displays or smart windows.

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1. Introduction

An electrochromic thin film is characterized by its ability to sustain reversible and persistent change in optical properties when a voltage is applied to it [1]. Such a function can be of considerable interest for the film and can be applied to various electro-optical devices such as information displays, light shutters, smart windows, and variable reflectance mirrors [2–5]. As a well-known inorganic electrochrome, WO₃ films can display colorless and blue colored states by alternately applying positive and negative electrical voltages [6–8]. In the past, amorphous WO₃ was widely studied owing to fast electrochromic switching response arising from its large specific surface areas [4]. Electrochromic WO₃ films can be prepared by several methods such as

sputtering, evaporation, chemical vapor deposition (CVD), pulsed laser deposition (PLD), sol-gel, electrochemical deposition, hydrothermal reaction, and layer-by-layer (LbL) fabrication [9–13]. Layer-by-layer deposition of polymeric thin films was developed by Decher *et al.* wherein a substrate is immersed in alternating solutions of polycations and polyanions, resulting in linear film growth with the ultimate thickness being controlled by the number of bilayers deposited [14,15]. Optically active multilayers deposited by LbL have been shown to exhibit high-contrast ratios and excellent electrochemical stability [16]. LbL films composed of bilayers of chitosan/WO₃ were obtained via ionic attraction of oppositely charged materials [17]. Poly(aniline)-WO₃ hybrid thin films were synthesized via a molecular assembling route in a solution of aniline using peroxotungstic acid (PTA) as the dopant [18]. In yet another study, WO₃ films were fabricated using poly(acrylic acid) (PAA) and ammonium tungstate solutions through alternative dip coating method [19]. Previously, a LbL assembly of poly(butyl viologen)-poly(styrene sulfonate) was fabricated as a

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solid thin film; however, the electrochromism of the film was not studied by the authors [20]. Dual electrochrome composites are attractive, as both constituent species undergo coloration or bleaching simultaneously and as a consequence very high optical contrast ratios can be realized. In a previous report, DeLongchamp and co-workers studied a dual electrochromic multilayer films by combining two electrochromic polymer composites, namely poly(hexyl viologen) (PXV) and poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PSS) PEDOT:PSS colloid and obtained a 82% transmittance contrast at 525 nm [21]. In this context, viologens, which are salts of 1,1'-diquaternized 4,4'-bipyridyl compounds and are typically solution based cathodically coloring electrochromes [22,23], can be used in conjunction with WO_3 by using an appropriate deposition strategy to yield a composite capable of exhibiting large electrochromic contrast.

Among anodically coloring electrochromes, Prussian blue (PB), an inorganic coordination polymer, has been widely used and a variety of methods such as solution based routes, electrodeposition, and PB nanoparticle preparation are well reported [9,24,25]. In the past, PB/poly(aniline) LbL composite films have also been fabricated and multiple-hue electrochromism, fast switching, and high contrast ratios were achieved [26]. Prussian blue analogues involving the use of 3d and 4d group elements have been reported in the past [27–29]. Ruthenium purple (RP), a Prussian blue analogue, is relatively less investigated; it is also a dye, which strongly absorbs in the visible region with an absorption maximum positioned at 550 nm and appears purple in color [30]. The origin of color in RP is attributed to charge transfer between Ru^{2+} and Fe^{3+} centers. RP can be synthesized in two different forms, soluble and insoluble forms, namely $\text{KFe}[\text{Ru}(\text{CN})_6]$ and $\text{Fe}_4[\text{Ru}(\text{CN})_6]_3$ [31,32]. In the past, RP thin films were electrodeposited from a solution containing a soluble RP colloid, prepared by dissolving FeCl_3 and potassium hexacyanoruthenium(II) in water [30]. Linear polyethylene imine (LPEI)-RP multilayered nanocomposites were also fabricated in the past using LbL technique and a transmittance change of 84% at 560 nm and a coloration efficiency of $205 \text{ cm}^2 \text{ C}^{-1}$ were reported [33].

In view of the above-described developments in thin films for cathodic and anodic electrochromes, herein we present for the first time an electrochromic device configuration comprising of a LbL assembly of poly(peroxotungstate) and poly(butyl viologen) or PBV as the dual electrochrome cathodic layer and an anodically coloring RP film electrosynthesized from a novel precursor bath. The cathodic dual electrochrome film is initially made of $(\text{W}_2\text{O}_{11}^{2-})_n$ and PBV species, alternatively serving as negatively and positively charged layers respectively, which is transformed to a WO_3 -PBV LbL film, subsequent to the decomposition of peroxy groups. In the present article, a RP film was electrochemically deposited from a precursor solution containing an inorganic salt: potassium hexacyanoruthenium(II) which served as the source for Ru^{2+} color centers, and an organometallic compound, ferrocenecarboxaldehyde which furnished the Fe^{3+} species. Herein, the precursor solution is unlike the previously reported RP colloids [30]; it formed a pale yellow transparent homogeneous formulation in aqueous/non-aqueous solvents and yielded a colored deposit in the form of a thin film on conducting glass substrates under potentiodynamic conditions. This new deposition solution yielded purple colored (RP) films of high uniformity. The films were characterized in terms of absorption/transmission modulation, electrochemical redox potentials and reversibility, Fourier transform infrared (FTIR) spectroscopy, and scanning electron microscopy (SEM). The structure of the RP film was established by X-ray photoelectron spectroscopy (XPS). Nanoscale current carrying capabilities of the two films, which are essentially mixed conductors, capable of conducting both ions and electrons during coloration and bleaching, were studied by conducting atomic force

microscopy (C-AFM). Electrochromic devices based on WO_3 -PBV LbL film and RP film as the cathodic and anodic layers were constructed using an aqueous electrolyte, and potential induced reversible transitions between transparent, blue, and purple hues were followed by *in situ* spectroelectrochemistry, cyclic voltammetry, color switching speeds, and color cycling stability measurements, which demonstrated the feasibility of using this novel and highly scalable WO_3 -PBV/RP device for practical electrochromic applications.

2. Experimental procedure

2.1. Materials

Ferrocenecarboxaldehyde, potassium hexacyanoruthenium(II) ($\text{K}_4[\text{Ru}(\text{CN})_6]$), (3-aminopropyl)triethoxysilane (APS), 4,4'-bipyridyl, and 1,4-dibromobutane were procured from Sigma Aldrich. Hydrogen peroxide 30%, potassium chloride (KCl), tungsten (W) metal powder ($< 100 \mu\text{m}$), toluene, methanol, acetonitrile, 2-propanol, and n-hexane are procured from Merck. Ultrapure water (resistivity $18.2 \text{ M}\Omega \text{ cm}$) obtained through the Millipore Direct-Q 3 UV system was used as the solvent. Fluorine doped tin oxide ($\text{SnO}_2:\text{F}$ or FTO) coated glass substrates were purchased from Pilkington (sheet resistance: $14 \Omega \text{ sq}^{-1}$) and used after cleaning with 10 % HCl, soap solution, and distilled water and acetone.

2.2. Synthesis of precursor solutions

To a solution of ferrocenecarboxaldehyde (5 mM, 25 mL) prepared in methanol and 2-propanol mixed in a 1:1 v/v ratio, 25 mL of an aqueous solution of $\text{K}_4[\text{Ru}(\text{CN})_6]$ (5 mM) and KCl (50 mM) was added. All the contents were mixed and sonicated for 10 min to obtain a clear transparent orange yellow solution. This solution was used as a precursor solution for the electrochemical deposition of RP films.

A poly(peroxotungstic acid) or poly(PTA) solution was prepared by dissolution of $\sim 6.5 \text{ g}$ of W powder in 80 mL of H_2O_2 by gentle heating at 50–60 °C for a duration of 2–4 h with constant stirring. The obtained solution was a clear transparent solution and diluted with water so as to achieve a total volume of 120 mL. This solution was used as a stock solution for the LbL film. An APS solution was prepared by dissolving 100 mg of APS in 100 mL of toluene. A poly(butyl viologen) bromide solution was prepared by dissolving 50 mg PBV in 50 mL of water via sonication. Poly(butyl viologen) bromide or PBV was synthesized according to reported literature [34]. Briefly, to a 3.2 mmol solution of 4,4'-bipyridyl (500 mg) in acetonitrile (4 mL), a 3.2 mmol solution of 1,4-dibromobutane (690 mg) was added and microwave irradiation was performed for 10 min at 300 W, at a temperature of 100 °C. The crude was filtered and washed with acetonitrile and vacuum dried to obtain a yellow solid powder of PBV.

2.3. LbL assembly of WO_3 -PBV and RP films

Conductive FTO glass substrates were subjected to a surface cleaning by ultrasonication through successive immersions in distilled water, ethanol, and acetone prior to LbL fabrication. The cleaned FTO glass substrates were dipped in an APS solution for 1 h to graft the silane to the FTO/glass substrate. The aminopropyl groups of APS are protonated (NH_3^+) even in neutral pH and are available for electrostatic interaction with the poly(PTA)anion. The APS grafted FTO/glass substrate was dried and dipped in the poly(PTA) solution and the NH_3^+ groups of APS link to $\text{W}_2\text{O}_{11}^{2-}$ species via electrostatic attraction and a layer of $\text{APS}/(\text{W}_2\text{O}_{11}^{2-})_n$ is formed and this film was rinsed in water. This single layer with residual negative charges on the surface was used to create next

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