

Influencing factors on electrochromic hysteresis performance of ruthenium purple produced by a WO₃/Tris(2,2'-bipyridine)ruthenium(II)/polymer hybrid film

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ABSTRACT

A [Ru(bpy)₃]²⁺ (bpy = 2,2'-bipyridine)/WO₃ hybrid (denoted as Ru-WO₃) film was prepared as a base layer on an indium tin oxide electrode by electrodeposition from a colloidal solution containing peroxotungstic acid, [Ru(bpy)₃]²⁺ and poly(sodium 4-styrenesulfonate). A ruthenium purple (RP, Fe^{III}₄[Ru^{II}(CN)₆]₃, denoted as Fe^{III}-Ru^{II}) layer was electrodeposited on a neat WO₃ film or a Ru-WO₃ film from an aqueous RP colloid solution to yield a WO₃/RP bilayer film or a Ru-WO₃/RP bilayer film, respectively. The spectroscopic voltammetry measurement reveals that Fe^{II}-Ru^{II} is oxidized to Fe^{III}-Ru^{II} by a geared reaction of [Ru(bpy)₃]^{2+/3+} and Fe^{III}-Ru^{II} is reduced by a geared reaction of H_xWO₃/WO₃ in the Ru-WO₃/RP film. These geared reactions produced electrochromic hysteresis of the RP layer. However, the absorbance change in the hysteresis was smaller than that for the Ru-WO₃/Prussian blue bilayer film reported previously, resulting from the lower electroactivities of any redox component for the Ru-WO₃/RP film. The lower electroactivities could be explained by the specific interface between the Ru-WO₃ and RP layers. It might contribute to either an increase of the interfacial resistance between the Ru-WO₃ and RP layers, or formation of the physically precise interface between the layers to make it difficult for counter ions to be transported in the interfacial liquid phase involved in the redox reactions in the film. The specific interface at the Ru-WO₃ and RP layers could be formed possibly by the electrostatic interaction between [Ru(bpy)₃]²⁺ and terminal [Ru(CN)₆]⁴⁻ moieties of RP. It could be suggested by the decreased redox potential of [Ru(bpy)₃]²⁺ in the Ru-WO₃ layer from 1.03 to 0.61 V by formation of the RP layer.

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1. Introduction

Hybridization of functional molecules with solid materials such as polymers [1,2], clay compounds [3–6] and semiconductors [7–12] has been studied extensively to develop advanced functional materials that are applicable to molecule-based electronic and photoelectronic devices, e.g., solar cells [7–10,13], sensors [14–18], displays [19–21], and catalysts [5,6]. WO₃ is an n-type semiconductor as well as potential electrochromic material with the distinct color change from colorless WO₃ to blue H_xWO₃ (so called tungsten bronze) by electrochemical reduction accompanying intercalation of cations (H⁺ or Li⁺) [22–24] (Eq. (1)).



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[Ru(bpy)₃]²⁺ (bpy = 2,2'-bipyridine) is a stable redox molecule with an intense metal-to-ligand charge transfer (MLCT) absorption band at 453 nm in water [25,26], and it reversibly disappears by oxidation to [Ru(bpy)₃]³⁺. Hybridization of [Ru(bpy)₃]²⁺ with WO₃ has been achieved by an electrochemical technique from an aqueous colloid solution containing peroxotungstic acid (PTA), [Ru(bpy)₃]²⁺ and poly(sodium 4-styrenesulfonate) (PSS) to yield a [Ru(bpy)₃]²⁺/WO₃ hybrid (Ru-WO₃) film, demonstrating multi-color electrochromism based on redox reactions of [Ru(bpy)₃]^{2+/3+} and H_xWO₃/WO₃ [11,12]. The charge transport by [Ru(bpy)₃]^{2+/3+} redox in the film was found to occur rapidly through the conduction band of WO₃ [27].

A Prussian blue (Fe^{III}₄[Fe^{II}(CN)₆]₃, denoted as Fe^{III}-Fe^{II}) layer was formed on the Ru-WO₃ film to fabricate the Ru-WO₃/Prussian blue bilayer film. This film first produced unique hysteretic potential profile of the absorbance due to Prussian blue, which was defined as electrochromic hysteresis performance [28]. However, this phenomenon is not sufficiently understood yet because it is only an example for the Ru-WO₃/Prussian blue film. Ruthenium purple (RP)

is a macromolecule composing a repeating unit of $\text{Fe}^{\text{III}}_4[\text{Ru}^{\text{II}}(\text{CN})_6]_3$ (denoted as $\text{Fe}^{\text{III}}\text{-Ru}^{\text{II}}$), similar to Prussian blue. RP exhibits an intense absorption band (at 556 nm) assigned to intervalence charge transfer (IVCT) of $\text{Fe}^{\text{III}}\text{-NC-Ru}^{\text{II}}$ [29,30], and it disappears by reduction to $\text{Fe}^{\text{II}}\text{-Ru}^{\text{II}}$ or oxidation to $\text{Fe}^{\text{III}}\text{-Ru}^{\text{III}}$ [29–32]. The bilayer film (WO_3/RP or $\text{Ru-WO}_3/\text{RP}$) of RP layered on the WO_3 or Ru-WO_3 film could yield new multi-color electrochromism involving the color change by redox of the RP layer, and especially the latter providing insight into the electrochromic hysteresis of bilayer films induced by the Ru-WO_3 film. The electrochemical aspects of the $\text{Ru-WO}_3/\text{RP}$ film were preliminarily reported [32]. However, they were neither discussed quantitatively nor compared with WO_3/RP film and $\text{Ru-WO}_3/\text{Prussian blue}$. Herein, we report electrochromic reactions of the WO_3/RP and $\text{Ru-WO}_3/\text{RP}$ bilayer films prepared by a two-step electrochemical deposition technique. The electrochemical reactions responsible for the electrochromic hysteresis performance of RP on the $\text{Ru-WO}_3/\text{RP}$ film are revealed using a spectroscopic voltammetric (SCV) technique, and compared with the $\text{Ru-WO}_3/\text{Prussian blue}$ film to discuss influencing factors on the hysteresis.

2. Experimental

2.1. Materials

$[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$, PSS ($M_w = 70,000$) and $\text{K}_4[\text{Ru}(\text{CN})_6]$ were purchased from Aldrich Chemical Co., Inc. Tungsten powder, hydrogen peroxide (30%) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were purchased from Kanto Chemical Co., Inc. An indium tin oxide (ITO)-coated glass ($10 \Omega/\square$) was purchased from Asahi Glass Co., Ltd. All reagents were used as received.

2.2. Preparations

2.2.1. WO_3 film and Ru-WO_3 film [12]

0.92 g (5.0 mmol) of tungsten powder was dissolved in a 30% hydrogen peroxide to prepare a PTA solution. After excess hydrogen peroxide was decomposed by Pt black, ethanol was added to the solution for stabilizing PTA to prepare an aqueous ethanol solution (30 vol%) containing 100 mM PTA (based on tungsten atom) as a stock solution. $[\text{Ru}(\text{bpy})_3]^{2+}$ and PSS solutions were added to the PTA solution to prepare an aqueous ethanol solution (30 vol%) containing 1 mM $[\text{Ru}(\text{bpy})_3]^{2+}$, 50 mM PTA and 30 mM PSS. After standing the solution at room temperature, it turned into a colloid solution. A Ru-WO_3 film was electrodeposited from the colloid solution on an ITO electrode with stirring under the potentiostatic conditions ($-0.45 \text{ V vs. Ag/AgCl}$) to 1.0 C cm^{-2} , using a conventional single-compartment electrochemical cell equipped with an ITO working electrode, an Ag/AgCl reference electrode and a platinum wire counter electrode. The prepared film was cathodically polarized at $-0.5 \text{ V vs. saturated calomel reference electrode (SCE)}$ in a 0.1 M HNO_3 aqueous solution to complete electrodeposition of PTA. A neat WO_3 film was also cathodically electrodeposited from a 30 vol% ethanol solution containing 50 mM PTA and 30 mM PSS (without $[\text{Ru}(\text{bpy})_3]^{2+}$) on an ITO electrode under the same conditions as the Ru-WO_3 film.

X-ray diffraction measurement indicated that WO_3 is amorphous in either the neat WO_3 film or the Ru-WO_3 film [12]. The thickness of these films was measured by a scanning electron microscopic technique to be $560 (\pm 24) \text{ nm}$ (in average) [12]. The UV-visible absorption spectrum of the Ru-WO_3 film exhibited a MLCT band of $[\text{Ru}(\text{bpy})_3]^{2+}$ at $\lambda_{\text{max}} = 459 \text{ nm}$. The coverage (Γ_{Ru}) of $[\text{Ru}(\text{bpy})_3]^{2+}$ on the film was calculated to be $3.4 \times 10^{-8} \text{ mol cm}^{-2}$

from the absorbance (A_{459}) at 459 nm and its molar absorption coefficient ($14,600 \text{ M}^{-1} \text{ cm}^{-1}$) in an aqueous solution.

2.2.2. RP film, WO_3/RP film and $\text{Ru-WO}_3/\text{RP}$ film

The RP film was electrodeposited on an ITO electrode from an aqueous RP colloid solution (pH 2.0) containing 0.5 mM FeCl_3 , 0.5 mM $\text{K}_4[\text{Ru}(\text{CN})_6]$ and 40 mM KCl by a potentiodynamic multi-sweep (100 cycles) in a range of -0.3 to $1.0 \text{ V vs. Ag/AgCl}$. A RP colloid is formed from FeCl_3 and $\text{K}_4[\text{Ru}(\text{CN})_6]$ in an equimolar ratio in an aqueous solution. As is the case of the RP film, the RP layer was formed on the WO_3 film or Ru-WO_3 film by a potentiodynamic multi-sweep (200 cycles) in a range of -0.5 to 1.5 V to yield the WO_3/RP film or $\text{Ru-WO}_3/\text{RP}$ film, respectively.

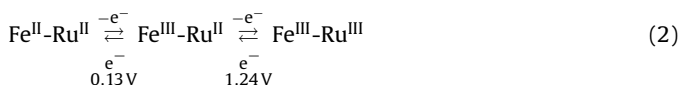
2.3. Measurements

SCV measurements were conducted by combining a photodiode array spectrophotometer (Shimadzu, Multispec-1500) with a potentiostat (Hokuto Denko, HA-501G) and a function generator (Hokuto Denko, HB-104). A single-compartment spectroelectrochemical cell (1 cm path length) was equipped with a modified working electrode, an SCE reference electrode and a platinum wire counter electrode for SCV measurements.

3. Results

3.1. RP film

The UV-visible absorption spectrum of an RP film exhibited the intense IVCT band at $\lambda_{\text{max}} = 556 \text{ nm}$. The coverage (Γ_{RP} , mol cm^{-2}) of the RP unite (containing a Fe^{III} ion and a Ru^{II} ion) in the film was calculated to be $1.5 \times 10^{-8} \text{ mol cm}^{-2}$ from absorbance ($A_{556} = 0.17$) and the molar absorption coefficient ($\epsilon_{\text{RP}} = 11,400 \text{ M}^{-1} \text{ cm}^{-1}$) [32] at 556 nm according to the Lambert-Beer law, $A_{556} = \epsilon_{\text{RP}} \Gamma_{\text{RP}} \times 10^3$. The cyclic voltammogram (CV) of the RP film in a 40 mM KCl aqueous solution gave a reversible redox response of $\text{Fe}^{\text{II}}\text{-Ru}^{\text{II}}/\text{Fe}^{\text{III}}\text{-Ru}^{\text{II}}$ at 0.13 V vs. SCE in a range of -0.2 to 0.7 V , as shown in Fig. S1a (“Reversible” means consistence in the charge amount between anodic (1.5 mC cm^{-2}) and cathodic (1.4 mC cm^{-2}) waves). An *in situ* UV-visible absorption spectral technique is useful to directly observe the electrochemical reactions of redox centers. In an *in situ* UV-visible absorption spectral change recorded simultaneously with the CV measurement, the absorption band at 556 nm decreased during the reductive scan from 0.3 V (inset of Fig. S1). The A_{556} decrease corresponded to the increase of the cathodic current at 0.25 V, as indicated by the potential profile of A_{556} in Fig. S1. The disappearance of the IVCT band of $\text{Fe}^{\text{III}}\text{-Ru}^{\text{II}}$ in the spectral change (inset of Fig. S1) corroborates that $\text{Fe}^{\text{III}}\text{-Ru}^{\text{II}}$ is completely reduced during the reductive scan to -0.2 V . In an extended scan from -0.2 to 1.5 V (Fig. S2), a redox wave assigned to further oxidation of $\text{Fe}^{\text{III}}\text{-Ru}^{\text{II}}$ to $\text{Fe}^{\text{III}}\text{-Ru}^{\text{III}}$ was observed at 1.24 V, overlapping with an anodic current based on chloride oxidation. The electrochemical reactions of the RP film are summarized in Eq. (2).



3.2. WO_3/RP bilayer film

The CV of an aqueous 0.5 mM RP colloid solution containing 40 mM KCl as measured using an ITO electrode clearly exhibited redox responses at 1.24 and 0.77 V in the potential range of -0.5 to 1.5 V (not shown), both of which are assigned to $\text{Fe}^{\text{III}}\text{-Ru}^{\text{II}}/\text{Fe}^{\text{III}}\text{-Ru}^{\text{III}}$ of RP colloid and $[\text{Ru}(\text{CN})_6]^{4-/3-}$ existing in equilibrium in the solu-

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