Spectrocyclic Voltammetry of Ruthenium Purple Electrodeposited on a WO_3/Tris(2,2′-bipyridine)-ruthenium(II)/Polymer Hybrid Film

*Koji Sone, Masayuki Yagi**

Summary: Electrochemical reactions of Ruthenium purple, $Fe_4^{III}[Ru^{II}(CN)_6]_3$ (RP; Fe^{III}-Ru^{II}) were studied using a spectrocyclic voltammetry (SCV) technique. The SCV measurement for an RP film coated on an ITO electrode showed a reversible redox between RP and Ruthenium white (RW; Fe^{II}-Ru^{II}) at 0.14 V vs saturated calomel reference electrode (SCE). An RP film was electrodeposited on a hybrid film of tungsten trioxide (WO_3)/tris(2,2′-bipyridine)ruthenium(II) ($[Ru(bpy)_3]^{2+}$; bpy = 2,2′-bipyridine)/poly(sodium 4-styrenesulfonate) (PSS) (denoted as WRP film) from a colloidal solution containing 0.5 mM $FeCl_3$, 0.5 mM $K_4[Ru(CN)_6]$ and 40 mM KCl using a potentiodynamic multi-sweep technique. In a cyclic voltammogram (CV) of a WRP/RP film, a redox response was observed at 0.61 V in addition to essential redox responses of WRP hybrid film (a $[Ru(bpy)_3]^{2+}/[Ru(bpy)_3]^{3+}$ redox at 1.03 V and a H_xWO_3/WO_3 redox below 0.09 V), but a redox response of RW/RP was not observed at 0.14 V. The SCV measurement for the WRP/RP film suggested that the redox response at 0.61 V is attributed to a redox of $[Ru(bpy)_3]^{2+}/[Ru(bpy)_3]^{3+}$ interacted electrostatically with RP. It also showed that RW is oxidized to RP *via* $[Ru(bpy)_3]^{2+}/[Ru(bpy)_3]^{3+}$ redox and RP is reversibly reduced to RW *via* H_xWO_3/WO_3 redox. This unique geared electrochemical reaction for the WRP/RP film leads to a hysteresis property of an RW/RP redox.

Keywords: charge transfer; electrochemistry; Ruthenium purple; spectrocyclic voltammetry; tungsten trioxide

Introduction

WO_3 is a promising electrochromic material giving a reversible color change in a redox reaction between WO_3 (colorless) and H_xWO_3 (dark blue), and is expected to be applied to electronic devices such as smart windows,[1–5] displays[6–10] and electronic papers.[11,12] Hybridization of WO_3 with other electrochromic materials is anticipated to expand the application of WO_3 to a large variety of electronic devices. $[Ru(bpy)_3]^{2+}$ is a well-studied electrochromic molecule giving a reversible redox between $[Ru(bpy)_3]^{2+}$ (orange) and $[Ru(bpy)_3]^{3+}$ (colorless). Recently, we reported hybridization of WO_3 with $[Ru(bpy)_3]^{2+}$ by a unique electrodeposition from a colloidal triad solution containing peroxotungstic acid, $[Ru(bpy)_3]^{2+}$ and PSS, yielding a $WO_3/[Ru(bpy)_3]^{2+}$/PSS (denoted as WRP) hybrid film with a multicolor electrochromic performance by combination of WO_3 and $[Ru(bpy)_3]^{2+}$.[13,14] The unique electrochemical features of the WRP film have been revealed by the spectroelectrochemical measurements. All $[Ru(bpy)_3]^{2+}$ in the film is electrochemically oxidized to $[Ru(bpy)_3]^{3+}$ in the film owing to an ohmic contact formed at the interface between $[Ru(bpy)_3]^{2+}$ and WO_3, and electrons from $[Ru(bpy)_3]^{2+}$ are transferred rapidly through a conduction band of WO_3 to the corrector electrode. Moreover

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the flat band (FB) potential of WO_3 was found to decrease from 0.26 to 0.09 V vs SCE by hybridization of $[Ru(bpy)_3]^{2+}$.[14]

RP is known to be a macromolecule with a repeating unit of $Fe_4^{III}[Ru^{II}(CN)_6]_3$ and to afford a reversible redox response between RP (Fe^{III}-Ru^{II}, purple) and RW (Fe^{II}-Ru^{II}, colorless) with an electrochromic performance.[15–17] A new hybrid film with three different redox components, WO_3, $[Ru(bpy)_3]^{2+}$ and RP is herein prepared by a simple electrochemical technique on the WRP hybrid film. In the present paper, electrochemical reactions on the WRP/RP film are studied using a SCV technique that is useful to observe directly real changes of the redox molecule in electrochemical reactions.[18,19]. The SCV results are reported to show unique electrochemical reactions of RW/RP which are geared by $[Ru(bpy)_3]^{2+}$/$[Ru(bpy)_3]^{3+}$ and H_xWO_3/WO_3 in the WRP/RP film, leading to a hysteresis property of an RW/RP redox.

Experimental

Materials

$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$, poly(sodium 4-styrenesulfonate) (PSS) (Mw = 70000) and $K_4[Ru(CN)_6]$ were purchased from Aldrich Chemical Co. Inc. $FeCl_3 \cdot 6H_2O$ was purchased from Kanto Kagaku Co., Ltd. All the reagents were used as received.

Preparations

An RP film was electrodeposited on an ITO electrode from a colloidal aqueous solution (pH = 2.0) containing 0.5 mM $FeCl_3$, 0.5 mM $K_4[Ru(CN)_6]$ and 40 mM KCl by a potentiodynamic multi-sweep between −0.3 and 1.0 V vs Ag/AgCl.[16,17] A WRP hybrid film was prepared according to the procedure reported elsewhere.[14] Tungsten powder was dissolved in a 30% hydrogen peroxide to prepare a peroxotungstic acid (PTA) solution. After excess hydrogen peroxide was decomposed by Pt black, ethanol was added to the solution for stabilizing PTA to prepare finally an aqueous ethanol solution (30 vol.%) containing 100 mM PTA (based on W concentration) as a stock solution. $[Ru(bpy)_3]^{2+}$ and PSS solutions were added to the PTA solution to prepare an aqueous ethanol solution (30 vol.%) containing 1 mM $[Ru(bpy)_3]^{2+}$, 50 mM PTA and 30 mM PSS. After standing the solution at room temperature, it turned into a colloidal triad solution of $[Ru(bpy)_3]^{2+}$, PTA and PSS. A WRP film was electrodeposited on an ITO electrode from the colloidal triad solution with stirring under the potentiostatic conditions (−0.45 V vs Ag/AgCl) up 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 thickness of the WRP film was measured by a scanning electron microscopic technique to be 560 (±24) nm (in average) in electrodeposition with 1.0 C cm^{-2}. $[Ru(bpy)_3]^{2+}$ is uniformly confined in the film, and its coverage of $[Ru(bpy)_3]^{2+}$ was calculated to be 2.2×10^{-8} mol cm^{-2} (in electrodeposition with 1.0 C cm^{-2}) from the absorbance ($A_{459} = 0.33$) at $\lambda_{max} = 459$ nm and the molar absorption coefficient of 14600 M^{-1} cm^{-1} for its aqueous solution. For preparation of a WRP/RP film, an RP film was electrodeposited on the WRP hybrid film from the same colloidal solution by a potentiodynamic multi-sweep between −0.5 and 1.5 V vs Ag/AgCl.

Measurements

SCV measurements were carried out 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 was equipped with a modified working electrode, SCE as a reference electrode and a platinum wire counter electrode.

Results and Discussion

SCV of a Ruthenium Purple Film

Figure 1 shows repetitive CVs of an ITO electrode in a colloidal solution (pH = 2.0)

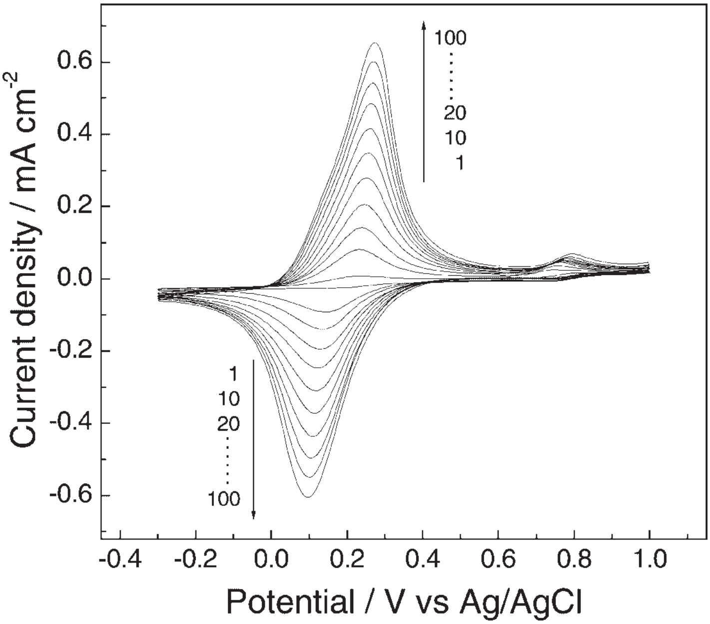

Figure 1.
Repetitive CVs of an ITO electrode in a colloidal aqueous solution (pH = 2.0) containing 0.5 mM $FeCl_3$, 0.5 mM $K_4[Ru(CN)_6]$ and 40 mM KCl as measured at 50 mV s^{-1} of a scan rate. The number of potential cycles is 100.

containing 0.5 mM $FeCl_3$, 0.5 mM $K_4[Ru(CN)_6]$ and 40 mM KCl. A reversible redox assigned to RW/RP was observed at 0.18 V,[15–17] and the anodic peak current at 0.27 V increased with repetition of a continuous potential sweep, indicating the electrochemical formation of the RP film. The CV of the RP film on an ITO electrode exhibited a reversible response at 0.14 V for a RW/RP redox, as shown by a solid line in Figure 2. The coverage (Γ_{RP}) of the RP unit electrodeposited was calculated as 2.1×10^{-8} mol cm^{-2} from the anodic wave area in the CV. A UV-visible absorption spectrum of the RP film exhibits an intense band at $\lambda_{max} = 565$ nm, which is close to that ($\lambda_{max} = 559$ nm) of an aqueous solution of RP colloid and is assigned to an intervalence charge transfer (IVCT) band of Fe^{III}-NC-$Ru^{II} \rightarrow Fe^{II}$-NC-$Ru^{III}$.[15,16] The molar absorption coefficient (ε_{RP}/M^{-1} cm^{-1}) at 565 nm was given to be 11400 M^{-1} cm^{-1} from the absorbance ($A_{565} = 0.24$) at 565 nm and $\Gamma_{RP} = 2.1 \times 10^{-8}$ mol cm^{-2} according to the Lambert-Beer equation, $A_{565} = \varepsilon_{RP}\ \Gamma_{RP} \times 10^3$. It is consistent with that (9700 M^{-1} cm^{-1}) of a colloidal RP solution at $\lambda_{max} = 559$ nm in a literature reported earlier.[20]

In situ UV-visible absorption spectral changes during the CV measurement of the RP film are shown in Figure 3A and B. In applying 0.7 V, the spectrum showed a band at 565 nm due to RP in a visible region. A_{565} decreased with a potential sweep from 0.7 V to −0.2 V by reduction of RP to RW (Figure 3A). A reverse scan from −0.2 V to 0.7 V (Figure 3B) showed that the electrochemical reaction of RW/RP is completely reversible. The change of A_{565} with the potential sweep is shown together with the CV of the RP film in Figure 2.

A_{565} decreased at the close potential (0.22 V) to that for the rise of the cathodic current, and it increased with the rise of the anodic current at 0.04 V. A_{565} came back to the original value before the potential scan. The A_{565} change thus corresponds to a redox reaction of RW/RP in the CV measurement, indicating that the absorbance change is available in following the electrochemical reactions.

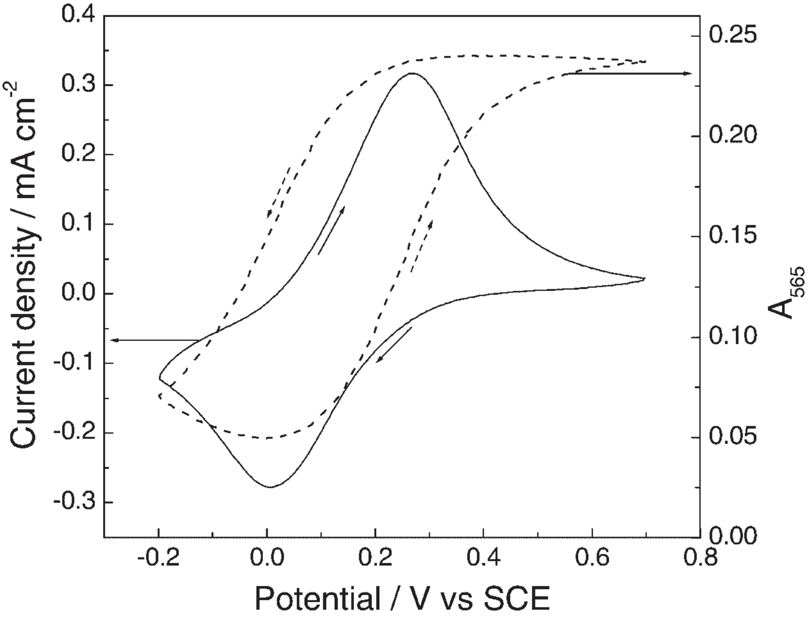

Figure 2.
SCV of the RP film coated on an ITO electrode in a 40 mM KCl aqueous solution (pH = 2.0) as measured at 50 mV s^{-1} of a scan rate.

In an extended oxidative scan to 1.5 V, the anodic response was observed at 1.24 V due to further oxidation of RP to Fe^{III}-Ru^{III}, showing the A$_{565}$ decrease. However, the latter is not very stable to result in a decrease of the anodic current at 1.24 V with a repetitive potential scan. The redox reactions of the RP film on the ITO electrode are summarized in Eq (1).

$$\underset{\text{(RW)}}{\mathrm{Fe^{II}\text{-}Ru^{II}}} \overset{0.14\,\mathrm{V}}{\rightleftharpoons} \underset{\text{(RP)}}{\mathrm{Fe^{III}\text{-}Ru^{II}}} \overset{0.24\,\mathrm{V}}{\rightleftharpoons} \underset{\text{not very stable}}{\mathrm{Fe^{III}\text{-}Ru^{III}}} \tag{1}$$

SCV of a WRP/RP Film

UV-visible absorption spectrum of the WRP/RP film showed two peaks at

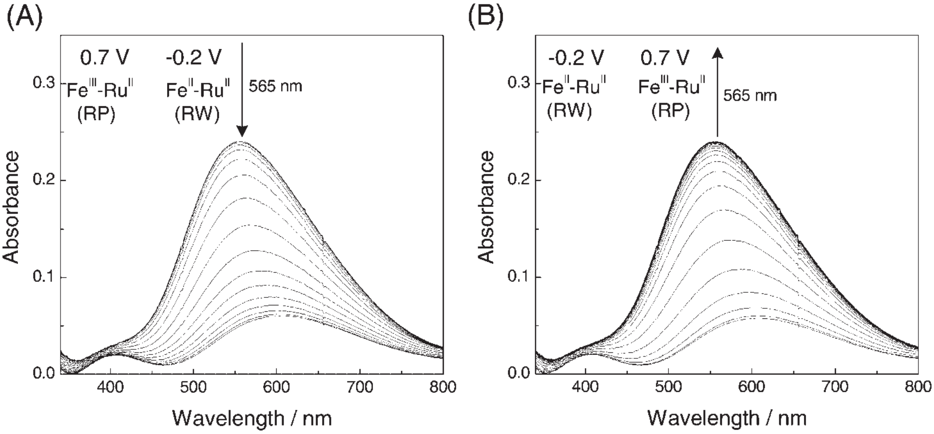

Figure 3.
In situ UV-visible absorption spectral changes during the CV measurement of the RP film coated on an ITO electrode in a 40 mM KCl aqueous solution (pH = 2.0) as measured at 50 mV s^{-1} of a scan rate.

$\lambda_{max} = 470$ and 549 nm. The former is assigned to a metal-to-ligand charge transfer (MLCT) band of $[Ru(bpy)_3]^{2+}$, and the latter being to the IVCT band of RP. The λ_{max} (470 nm) for the former shifts to a higher wavelength compared with that (459 nm) for the WRP film. By association, the λ_{max} (549 nm) for the latter shifts to a lower wavelength compared to that (565 nm) for the RP film. This is indicative of strong interaction between $[Ru(bpy)_3]^{2+}$ and RP in the WRP/RP film. Γ_{RP} in the WRP/RP film was estimated to 2.9×10^{-8} mol cm^{-2} from $A_{549} = 0.33$ and $\varepsilon_{RP} = 11400$ M^{-1} cm^{-1} (*vide supra*) since the contribution of the absorption by $[Ru(bpy)_3]^{2+}$ to the absorbance (A_{549}) at 549 nm of the film is 5%. A CV of the WRP film coated on an ITO electrode was reported; it exhibited a reversible redox wave at 1.03 V on $[Ru(bpy)_3]^{2+}/[Ru(bpy)_3]^{3+}$ and a redox response of H_xWO_3/WO_3 below a flat band potential (0.09 V) of WO_3.[14] A CV of the WRP/RP film on an ITO electrode is shown by a solid line in Figure 4. The CV gave a redox wave at 0.61 V in addition to redox responses on $[Ru(bpy)_3]^{2+}/[Ru(bpy)_3]^{3+}$ and H_xWO_3/WO_3, but a redox based on RW/RP was not observed at 0.14 V.

Since *in situ* UV-visible absorption spectral change during the CV measurement of the WRP/RP film includes several electrochemical reaction phases, it was segmented into each phase as shown in Figure 5A~F. In Figure 5A, absorbance over 500 nm decreased due to oxidation of H_xWO_3 to WO_3 during the potential sweep from −0.5 V to 0.2 V. During the potential scan from 0.2 V to 0.92 V, absorbance at 470 nm (A_{470}) decrease by oxidation of $[Ru(bpy)_3]^{2+}$ as shown in Figure 5B. In Figure 5C A_{549} increased during the potential scan from 0.92 V to 1.15 V, showing that RP is formed from RW though the corresponding electrochemical reaction can not be observed in the CV measurement. In Figure 5D A_{470} decreased again during the potential scan from 1.15 V to 1.5 V. During the reverse scan from 1.5 V to 0.0 V, $[Ru(bpy)_3]^{3+}$ was reduced to $[Ru(bpy)_3]^{2+}$, leading to the increase of A_{470} (Figure 5E), and in the cathodic scan to −0.5 V the

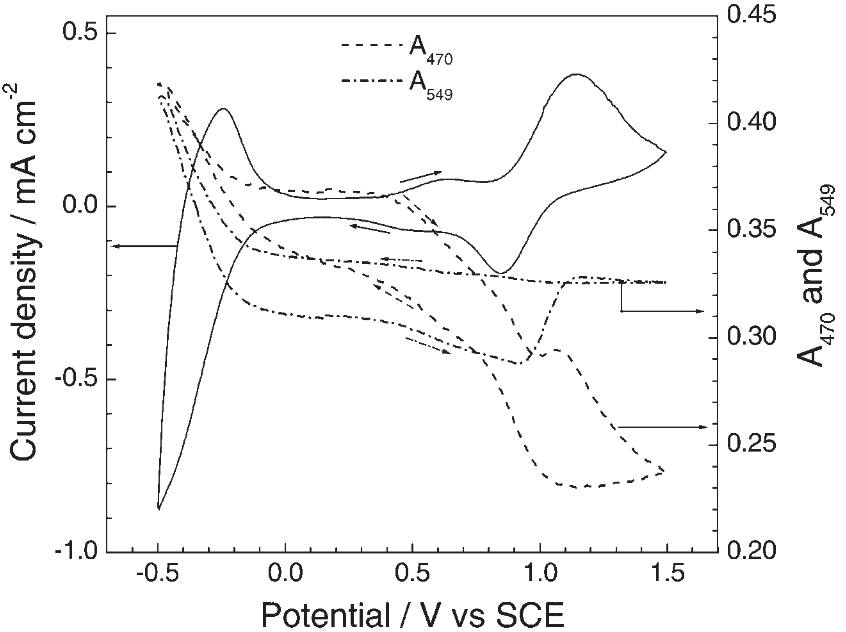

Figure 4.

SCV of the WRP/RP film coated on the ITO electrode in a 40 mM KCl aqueous solution (pH = 1.6) as measured at 50 mV s^{-1} of a scan rate.

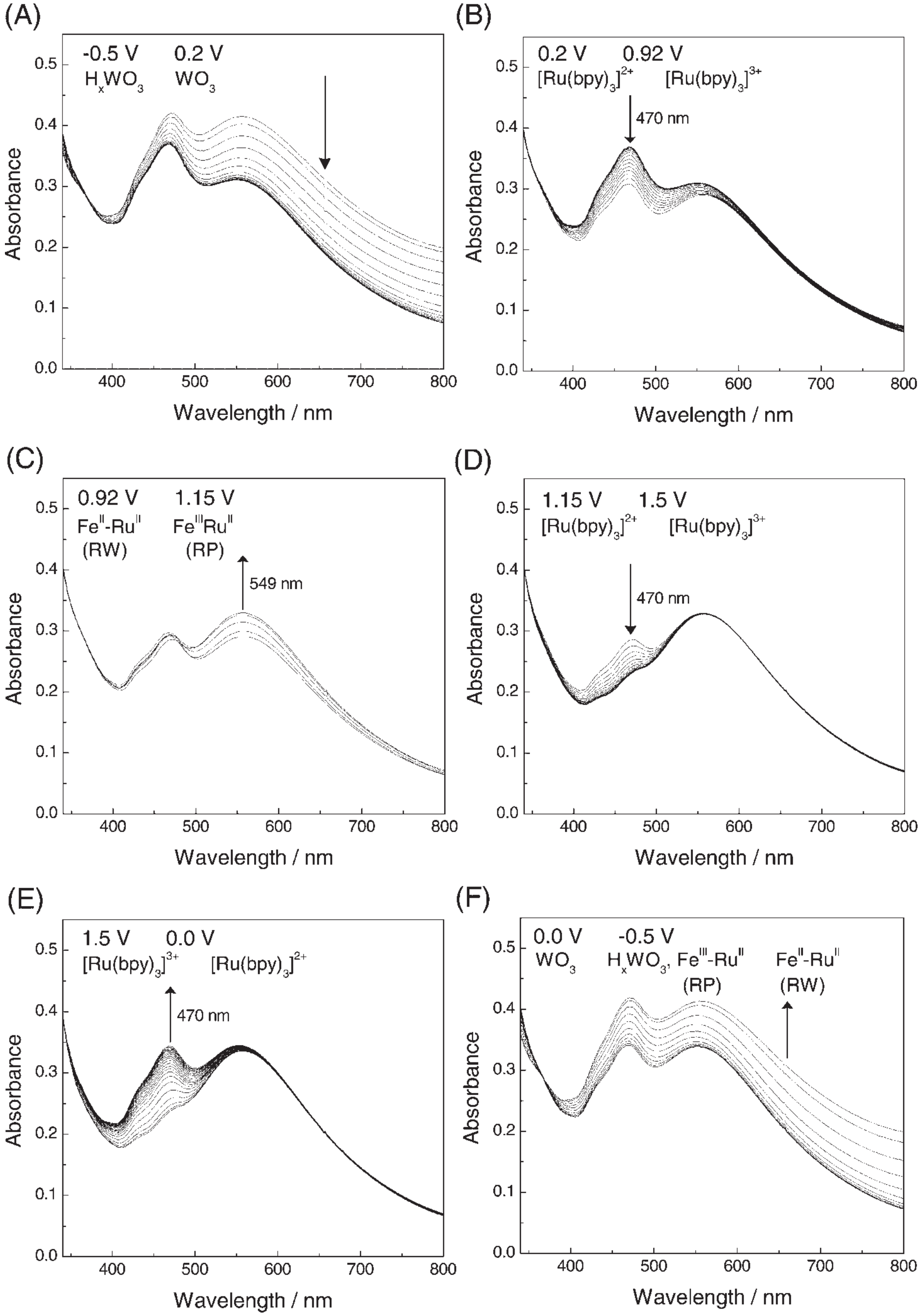

Figure 5.

In situ UV-visible absorption spectral changes during the CV measurement of the WRP/RP film coated on the ITO electrode in a 40 mM KCl aqueous solution (pH = 1.6) as measured at 50 mV s^{-1} of a scan rate.

absorption spectrum completely came back to the original spectrum before a potential scan. (Figure 5F)

In order to correlate the absorbance data to electrochemical reactions, the potential profiles of A_{470} and A_{549} (mainly due to

$[Ru(bpy)_3]^{2+}$ and RP, respectively) are shown together with the CV of the WRP/RP film in Figure 4. As for the redox response at 0.61 V in the CV, A_{470} decreased with the increase in the anodic current at 0.61 V, indicating that it is based on oxidation of $[Ru(bpy)_3]^{2+}$. It should be pointed out that the redox potential (0.61 V) of $[Ru(bpy)_3]^{2+}$/$[Ru(bpy)_3]^{3+}$ in the WRP/RP film is lower by 0.42 V than that (1.03 V) in the WRP film. This is consistent with the significant red shift of λ_{max} (470 nm) for the MLCT band of $[Ru(bpy)_3]^{2+}$ for the WRP/RP film compared with that (459 nm) for the WRP film. This reveals that the red shift is mainly contributed to the increase of the d level energy of the Ru center rather than the decrease of π^* level energy of bpy ligands. The lower redox potential could be ascribed to strong electrostatic interaction of $[Ru(bpy)_3]^{2+}$ with terminal anionic $Ru^{II}CN^-$ of RP to stabilize $[Ru(bpy)_3]^{3+}$.

In an anodic scan, A_{470} decreased at 0.4 V and suspended at 0.95 V. Alternatively A_{549} increased at the same potential (0.95 V). A_{470} decreased again after saturation of the A_{549} increase at 1.1 V. The profiles of A_{470} and A_{549} suggested that RW is oxidized to RP by $[Ru(bpy)_3]^{3+}$ generated electrochemically in the film. While, during the reverse cathodic scan A_{470} drably increased from 1.5 V to 0.0 V, with keeping A_{549} which is higher than that during the anodic scan at 0 V ~ 0.95 V. This shows that the WRP/RP film stays in RW (Fe^{II}-Ru^{II}) and RP (Fe^{III}-Ru^{II}) states during anodic and cathodic scans, respectively, under the same potential conditions in the range of 0 V ~ 0.95 V. The higher A_{549} decreased to the low value after reduction of WO_3 to H_xWO_3 at –0.2 V, indicating that RP is reduced to RW by H_xWO_3 formed electrochemically from WO_3. The electrochemical reactions of RW/RP geared by $[Ru(bpy)_3]^{2+}$/$[Ru(bpy)_3]^{3+}$ and H_xWO_3/WO_3 were demonstrated in the WRP/RP film, leading to a hysteresis property of an RW/RP redox.

Conclusion

A WRP/RP film on an ITO electrode was prepared by electrodeposition of a Ruthenium purple (RP; Fe^{III}-Ru^{II}) film on a $WO_3/[Ru(bpy)_3]^{2+}$/PSS (WRP) hybrid film using a potentiodynamic multi-sweep technique. The SCV measurement for the WRP/RP film showed that RW is oxidized to RP *via* $[Ru(bpy)_3]^{2+}$/$[Ru(bpy)_3]^{3+}$ redox and RP is reversibly reduced to RW *via* H_xWO_3/WO_3 redox. The SCV technique was demonstrated to be useful to reveal such geared electrochemical reactions that are difficult to be investigated using a conventional CV technique. The unique geared electrochemical reactions for the WRP/RP film led to a hysteresis property of an RW/RP redox that could provide a prospective possibility for development of new memory devises based on the WRP hybrids, as well as display devises with advanced multicolor electrochromic performances.

Acknowledgements: Research was partially supported by Grant for Promotion of Niigata University Research Projects. Fellowship grant was provided by The Niigata Engineering Promotion, Inc. (KS)

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