Electron Transfer in Tris(bipyridine)ruthenium(II) Complex Films on ITO

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The packing density of Ru(bpy)$_3$ units was shown to be a crucial factor in constructing thin films having reversible redox functions. We have succeeded in controlling the surface of Ru(bpy)$_3$ thin films using a bottom-up fabrication procedure. The redox function of the resulting multilayered films is highly predictable and reliable, although the productivity of the stepwise film growth of **1** is not high.

Surface control with immobilized redox-active molecules in thin films is one of the most important issues for the development of molecular-based electronic/optic devices.[1] It is an important elementary concept for electron-transfer phenomena that a reversible redox cycle takes place in association with the motion of counter-ions. Taking this basic principle into consideration, we can anticipate that the packing density of immobilized redox-active molecules is a crucial factor in realizing efficient reversible redox cycles, i.e., ensuring a smoother migration of counter-ions in solid films occurs. Self-assembled monolayers (SAMs) and related thin films consisting of redox-active molecules have recently become of increasing interest.[2–7] However, there has been little study of the density control of redox-active molecules in these films. Herein, we report on a simple bottom-up method that enables us to control the density of redox-active molecules at the surface. This will help achieve efficient electron-transfer reactions in thin film redox systems.

Tris(bipyridine)ruthenium(II) (Ru(bpy)$_3$) derivatives containing phosphonic acid groups were employed in this study. Ru(bpy)$_3$ shows intriguing photophysical and electrochemical features, in addition to its inherent chemical stability.[8] Therefore, this metal complex has been widely used in research on constructing molecular-based electronic/optic devices, such as photosensitized solar cells and electrogenerated chemiluminescence devices.[7] Methods that have been utilized for fabricating Ru(bpy)$_3$ thin films include molecular-based techniques, such as SAMs,[2–6] Langmuir–Blodgett (LB) multilayers, and conventional spin-casting methods.[7] In this study, we used a bottom-up procedure utilizing the sequential deposition of phosphonate-containing Ru(bpy)$_3$ with ZrOCl$_2$ acting as an interlayer cross-linking reagent.[2]

The chemical structures of the phosphonate-containing Ru(bpy)$_3$ used are shown in Figure 1, which also outlines the steps used in our approach. In general, this type of stepwise adsorption technique uses a phosphonate molecule. However, as reported previously, it was shown that this approach was very effective for the sequential multilayer formation of a bulky phosphonate molecule, such as **2**.[2] This procedure consists of a two-step fabrication route, as follows. Pretreated indium tin oxide (ITO) substrates having phosphonate surfaces were initially immersed in an aqueous ZrOCl$_2$ solution. They were then treated with an aqueous solution of **2**. This repetitive two-step process was applied to laminate the Ru(bpy)$_3$ units (each repetition of this process is hereafter denoted as a “cycle”).

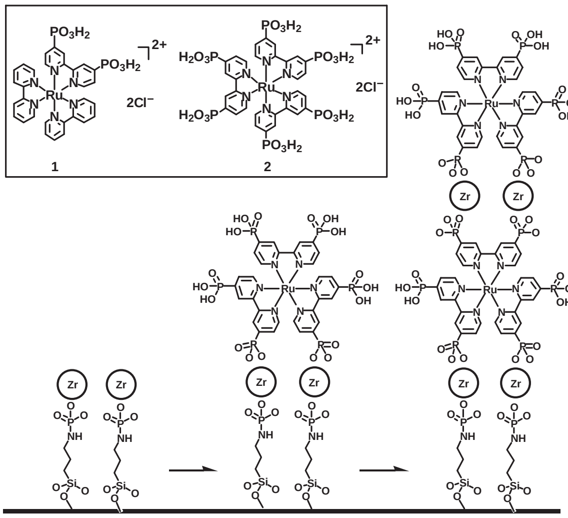

Figure 1. Schematic illustration of the bottom-up fabrication process used to prepare Ru(bpy)$_3$ films (This scheme shows that **2** is a Ru(bpy)$_3$ molecule).

An electrochemical investigation into a one-cycle film (middle of the bottom scheme shown in Figure 1) indicated the high efficiency of the deposition of **2** onto ITO electrodes. A reversible peak of the Ru^{III}/Ru^{II} redox couple appeared at a potential of 1.18 V vs Ag/Ag$^+$ in Bu$_4$NClO$_4$–acetonitrile. The anodic charge integration under the voltammetric wave yielded a surface coverage of $\Gamma = 3.4 \times 10^{-10}$ mol·cm^{-2} (in SI units). This value is close to that determined from the UV–vis spectra.[2] The differential pulse voltammograms (DPVs) of the multilayered films showed that the current density increased by only a small amount with an increasing number of deposition cycles (Figure 2B). This implies that participation in the redox event was limited to only a small number of complexes in the multilay-

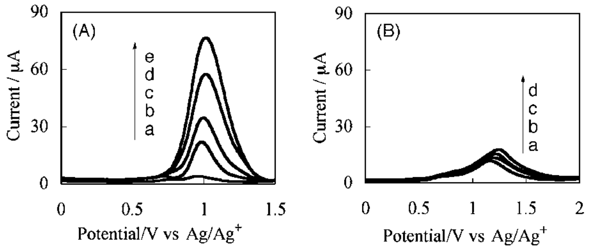

Figure 2. (A) DPVs of multilayer films of **1** on ITO electrodes in 0.1 M Bu$_4$NClO$_4$–acetonitrile (a = 1-, b = 4-, c = 8-, d = 14-, and e = 20-cycle films). (B) DPVs of multilayer films of **2** on ITO electrodes in 0.1 M Bu$_4$NClO$_4$–acetonitrile (a = 1-, b = 5-, c = 10-, and d = 14-cycle films).

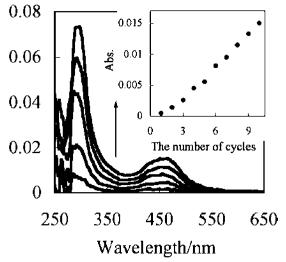

Figure 3. UV–vis absorption spectra of multilayered films of **1** on quartz plates with increasing number of fabrication cycles (2, 4, 6, 8, and 10 cycles). The inset shows a plot of the absorbance at 457 nm vs the number of cycles.

ered films. A possible interpretation of this phenomenon is that the migration of counter-anions is considerably restricted in dense films of **2**.

We subsequently tried to reduce the density of the Ru(bpy)$_3$ thin film, aiming to enhance the accessibility of the counter-anions into the films. After several trials, replacing **2** with **1** was found to be the most effective approach. Indeed, **2** has often been used in photoelectrochemical studies as a monomolecularly adsorbed photosensitizing agent on electrodes.[9] However, it is of great interest that the sequential deposition of **1** was successfully performed by interacting with $ZrOCl_2$ successively over at least 20 cycles.

A reversible peak of the Ru^{III}/Ru^{II} redox couple was observed at a potential of 0.98 V for a one-cycle film of **1**. The negative shift of the redox potential of **1** compared with that of **2** was probably caused by a difference in the number of electron-withdrawing phosphonic acid groups in the two cases. The anodic charge integration under the voltammetric wave yielded a value of $\Gamma = 5.6 \times 10^{-11}$ mol·cm^{-2}.

Multilayered films of **1** revealed a very interesting electrochemical behavior, which was in sharp contrast with that of multilayered films of **2**. As shown in Figure 2(A), the current response of the DPVs increased with an increasing number of deposition cycles, up to 20 cycles, indicating that migration of the counter-ions was fast enough to follow the electron-transfer reactions in the films. Thus, it was found that the net number of redox-active complexes monotonically increased with increase in film growth for **1**.

The stepwise multilayer fabrication of **1** was performed in a manner that was essentially identical to that described for **2**. A quartz substrate was also used to determine the stepwise molecular fabrication of the complex. We consider the hydroxy groups on the ITO surface and a quartz surface to react similarly with silane-coupling reagents, and so similar multilayers would form on these surfaces.[10]

Figure 3 shows changes in the spectrophotometric data for the films on quartz, revealing a successive increase in absorbance following a fabrication cycle in the wavelength range $\lambda = 250$–600 nm. As shown in the inset of Figure 3, a plot of the absorbance at $\lambda = 457$ nm (the MLCT band maximum) vs immersion cycle was linear, with a gradient of 1.7×10^{-3} absorbance units per deposition cycle. Provided that the molar absorption coefficient of **1** ($\varepsilon = 1.5 \times 10^{4}$) remained unchanged in the films, then the surface coverage of Ru(bpy)$_3$ units was estimated to be 5.7×10^{-11} mol·cm^{-2} per deposition cycle. This value corresponds to only 18% of the surface coverage of a film consisting of **2**. Nevertheless, the thickness of the 20-cycle film of **1** reached a depth of 14 nm, which is over one-third that of a film of **2** (The thickness of a 20-cycle film of **2** was found to be 37 nm from an investigation using a surface profiler). These results suggest that **1** is more loosely assembled in multilayered films than **2**.[2] Figure 4 shows an illustration of the interaction of the electrolyte at the film interface.

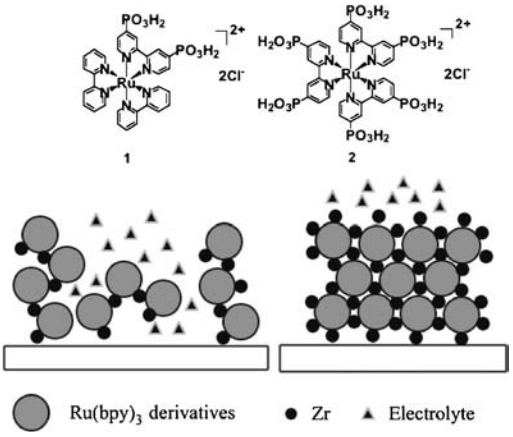

Figure 4. Side view images of multilayered films composed of ruthenium complexes and zirconium on electrodes in an electrolytic solution. The electrolyte can enter the multilayer of **1** smoothly. On the other hand, the electrolyte remains near the surface of a film of **2**.

In summary, the packing density of Ru(bpy)$_3$ units has been shown to be a crucial factor in constructing thin films having reversible redox functions. The redox function of the resulting multilayered films was highly predictable and reliable, although the productivity of the stepwise film growth of **1** was not high. Thus, the film growth efficiency and the density of the resulting thin films should be controllable using a simple design of the periphery of the Ru(bpy)$_3$ molecule. Based on the present findings, work is now in progress to control electron-transfer reactions precisely in Ru(bpy)$_3$ thin films, and to apply them to the construction of highly functional photoelectrochemical devices.

This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas (417) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government. We also thank Japan Science and Technology Agency, CREST and Tokyo Ohka Foundation for the Promotion of Science and Technology for financial support.

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