

Electrochemical Charge Storage Using Layer-by-Layer Deposited Film Composed of Redox Polymer and Inorganic Nanoparticle

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We demonstrated electrochemical charge storage in a Layer-by-layer assembled hybrid film. A cationic polymer, which contain ruthenium complex (pCM/Ru) and negatively charged Prussian blue (PB) nanoparticles, were assembled onto an ITO electrode a using layer-by-layer technique, so that pCM/Ru layer located in an inner layer and PB located in an outer layer. The electrochemical property of the hybrid film was studied by cyclic voltammetry (CV) measurement. The first scan of CV cycle showed an asymmetric spectrum in which oxidation current was about 1.7 times larger than reduction current, whereas those current values were almost identical for 2nd and 3rd CV cycles. The asymmetric CV spectrum indicates that PB at the outer layer was catalytically oxidized by pCM/Ru layer and stored positive charges at the first CV cycle.

Keywords: Bilayer electrode, Electrochemical diode, Electrochromism

1. Introduction

It has been reported that two redox active polymers deposited in a bilayer fashion produce a rectifying property similar to p-n junction in semiconductor devices [1-3]. The concept is called bilayer electrodes, which was first reported by Murray et al [1]. Bilayer electrodes consist of a conducting electrode coated with two redox active polymers that have different redox potentials [4]. The bilayer interface between the films acts as a “chemical free-energy-based rectifying junction”. The rectification is the result of the difference of redox potential between the two redox polymers. Murray et al. prepared bilayer electrode by sequential electropolymerization of two redox polymers [3]. We have prepared a molecular bilayer electrode from polymer nanosheets assembly using Langmuir-Blodgett (LB) film. Polymer nanosheets, which composed redox and photo active molecules

were deposited in a bilayer manner to produce monolayer bilayer electrodes, which act as molecular diode [5,6], molecular logic gates [7-11] and molecular charge trapping devices [5]. The LB technique enables to prepare ultrathin and high uniformity polymer assemblies, whereas the materials to be processed are limited to amphiphilic molecules and special equipment is required [12]. On the other hand, the layer-by-layer (LbL) technique, which used an electrostatic interaction between positively and negatively charged polymers can also prepare ultrathin polymer multilayer films [13,14]. Although LbL films have much porosity, their simple process; alternatively dipping a substrate into a cationic polymer and anionic polymer solution, and material versatility; charged polymer [15] to charge nanoparticles [16,17] are attractive for preparation of molecular bilayer electrodes.

In this work, we prepare a molecular bilayer electrode using the layer-by-layer technique. A cationic charged polymer which contains ruthenium complex (pCM-Ru, Fig. 1) and anionic charged Prussian blue ($\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]$) nanoparticles (PB) were assembled in a bilayer fashion using the LbL technique. The redox properties of “monofunctional” LbL film consisted from cationic pCM-Ru and anionic poly(acrylic acid) (PAA) or anionic PB and cationic poly(ethylene imine) (PEI) was studied. These LbL film was deposited onto an electrode to prepare a LbL bilayer electrode. The redox property and the charge trapping phenomenon in the LbL bilayer electrode was studied.

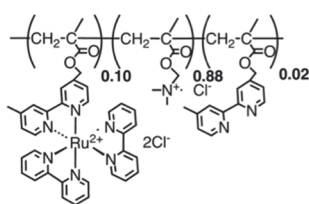


Fig. 1. Chemical structure of pCM/Ru.

2. Experimental

4-(Methacryloylmethyl)-4'-methyl-2,2'-bipyridyl (Mbpy) was synthesized by reaction of 4-hydroxymethyl-4'-methyl-2,2'-bipyridil (TCI) with methacryloyl chloride in the presence of trimethylamine. A copolymer of methacryloylcholine chloride (CM, 80 wt% water solution, Aldrich) with Mbpy was prepared using free radical polymerization in ethanol at 60 °C with AIBN. The mole fraction of Mbpy in the copolymer was determined according to the UV-vis spectrum using the molar absorption coefficient of 4-vinyl-4'-methyl-2,2'-bipyridil ($\epsilon = 1.43 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 283 nm) [18,19]. The Mbpy content was determined to be 12 mol%. Then the copolymer was refluxed with $\text{Ru}(\text{bpy})_2\text{Cl}_2$ in ethanol for 48 h. The content of $\text{Ru}(\text{bpy})_3^{2+}$ was determined to be 10 mol% by UV-vis spectrum measurement. PB was synthesized following a process described in a previous report [20]. Briefly iron(III)nitrate dissolved in water was quickly added to vigorously stirred potassium ferrocyanide water solution. The prepared PB nanoparticles were collected by centrifugation. The collected PB nanoparticles were dissolved in water in which potassium ferrocyanide water solution was added to form a PB ink. An ITO and quartz substrate was washed by sonication in acetone then cleaned

by treatment with a UV-O₃ cleaner (SSP16-110, SEN Lights Corp). LbL deposition was carried out using dipping machine (MC4000, AIDEN). Ten mM water solution of each compounds were prepared and a substrate was dipped into each solution for 5 min. PAA and PEI was purchased from Wako and used as received.

3. Results and discussion

3.1. Optical and redox property of “monofunctional” LbL film

“Monofunctional” LbL films which contain pCM/Ru or PB were fabricated using PAA or PEI as a counter polymer. UV-O₃ treated quartz and ITO substrates were negatively charged, therefore substrates were initially dipped into a cationic solution and then dipped into an anionic solution. This combination was defined as one layer. Figure 2a shows a UV-vis spectrum of three-layer LbL film of pCM/Ru-PAA. The UV-vis spectrum displayed a strong absorption centered at 454 nm, which was assigned to MLCT band of $\text{Ru}(\text{bpy})_3$. The result indicates that pCM/Ru-PAA pair was successfully deposited onto quartz substrate. Three layers of pCM/Ru-PAA LbL film were deposited onto an ITO electrode to studied the electrochemical property. Figure 2b shows a cyclic voltammogram of the LbL film. The LbL film showed a well-defined surface wave consisting of symmetric oxidation and reduction peaks of Ru at 1.1 V vs. Ag/AgCl). The CV spectra are identical in the three scan cycles, which indicate that the LbL film was stably

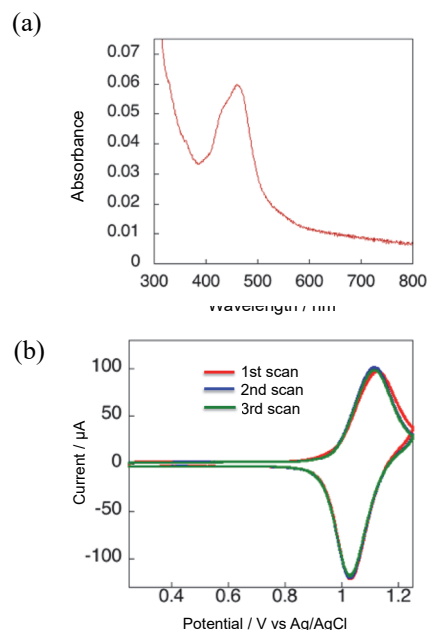


Fig. 2. (a) UV-vis spectrum and (b) cyclic voltammogram for tri-layer pCM/Ru-PAA LbL film.

adsorbed onto ITO electrode and did not desorb during the potential cycle.

UV-vis spectrum of three-layer LbL film of PB-PEI pair display a strong absorption around 700 nm, due to intervalence charge transfer absorption of PB (Fig. 3a). The color is so intense and can be observed in a naked eye (inset in Fig. 3a). The CV spectra of PB-PEI contained two reversible symmetric redox peaks at 0.1 V and 0.8 V vs Ag/AgCl (Fig. 3b). The former peak is attributed to one-electron redox reaction between Prussian blue and Prussian white ($\text{K}_4\text{Fe}^{\text{II}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]$) and latter is attributed to Prussian blue to Prussian yellow ($\text{Fe}^{\text{III}}[\text{Fe}^{\text{III}}(\text{CN})_6]$). These peaks are negligibly changed within three potential cycle, which support that the PB-PEI LbL films are stable in the redox cycle.

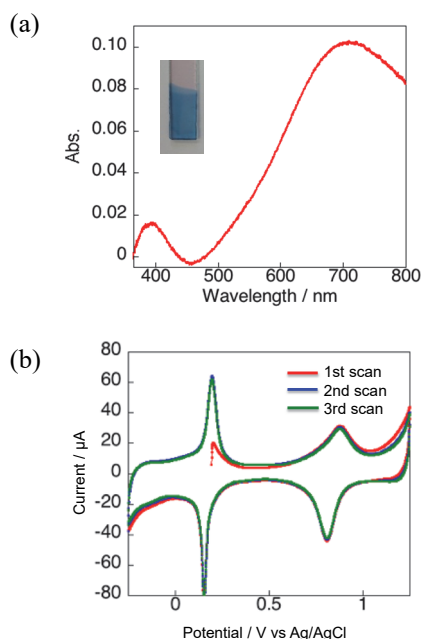


Fig. 3. (a) UV-vis spectrum and (b) cyclic voltammogram for tri-layer PB/PEI LbL film. Inset: digital camera image for the tri-layer film.

3.2. Molecular bilayer electrode prepared from LbL film

Molecular bilayer electrode was prepared by deposition of three-layer PB-PEI LbL film onto three-layer pCM/Ru-PAA LbL film (Fig. 4a). Cyclic voltammogram of the molecular bilayer film only showed a redox peak of Ru and redox peak related to $\text{PY} + \text{e}^- = \text{PB}$ was not observed (Fig. 4b). Moreover, oxidation current observed in 1st CV scan was larger

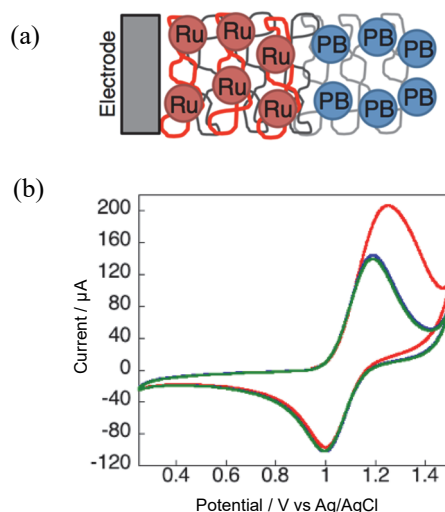


Fig. 4. (a) Molecular bilayer electrode structure and (b) cyclic voltammogram for the bilayer electrode.

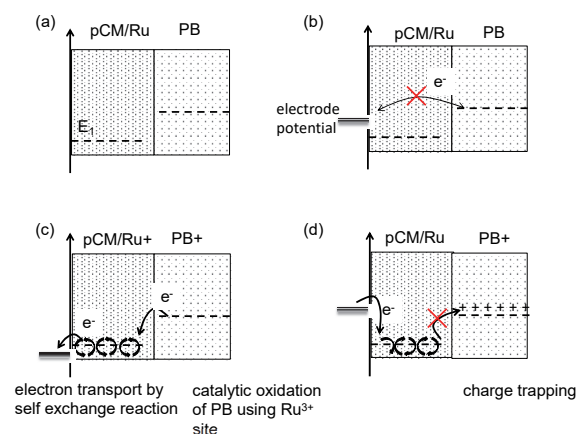


Fig. 5. Mechanism of charge trapping the molecular bilayer electrode. (a) Potential diagrams for the bilayer electrode. Dotted line indicates redox potentials for pCM/Ru and PB. (b) No direct electrochemical reaction of PB with the electrode. (c) Oxidation of pCM/Ru by the electrode and catalytic oxidation of PB. Electron was transported to the electrode by self-exchange reaction. (d) pCM/Ru was reduced by the reductive scan, whereas PB remains in the oxidation state even though the electrode potential is more negative than the redox potential of PB (charge trapped condition).

than that observed in 2nd and 3rd CV scan, whereas the reduction current of Ru^{3+} to Ru^{2+} was independent to the potential cycle. This result can be explained considering the potential diagram throughout the film (Fig. 5). The inner pCM/Ru-PAA is a “redox conductive” materials; the electron was transported by self-exchange reactions between adjacent oxidized and reduced Ru sites. Therefore, pCM/Ru-PAA layer is an insulator when the electrode potential is kept above the redox reaction of $\text{Ru}^{3+} + \text{e}^- = \text{Ru}^{2+}$ (E_1 in Fig. 5a). This means that a

direct electron transfer reaction of PB with the electrode is restricted by the pCM/Ru-PAA layer (Fig. 5b). Oxidation of PB requires mediation by pCM/Ru, which starts at the potential below oxidation potential of Ru. In this potential range, Ru^{2+} was oxidized to Ru^{3+} and PB was oxidized catalytically using the Ru^{3+} site. When the electrode potential was swept in the reverse direction, Ru^{3+} was reduced to Ru^{2+} , however, reduction of PY to PB at this potential was thermodynamically unfavorable (Fig. 5d). Thus, in the first oxidation scan, current include oxidation of Ru^{2+} and PB, whereas 2nd and 3rd scan the oxidation current was only derived from Ru^{2+} , which result in the decrease of oxidation current. On the other hand, reduction current was derived from Ru^{3+} to Ru^{2+} , and was constant because of the film stability. The CV results indicate that the electron flow in the LbL bilayer electrode was rectified and the charge was trapped at the PB-PEI layer in one potential cycle.

4. Conclusion

Molecular bilayer electrode was constructed using LbL deposition technique. The process is simple in applicable to other charge materials. Recently we proposed a new concept to achieve multicolor electrochromism applying the bilayer electrode [21]. Fabrication of full color electrochromism using this concept is now in progress.

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