Abstract

The novel multifunctional thin films composed of transition metal complex tris(1,10-phenanthroline)ruthenium(II) Ru(phen)3Cl2 (abbr Ru(phen)3, phen = 1,10-phenanthroline), and Dawson-type polyoxometalate [P2Mo18O62]6− (abbr P2Mo18) were fabricated on quartz, silicon and ITO substrates by layer-by-layer (LBL) method. The LBL films deposition were found to be linearly related to the number of bilayers as monitored by UV–vis spectroscopy. And the compositions of the films were measured by X-ray photoelectron spectra (XPS). The result of atomic force microscopy (AFM) revealed a relatively uniform surface morphology of the multilayer films. In particular, the films exhibited the photo-luminescence arising from \((\pi \rightarrow \pi^*)\) ligand-to-metal transition of Ru(phen)3 and catalytic activity to the reduction of NO2− attributing to molybdenum-centered redox processes of P2Mo18.

Keywords: Layer-by-layer self-assembly; Polyoxometalate; Luminescent film; Ruthenium; Electrocatalysis

1. Introduction

Polyoxometalates (POMs) represent a well-defined class of inorganic compounds with remarkable structural, and electronic versatility [1–3], and possess diverse properties such as catalytic activity, molecule-based conductivity, magnetism, photochromism, electrochromism and luminescence, etc. [4–7]. However, practical applications of polyoxometalates in these areas depend on the successful preparation of thin polyoxometalate-containing films [8,9]. The layer-by-layer (LBL) method, being based on sequential adsorption of oppositely charged species from dilute solutions and relying primarily on electrostatic attraction of the oppositely charged components, provides a facile synthetic route towards uniform POM based multilayer films [10–13]. This method permits the combination of POMs with many other functional components as part of the polycationic macromolecules with good control over the layer composition and thickness, which renders them potentially attractive for a host of applications in photochemistry, electrochemistry, catalysis, and sensing [14,15].

Transition metal complexes have been the subject of extensive electrochemical and spectroscopic studies, due to their excellent photo-luminescence properties and excellent stability in multiple redox states. In particular, ruthenium(II) polypyridyl complexes can display strong luminescence with high quantum yield and long natural lifetime, and serve as luminescence sensors for monitoring oxygen concentration, pH, chloride, or temperature [16–22]. Meanwhile, the intercalation of chiral metal complex tris[1,10-phenanthroline](ruthenium(II)) by a smectite has been studied to understand the nature of the host–guest systems as well as to construct an adsorbent, optical resolving agent, and a chiral catalysis [23–25]. It has been found that cationic ruthenium(II) polypyridyl complexes can be combine with POM anion in film materials by LBL method [26–28]. To develop multifunctional films, in the present work, we fabricated organic–inorganic composite self-assembled ultrathin films from tris(1,10-phenanthroline)(ruthenium(II) Ru(phen)3Cl2 (Ru(phen)3) and Dawson-type polyoxometalate [P2Mo18O62]6− (P2Mo18) (shown in Fig. 1) by LBL method. The growth process of the film was monitored by UV–vis spectra and the morphology of the film was observed by atomic
force microscopy (AFM). Photo-luminescent property and electrochemical behavior of the multilayer films were studied. The combination of the unique properties of POM and functional molecule Ru(phen)3 might provide an opportunity in the applications of luminescence sensors, electrontransfer, electrocatalysis, and so on.

2. Experimental

2.1. Materials and instruments

Poly(ethyleneimine) (PEI; MW 750,000) and tris(1,10-phenanthroline)ruthenium(II) Ru(phen)3Cl2 were commercially obtained from Aldrich and used without further purification. Polyoxometalate/H9251/K6P2Mo18O62·14H2O was synthesized by the literature[29]. The water used in all experiments was deionized to a resistivity of 16–18 MΩ cm−1. All other reagents were of reagent grade.

UV–vis spectra were recorded on a U-3010 UV–vis spectrophotometer made in Japan. X-ray photoelectron spectra (XPS) were performed on an Escalab MKII photoelectronic spectrometer with Mg Kα (1253.6 eV) as X-ray source. AFM image were obtained by using Digital Nanoscope IIIa instrument operating in the tapping mode with silicon nitride tips. Fluorescence spectra were performed with a SPEX FL-2T2 fluorescence spectrophotometer using a 450 W xenon lamp as excitation source. A CHI 660 electrochemical workstation was used for control of the electrochemical measurements and data collection. A conventional three-electrode system was used, with a bare ITO electrode or a {PEI/[P2Mo18/Ru(phen)3]n} multilayer film coated ITO electrode as a working electrode, platinum foil as a counter electrode, and Ag/AgCl as a reference electrode.

2.2. Layer-by-layer assembly

The fabrication of the multilayer film was carried out as follows. The substrate (silica or quartz glass slide) was cleaned according to the literature[30], which made its surface become hydrophilic, rinsed with deionized water, and dried under a nitrogen stream. The hydrophilized substrate slide was immersed in 1 × 10−3 M PEI solution (the concentration was calculated based on their repeating units) for 20 min, followed by washing with deionized water. After washing, a nitrogen stream was blown over the film surface until the adhering water layer was completely removed. The PEI-coated substrates then were alternately dipped into 1 × 10−3 M P2Mo18 and 1 × 10−3 M Ru(phen)3 for 20 min, also rinsed with deionized water, and dried in a nitrogen stream after each dipping. Multilayer film {PEI/P2Mo18/Ru(phen)3}n was formed on polymer matrix.

ITO glass (on one side only) substrate was cleaned by immersing into a H2SO4:H2O2 = 7:3 (v/v) solution for a few minutes followed by rinsing copiously with deionized water and drying in a nitrogen stream[31]. Layer-by-layer deposition was performed according to the process as described above.

3. Results and discussion

3.1. Ultraviolet–visible absorption spectra

UV–vis spectroscopy was used to monitor the assembling process of the films, the absorbencies of per two-layer cycle being obtained for film assembled on two sides of a quartz slide. Fig. 2a exhibits the UV spectra of {PEI/P2Mo18/Ru(phen)3}n multilayer film (n = 1–20 and 50) deposited on quartz substrate (on both sides). Bottom to top: n = 0, 1, 2, 3, ..., 20, and 50, respectively. Insert: plots of the absorbance values at 203, 225, 269, 293, and 317 nm. (b) Comparative UV spectra of P2Mo18, Ru(phen)3, and PEI/P2Mo18/Ru(phen)3 multilayer films.
(n = 0–20 and 50) multilayer film. The spectra showed the five characteristic absorptions in 190–350 nm at 225, 269 and 293 nm owing to ligand-centered π–π* and metal-centered d–d transitions of Ru(phen)$_3$ cation, and at 203 and 317 nm assigned to the overlap peaks of both Ru(phen)$_3$ and P$_2$Mo$_{18}$, which confirms the incorporation of Ru(phen)$_3$ and P$_2$Mo$_{18}$ into the multilayer films. However, there is a slight red shift of 2–6 nm for every absorption peak of the multilayer films compared to that of the Ru(phen)$_3$ solution (Fig. 2b), which may be associated with the strong interactions between Ru(phen)$_3$ cation and the polyoxometalate anion. Further, one can see from the inset of Fig. 2a that the absorbance values of the multilayer films at 203, 225, 269, 293, and 317 nm increase linearly with the number of P$_2$Mo$_{18}$/Ru(phen)$_3$ bilayers, suggesting that the growth of the films for each deposition cycle was uniform up to at least 20 bilayers.

### 3.2. Atomic force microscopy

The morphology of the film was observed by AFM. Fig. 3 shows the AFM image of the thin film [PEI/P$_2$Mo$_{18}$/Ru(phen)$_3$]$_4$/P$_2$Mo$_{18}$. The surface of the film assembled on silica slide is uniform and smooth, consisting of a multitude of small grains with ca. 52 nm mean grain size. The mean interface roughness is ca. 1.9 nm, calculated from an area of $1.0 \times 1.0 \mu m^2$.

![AFM image](image)

**Fig. 3.** AFM image of [PEI/P$_2$Mo$_{18}$/Ru(phen)$_3$]$_4$/P$_2$Mo$_{18}$ multilayer film: (a) the planar image and (b) dimensional image.

### 3.3. Luminescent property

The excitation and emission spectra of the Ru(phen)$_3$ solid and [PEI/P$_2$Mo$_{18}$/Ru(phen)$_3$]$_{50}$ LBL film self-assembled on smooth quartz substrates at room temperature were showed in Fig. 4. Compared with the excitation spectrum of the Ru(phen)$_3$ solid, certain variations occurred in the band number, band position, band shape, and relative intensity of some individual bands in the spectrum of the film. Particularly, in contrast to the spectrum of Ru(phen)$_3$ solid, the most intense band arising from the singlet metal-to-ligand (MLCT) d–π* transitions [32], has a blue-shift of 11 nm, while the intense of broad band centered at 421 nm decrease greatly, and the much less intense bands at 472, 506, and 515 nm nearly disappear in the film. The emission spectra for Ru(phen)$_3$ solid and the thin film are quite similar and all show a characteristic broad band, arising from π→d$_{xy}$ ligand-to-metal transition of Ru(phen)$_3$ [32]. The luminescence band is, however, blue-shifted from 595 to 582 nm in thin film. All these changes as mentioned above may be associated with the strong interactions between tri(1,10-phenanthroline)ruthenium(II) and the polyanion, which have influence on the molecular orbitals of ligands and metal in Ru(phen)$_3$ [33–35]. The electroluminescence behavior of the multilayer film is underway.
3.4. X-ray photoelectron spectrum

XPS measurements were performed to identify elemental composition of \( \text{PEI/}[\text{P2Mo18/Ru(phen)3}]_6 \) LBL film deposited on the single-crystal silicon substrate. The film exhibited peaks corresponding to C 1s (BE = 284.6 eV), N 1s (BE = 399.5 eV), O 1s (BE = 532.2 eV), P 2p (BE = 132.6 eV), Mo 3d 5/2 (BE = 231.9 eV), and Mo 3d 3/2 (BE = 234.9 eV) shown in Fig. 1. Whereas that for Ru was not observed due to its very low percentages in the film (detection limit required by the instrument is \( \geq 2\% \)). The N 1s is attributed to the nitrogen atom of the N–Ru coordination bond in Ru(phen) 3. The C 1s signal can be assigned to the carbon in Ru(phen) 3; the O 1s is ascribed to the oxygen atoms in P2Mo18. These XPS results confirm the existence of the P2Mo18, and Ru in the multilayer film in conjunction with the results of UV–vis and fluorescent spectra.

3.5. Voltammetric behavior and electrocatalytic activity of the film assembled on ITO glass substrate

The electrochemical studies of \( \text{PEI/}[\text{P2Mo18/Ru(phen)3}]_{10} \) P2Mo18-modified ITO electrode were carried out in 0.5 M Na2SO4 + H2SO4 buffer solution (pH 0.5). The comparative cyclic voltammograms of a bare ITO electrode just after being immersed into 0.5 M Na2SO4 + H2SO4 buffer solution (pH 0.5) containing 0.1 mM P2Mo18 and a multilayer film \( \text{PEI/}[\text{P2Mo18/Ru(phen)3}]_{10} \) P2Mo18-modified ITO electrode in the same buffer solution were showed in Fig. 5. It can be seen that in the range \(-100 \text{ to } 700 \text{ mV} \), the thin film undergo three redox waves assigned to molybdenum-centered two-electron redox processes of P2Mo18 \[36\], while certain variation occurred in peak position, peak relative intensity, and peak-to-peak separation in contrast to that of P2Mo18 in aqueous solution perhaps due to strong interactions between Ru(phen) 3 cation and the polyoxometalate anion.

Fig. 5. Comparative cyclic voltammograms of 0.1 M P2Mo18 (dot line, ITO electrode), and a \( \text{PEI/}[\text{P2Mo18/Ru(phen)3}]_{10} \) P2Mo18 multilayer film-modified ITO electrode (solid line) in 0.5 M Na2SO4 + H2SO4 buffer solution (pH 0.5). Scan rate: 20 mV s\(^{-1}\).

In general, the reduction of polyoxometalate anions is accompanied by protonation, Fig. 6 exhibits the cyclic voltammograms for the multilayer film \( \text{PEI/}[\text{P2Mo18/Ru(phen)3}]_{10} \) P2Mo18-modified ITO electrode in 0.5 M Na2SO4 + H2SO4 aqueous solutions with different pH. In the range of pH 0.5–3, the peak potentials for all three redox couples shift negatively with the increase in pH, and plots of peak potentials of the three successive redox waves versus pH show good linearity (see inset). The slopes of the E/pH lines are about 61 mV for wave I, 59 mV for wave II, and 61 mV for wave III, respectively, indicating the addition of one proton to the reduced forms of P2Mo18 when one electron is transferred \[37\]. So the electrochemical behavior of the multilayer film \( \text{PEI/}[\text{P2Mo18/Ru(phen)3}]_{10} \) P2Mo18-modified ITO electrode can be summarized by the following equations:

\[
P2Mo13O46^{6-} + 2e + 2H^+ \rightleftharpoons H2P2Mo15O46^{6-}
\]

\[
H2P2Mo15O46^{6-} + 2e + 2H^+ \rightleftharpoons H4P2Mo23O62^{6-}
\]

\[
H4P2Mo23O62^{6-} + 2e + 2H^+ \rightleftharpoons H6P2Mo31O62^{6-}
\]

Fig. 7 shows the cyclic voltammograms of the \( \text{PEI/}[\text{P2Mo13/Ru(phen)3}]_{10} \) modified ITO electrode at different scan rate in 0.1 M Na2SO4 + H2SO4 solution (pH 1.5), and plots of peak current (III) versus the square root of the scan rates. As can be seen from the inset that the anodic currents were proportional to the square root of the scan rates, which indicates that the redox process is diffusion-controlled.

Reduced POMs can be exploited extensively in electrocatalytic reductions due to their ability of delivering the electrons to other species. The multilayer film \( \text{PEI/}[\text{P2Mo13/Ru(phen)3}]_{10} \) also presents electrocatalytic activity toward the reduction of nitrite. Fig. 8 exhibits cyclic voltammograms for the electrocatalytic reduction of nitrite by \( \text{PEI/}[\text{P2Mo13/Ru(phen)3}]_{10} \) in...
Fig. 7. Cyclic voltammograms of {PEI/[P2Mo18/Ru(phen)]10} multilayer film in 0.1 M Na2SO4 + H2SO4 buffer solution (pH 1.5) at different scan rates (from inner to outer: 25, 50, 75, 100, 125, 150, 175, 200, 250, 300, 350, 400, 450, and 500 mV s\(^{-1}\)). The inset shows a linear dependence of the third anodic current with square root of the scan rates.

Fig. 8. Cyclic voltammograms of {PEI/[P2Mo18/Ru(phen)]10} multilayer film in pH 1.2 buffer solutions containing NO2\(^{-}\) in various concentrations: 0.0, 5.0, 10.0, 20.0, 40.0, and 80.0 mM, respectively. Scan rate: 25 mV s\(^{-1}\). The inset shows relationship between catalytic current and concentration of NO2\(^{-}\).

4. Conclusion

The well-defined organic–inorganic multilayer films composed of transition metal complex tris(1,10-phenanthroline) ruthenium Ru(phen) and Dawson-type polyoxometalate P2Mo18 were fabricated by layer-by-layer assembly method. The film exhibited photo-luminescence arising from \(\pi^*\rightarrow\delta_{O-M}\) ligand-to-metal transition of Ru(phen), and electrocatalytic activity on the reduction of nitrite attributable to molybdenum-centered redox processes of [P2Mo18O62]\(^{-}\). These preliminary results in this work represent potential applications in the field of luminescence sensors, electron transfer, electrocatalysis, and so on.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.electacta.2006.01.040.

References

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