Ultrathin Ruthenium(II) Complex–H$_4$SiW$_{12}$O$_{40}$ Multilayer Film

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A dipolar Ru(II) complex, [(bpy)$_2$Ru(bpbh)Ru(bpy)$_2$](ClO$_4$)$_4$ {where bpbh = 1,6-bis-[2-(2-pyridyl) benzimidazoyl]hexane, bpy = 2,2′-bipyridine}, was synthesized and characterized. A multilayer film of at least 18 layers was successfully prepared by alternating adsorption of H$_4$SiW$_{12}$O$_{40}$ and [Ru$_2$(bpy)$_4$(bpbh)](ClO$_4$)$_4$ by electrostatic layer-by-layer self-assembly. The multilayer films were studied by ultraviolet-visible and X-ray photoelectron spectroscopy, atomic force microscopy, and cyclic voltammetry.

Keywords: Self-Assembled Film, Ruthenium, Bipyridine, Optical Property, Atomic Force Microscopy.

1. INTRODUCTION

Polyoxometalates (POMs) are structurally rigid and well-defined inorganic metal-oxygen nanocluster compounds. They have attracted great attention in the areas of catalysis, energy storage, medicine, and materials science due to their ability to act as electron reservoirs, enormous tunability of size and shape, acid-base properties, charge density, and redox ability.[1] One of the most attractive research activities is directed at assembling POMs in ultrathin ordered films with well-controlled, nanometer-scale architectures and tailored properties for potential applications in molecular devices. POMs are anionic over a wide pH range, hence they are amenable to the fabrication of thin films through electrostatic interaction with the positively charged species by use of Langmuir-Blodgett (LB)[2] and electrostatic self-assembly techniques.[3]

Recently, POM-containing LB films with interesting magnetic and electrochemical properties have been successfully prepared,[4] but the LB technique requires a delicate and expensive apparatus, limiting its widespread use. Layer-by-layer (LBL) electrostatic assembly has the advantage of being easy to prepare, and film thickness and composition are readily controlled. Thus, the LBL technique has recently been widely adopted to fabricate POM-containing multilayers.[5, 6] However, this kind of self-assembled film usually employs functionality-lacking "silent" protonated organic amine cations as the counter ions of the POMs. The electrostatically self-assembled films formed by functionality-integrated cations and anions remain rare even though the potential occurrence of the charge transfer interaction between POMs and functional cations may affect the ferromagnetic, nonlinear optical, and conducting properties of the materials.[7] In contrast, the polypyridyl ruthenium(II) complexes possess intriguing ground- and excited-state photochemical, photophysical, and redox properties, and the LB films of the Ru(II) complexes[8] have received keen attention during the past three decades; however the electrostatically self-assembled films based on Ru(II) complexes have been very limited.[6]

In extending our research from the photochemically and electrochemically active metal complex-based LB films[8a, 9] to the electrostatically self-assembled films of these complexes with POMs,[6e, 7d] we successfully prepared a multilayer ultrathin film based on a polyoxometalate H$_4$SiW$_{12}$O$_{40}$ and a dipolar Ru(II) complex. In this paper, related details regarding the material synthesis, film preparation, characterization, and electrochemical properties of the film are reported.

2. EXPERIMENTAL DETAILS

2.1. Materials

Commercially available 3-aminopropyltriethoxysilane (99%, Acros), 1,6-dibromohexane (96%, Fluka) and H$_4$SiW$_{12}$O$_{40}$ (AR grade, Beijing Xinhua Chemical Factory) were used without further purification. The dried

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hexane and *N,N*-dimethylformamide (DMF) were obtained by distillation over CaH_2 and P_2O_5, respectively. 2-(2-Pyridyl)benzimidazole was synthesized as described previously.[10] The dipolar Ru(II) complex, [(bpy)$_2$Ru(bpbh) Ru(bpy)$_2$](ClO$_4$)$_4$ {where bpbh = 1,6-(Bis-(2-(2-pyridyl) benzimidazoyl))hexane and bpy = 2,2′-bipyridine}, was synthesized according to the approach described in Figure 1, and is hereafter abbreviated as RuBPBH. The synthetic details of RuBPBH are given below.

Synthesis of 1,6-Bis-((2-(2-pyridyl)benzimidazoyl))hexane (BPBH). Sodium hydride (50% dispersed in mineral oil) (0.77 g, 16 mmol) was washed with dried hexane under nitrogen in a 50 mL flask. After the solvent was eliminated by gentle heating, 20 mL of DMF and 2-(2-pyridyl)benzimidazole[11] (3.0 g, 15.4 mmol) were successively added. After the evolution of hydrogen gas ceased, 1,6-dibromhexane (1.2 mL, 7.7 mmol) was added, and the mixture was refluxed at 110 °C for 22 h. Upon cooling, sodium bromide precipitate was removed by filtration. After most of the solvent was removed under reduced pressure, a precipitation formed was collected by filtration, and was chromatographed on silicon gel by using dichloromethane and methanol (v/v, 9:1) as eluent, affording BPBH as a slightly yellow solid. Yield: 4.65 g (64%). M.p.: 142–143 °C, IR: 3051(w), 2927(s), 2856(s), 1586(s), 1566(m), 1466(s), 1441(s), 1390(m), 1365(s), 1330(s), 1293(m), 1259(m), 1247(m), 1146(m), 1093(w), 1007(w), 994(w), 832(w), 795(s), 732(vs) cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 Hz): δ8.12 (d, J = 7.7 Hz, 4H), 7.46 (m, 4H), 7.35 (d, J = 8.2 Hz, 4H), 7.25 (t, J = 7.8 Hz, 7.1 Hz, 4H), 4.27 (t, J = 7.1 Hz, 4H), 1.86 (t, J = 6.8 Hz, 4H), 1.41 (m, 4H).

Synthesis of RuBPBH. A solution of BPBH (0.24 g, 0.5 mmol) and Ru(bpy)$_2$Cl$_2$ · 2H$_2$O (0.53 g, 1 mmol) in ethylene glycol (15 mL) was heated at 100 °C for 20 h under a nitrogen atmosphere. The reaction mixture was allowed to cool to room temperature and filtered to remove insoluble impurities. To the filtrate, a four-fold excess of sodium perchlorate aqueous solution was added dropwise. (**Caution!** *All the perchlorate salts are potentially explosive and therefore should be handled in small quantities and with care.*) The red precipitate formed immediately

was filtered and washed with cold water and crystallized from 1,4-dioxane. Yield: 0.63 g (75%). M.p. >270 °C (decomposition). Anal. Calcd. for C$_{70}$H$_{60}$N$_{14}$Cl$_4$Ru$_2$O$_{16}$: C, 49.54; H, 3.56; N, 11.55. Found: C, 49.10; H, 3.76; N, 11.31. UV-vis in H$_2$O: λ$_{max}$ (ε/10^4 · mol^{-1} · dm^3 · cm^{-1}): 460(1.96); 325(sh, 3.54), 288(4.26), 244 nm (2.30). IR: 3075(w), 2925(w), 1602(m), 1514(w), 1485(w), 1462(m), 1442(s), 1090(vs), 764(s), 742(m), 731(w), 622(s) cm^{-1}. ^{1}H NMR (d$_6$-DMSO): δ8.85 (m, 6H), 8.72 (d, J = 8.2 Hz, 2H), 8.59 (d, J = 8 Hz, 2H), 8.26 (t, 2H), 8.20 (t, J = 7.7 Hz, 4H), 8.12 (t, 2H), 8.0 (t, 2H), 7.95 (t, J = 8.7 Hz, 6.1 Hz, 4H), 7.91(m, 2H), 7.84 (d, J = 5.3 Hz, 2H), 7.77 (d, J = 6.0 Hz, 6H), 7.58 (m, 6H), 7.45 (m, 6H), 7.10 (t, J = 7.7 Hz, 2H), 5.70 (d, J = 8.3 Hz, 2H), 4.91 (m, 4H), 1.85 (m, 4H), 1.35 (m, 4H).

2.2. Substrates

Quartz, glass, and indium-tin-oxide (ITO) slides, and mica flakes were used as substrates to fabricate self-assembled films for different purposes. The quartz wafers and glass slides were cleaned by immersion in a fresh piranha solution (v/v = 1:3, 30% H$_2$O$_2$/98% H$_2$SO$_4$) for 40 min, then rinsed in water and dipped into a solution containing one part NH$_3$ · H$_2$O (25 wt% aqueous solution), one part H$_2$O$_2$ (30 wt% aqueous solution), and five parts pure water at 70 °C for 20 min, followed by rinsing in copious deionized water.[12] The ITO substrates were cleaned by soaking in a saturated sodium hydroxide ethanolic solution overnight, and then rinsing in diluted HCl aqueous solution and distilled water. The freshly cleaved mica flakes were sonicated in distilled water, ethanol, and acetone successively immediately before use.

2.3. Instrumentation

The UV-vis spectra of the films on quartz slides were collected on a Cintra 10e UV-vis spectrophotometer using blank quartz as the reference. X-ray photoelectron spectra of the films on the glass slides were measured on an Axis Ultra X-ray photoelectron spectrometer [Kratos Co. (British)], using Al K$_\alpha$ radiation with energy of 1486.6 eV as the excitation source. For calibration, the C1s line was set at 286.4 eV as standard. The surface morphology of the films was visualized by atomic force microscopy (AFM). The measurements were taken on mica flakes using a Nanoscope III AFM (Digital Instruments) operating in the tapping mode with commercial silicon probes. Cyclic voltammetry experiments were performed with a CHI 420 voltammetric analyzer (CH Instruments) in a conventional three-electrode cell at room temperature (22 ± 2 °C). The working electrodes used here were the ITO glass modified with monolayer film. A platinum wire was used as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode (RE). Formal potentials (E_f) of redox couple in cyclic voltammograms were
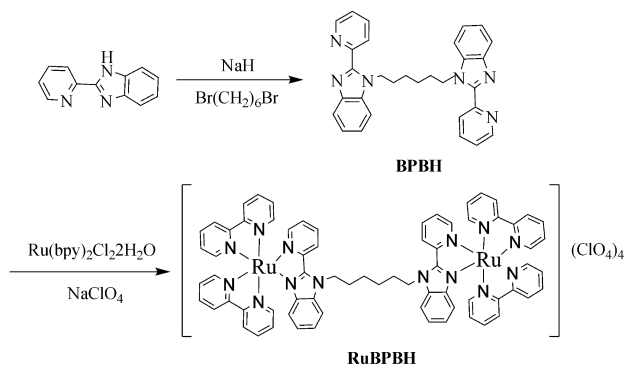

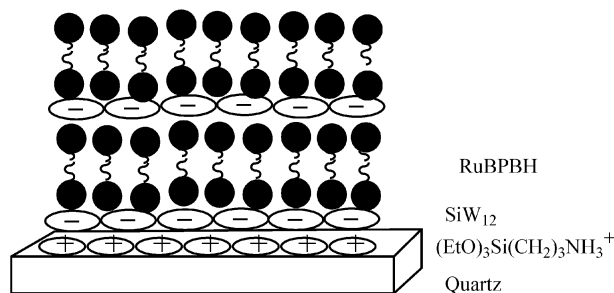**Fig. 1.** Synthetic route to the dipolar Ru(II) complex.

Fig. 2. The structure of the film $(SiW_{12}/RuBPBH)_n$.

estimated as average values of anodic (E_{pa}) and cathodic (E_{pc}) peak potentials, i.e., $E_f = (E_{pa} + E_{pc})/2$. All cyclic voltammograms were obtained in 0.125 M Na₂SO₄ (pH = 1.93) that was bubbled with nitrogen for at least 15 min prior to each measurement.

2.4. Preparation of Multilayer Film

The cleaned substrates were first silanized in 5% (v/v) 3-aminopropyltriethoxysilane-toluene solution for 5 h to create a surface covered with amino groups with reference to the literature.[13] The silanized substrates were immersed in HCl aqueous solution (pH = 2) to acheive the protonation of the surface amino group. The resulting protonated substrates were immersed in H₄SiW₁₂O₄₀ (hereafter abbreviated as SiW₁₂) (1 mmol/L) aqueous solution for 30 min, rinsed with distilled water of pH = 3 adjusted by HCl aqueous solution, and dried under a nitrogen stream. The substrates coated with SiW₁₂ were then dipped into a RuBPBH CH₃CN-H₂O (v/v, 1:1) solution (1 mmol/L) for 40 min, rinsed with copious CH₃CN-water (v/v, 1:1) solution, and blown dry with nitrogen. Repetitive immersions of the substrates in the SiW₁₂ and the RuBPBH solutions yielded multilayer films $(SiW_{12}/RuBPBH)_n$ (n = the number of repetitive deposition) with the film structure shown in Figure 2.

3. RESULTS AND DISCUSSION

3.1. Ultraviolet-Visible Spectra

The process of depositing multilayer films $(SiW_{12}/RuBPBH)_n$ on quartz slides was monitored by ultraviolet-visible (UV-vis) spectroscopy. Figure 3 shows the comparison of the UV-vis absorption spectra of the self-assembled multilayer film of $(SiW_{12}/RuBPBH)_{10}$ with those of the aqueous solutions of H₄SiW₁₂O₄₀ and the Ru(II) complex. Clearly, the multilayer film exhibits four absorption peaks at 247, 296, 326 (shoulder), and 471 nm, which are similar to those for RuBPBH aqueous solution [243, 289, 318 (shoulder), and 459 nm]. On comparison with the assignments for analogue Ru(II) complexes,[8b, 15] the bands at ~240 and ~460 nm for the film $(SiW_{12}/RuBPBH)_{10}$ film and the aqueous solution of
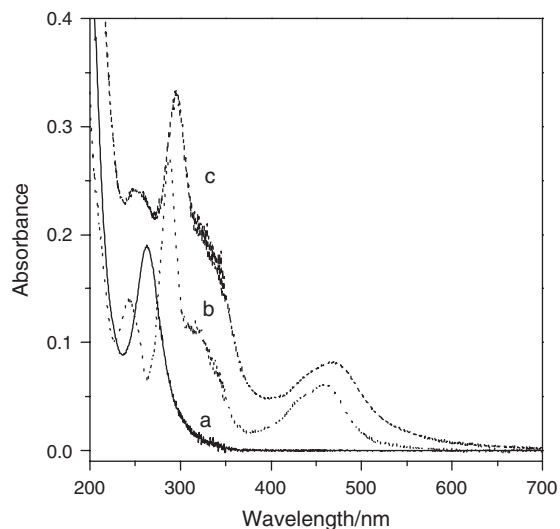

Fig. 3. UV-vis absorption spectra of (a) SiW₁₂, (b) RuBPBH, and (c) $(SiW_{12}/RuBPBH)_{10}$ film.

RuBPBH were assigned to metal-to-ligand charge-transfer (¹MLCT) transitions;[8b, 15] the UV band at ~240 was assigned to bpy-based $\pi \to \pi^*$ transitions and the UV band at ~290 nm was assigned to BPBH-based $\pi \to \pi^*$ transitions. The absorption (O → W charge transfer band[14] observed at 263 nm for SiW₁₂ aqueous solution) of SiW₁₂ is very weak compared to that of the Ru(II) complex and was obscured by the absorption of the RuBPBH in the UV absorption spectrum of the multilayer film. The MLCT absorption band centered at 471 nm with the absorption tail extending to 650 nm for RuBPBH in the film was red-shifted by 11 nm relative to the MLCT absorption band for the solution. These are characteristics of the charge transfer between SiW₁₂ and RuBPBH[7] and are not attributable to the protonation of imine on BPBH in RuBPBH caused by the possible proton transfer from H₄SiW₁₂O₄₀ to the Ru(II) complex during the film deposition, since pH spectral titration showed that the protonation of the amine nitrogen on BPBH in RuBPBH occurred below pH 1.9, accompanying spectral features of a slight increase in the intensities with almost unchanged absorption maxima.

The changes in the UV-vis absorption spectra of the $(SiW_{12}/RuBPBH)_n$ film as a function of the layer number n of the film $(SiW_{12}/RuBPBH)_n$ are shown in Figure 4. The absorption maxima were independent of the number of layers deposited, showing that the interlayer molecular interaction, i.e., the charge transfer between SiW₁₂ and RuBPBH, is independent of layer number. A good linear relationship between the number of layers and the absorbance at 297 and 471 nm (correlation factors of linear regression are 0.9944 for 297 nm and 0.9985 for 471 nm) is shown in the inset of Figure 4, demonstrating that the film deposition is uniform and reproducible. The absorbance per layer at 471 nm is calculated to be 4.23×10^{-3} from the slope in the linear relationship. From the

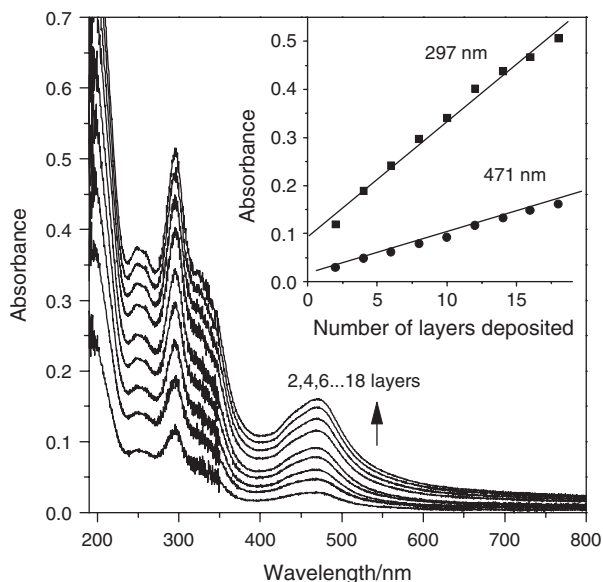**Fig. 4.** Dependence of UV-vis absorption spectra of $(SiW_{12}/RuBPBH)_n$ film on layer number. The inset is a plot of film absorbance at 297 and 471 nm versus layer number.

Lambert-Beer Law of modification for two-dimensional concentration,[16] $\Gamma = 10^{-3} A/\varepsilon$, where A is absorbance per layer; ε is the molar absorption coefficient (L mol^{-1} cm^{-1}) for RuBPBH aqueous solution, and Γ is the surface concentration (mol/cm^2) of RuBPBH in the multilayers calculated to be 2.16×10^{-10} mol/cm^2; a molecular area of 76.9 Å^2 was derived for RuBPBH, which is consistent with that (79.6 Å^2) obtained from the molecular modeling. It confirms that the ruthenium(II) complex was closely packed layer-by-layer, as shown in Figure 2.

3.2. X-Ray Photoelectron Spectra

In order to identify the elemental composition of the multilayer films and verify the charge transfer between SiW_{12} and RuBPBH in the film, X-Ray photoelectron spectra (XPS) of a monolayer SiW_{12} film without the Ru(II) complex layer, and a $(SiW_{12}/RuBPBH)_n$ $(n = 1)$ film were measured. For the SiW_{12} monolayer film, the W $4f_{5/2}$ and W $4f_{3/2}$ spin-orbit components were seen at 36.0 and 38.2 eV, respectively. For the SiW_{12}/RuBPBH film, the W $4f_{5/2}$ and W $4f_{3/2}$ components appeared at lower energies of 35.4 and 37.5 eV respectively, and binding energies at 280.8 eV for Ru $3d_{5/2}$, and 285.0 eV for Ru $3d_{5/2}$ were observed. The W $4f_{5/2}$ and W $4f_{3/2}$ components seen at low energy in the $(SiW_{12}/RuBPBH)_1$ film are consistent with the charge transfer from electron donor RuBPBH to the electron acceptor SiW_{12}.[7] The presence of W and Ru elements (C, Si, N and O are interferenced by the substrates and silanized reagent of 3-aminopropyltriethoxysilane) verifies the assembly process from both SiW_{12} and RuBPBH. A molar ratio of 1:4.17 for Ru:W in the $(SiW_{12}/RuBPBH)_1$ film is derived

on basis of the integration areas and sensitivity factors of their characteristic peaks, which is consistent with a molar ratio of SiW_{12}:RuBPBH = 2:3 in the ultrathin film. If we suppose the $SiW_{12}O_4^{4-}$ ion is a rigid ball and that SiW_{12} and RuBPBH are closely packed in the film, a molecular area of 73.3 Å^2 for RuBPBH is derived on basis of a cross section of 110 Å^2 for the $SiW_{12}O_4^{4-}$ ion[17] and the molar ratio of SiW:RuBPBH = 2:3. The molecular area of 73.3 Å^2 for RuBPBH estimated by XPS data is in agreement with those obtained from UV-vis spectroscopy and molecular modeling.

3.3. Atomic Force Microscopy

The AFM images on mica flakes could provide information about the surface morphology and homogeneity of the deposited films. From the AFM images, we can see that the silanized mica surface was uniform and smooth. After the polyoxometalate SiW_{12} and the Ru(II) complex were deposited, the surface became rough and the morphologies of the outer Ru(II) complex and the SiW_{12} layer were of distinctively different domain structures, as
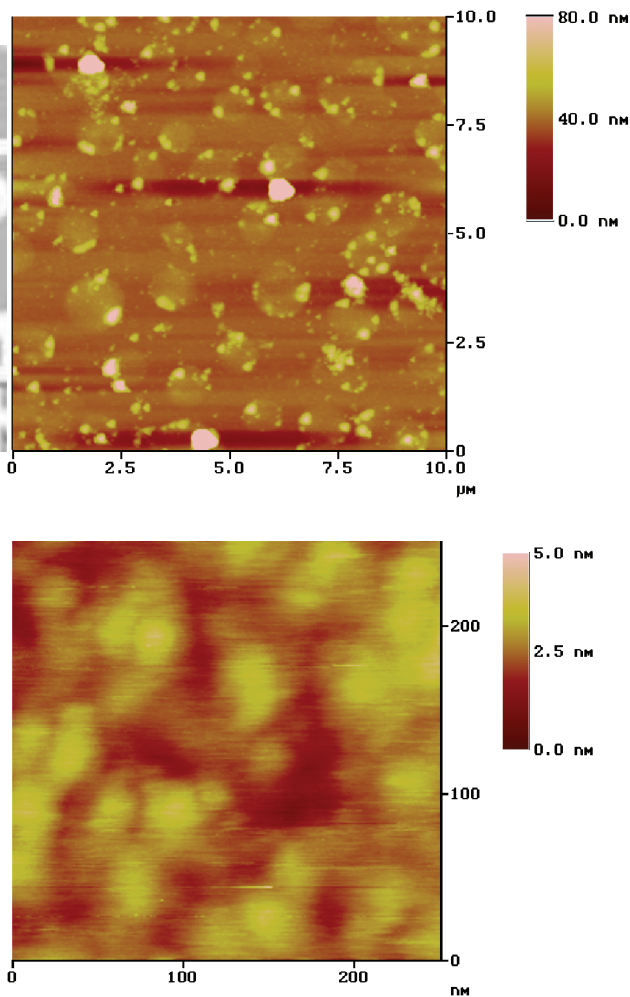

Fig. 5. AFM images of SiW_{12} (top) and SiW_{12}/RuBPBH (bottom) films.

shown in Figure 5. Many circular domains (Fig. 5(a)) in which the maximum diameter is as large as ~1 μm, can be observed for the SiW_{12} film, which is similar to the self-assembled films prepared from polycations and different heteropolyanions in the literature.[18] The AFM image for the RuBPBH film (Fig. 5(b)) shows that the quadrate domains ~20 × 50 nm appear, and some of them aggregate into clusters.

3.4. Cyclic Voltammetry

Cyclic voltammetry of a monolayer film of SiW_{12} deposited on an ITO electrode 3-aminopropyltriethoxy silanated, gave two pairs of redox waves with E_f at −0.239 and −0.488 V (not shown). The two redox pairs are assigned to two one-electron reductions and oxidations originating from $W^{VI/V}$, which are similar to the cyclic voltammetric results of the $SiW_{12}O_{40}^{4-}$ aqueous solution.[19] Figure 6 shows the cyclic voltammagrams of the SiW_{12}/RuBPBH film on the ITO electrode at various potential scan rates. The oxidation peak currents of the two $W^{VI/V}$ waves apparently decrease when SiW_{12} is coated by a RuBPBH layer, and the reduction waves almost disappeared. Moreover, a redox wave with E_f at 0.96 V, corresponding to the metal-based Ru^{2+}/Ru^{3+} redox reaction, is clearly observed. The oxidation peak currents for the Ru^{2+}/Ru^{3+} wave in the SiW_{12}/RuBPBH film increase linearly with the potential scan rates (inset of Fig. 5), indicating surface-confined redox reactions,[19–21] and as expected from the equation derived from an adsorbed redox species in a thin-layer cell[22] $i_c = n^2\Gamma F^2 v$ A/4RT, where n is the number of electrons, Γ is the surface concentration, F is the Faraday constant, v is the potential scan rate, and A is the electrode area. From the linear relationship in the

inset of Figure 6, the surface concentration Γ of the redox-active RuBPBH in the SiW_{12}/RuBPBH monolayer on the electrode was derived to be 2.08×10^{-10} mol/cm^2 at a potential scan rate of $v = 100$ mV/s; therefore, a molecular area of 79.9 Å^2 for RuBPBH was obtained, which is in good agreement with the values obtained from the UV-vis absorption spectroscopy and XPS.

4. CONCLUSIONS

A novel ruthenium(II) complex and $H_4SiW_{12}O_{40}$ have been successfully employed to fabricate a multilayer ultrathin film on solid supports using the electrostatic self-assembly technique. Studies of the hybrid organic-inorganic (SiW_{12}/RuBPBH)$_n$ film by means of UV-vis, XPS, AFM, and cyclic voltametry reveal that the multilayer film is uniformly prepared in a layer-by-layer fashion, SiW_{12} and RuBPBH are closely packed, and the charge transfer may occur between them. The SiW_{12} and RuBPBH species assembled in the film are redox active with surface confined characteristics. Currently, efforts are being directed at the applications of this organic-inorganic super lattice film in catalysis and electrochemical sensing.

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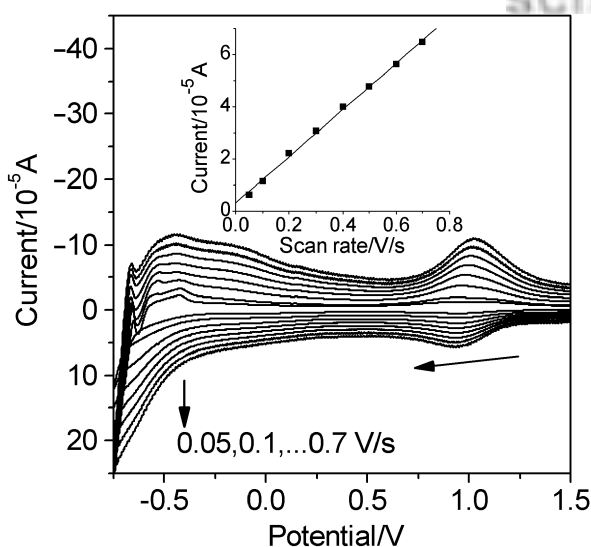

Fig. 6. Cyclic voltammagrams of film SiW_{12}/RuBPBH film on an ITO electrode at various scan rates. The inset is a linear plot of the oxidation peak currents against the potential scan rates.

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