Fabrication and Characterization of Luminescent Multilayer Films Based on Polyoxometalates and Fuchsin Basic

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Z. Naturforsch. **2011**, *66b,* 43 – 48; received June 29, 2010 / revised October 11, 2010

A luminescent multilayer film has been fabricated from the polyoxometalate anion α-$[PMo_{12}O_{40}]^{3-}$ (α-PMo_{12}) and the cation Fuchsin Basic (FB) through an electrostatic layer-by-layer (LbL) self-assembly method and characterized by UV/Vis spectra, atomic force microscopy and X-ray photoelectron spectra. The fluorescence properties of the LbL film have also been investigated. Cyclic voltammetry measurements have demonstrated that the electrochemical properties of the polyoxometalate and FB are maintained in the multilayer film, which exhibits electrocatalytic activity for the reduction of bromate.

Key words: Layer-by-Layer Self-Assembly, Thin Film, Polyoxometalates, Fuchsin Basic, Fluorescence

Introduction

Polyoxometalates (POMs), as a rich class of inorganic metal-oxygen cluster compounds, have been variously applied in catalysis, molecular conduction, magnetism, medicine, and luminescence [1 – 5], due to their well-defined molecular structures and electronic versatility. Especially, the Keggin-type POMs have various applications in catalysis and molecular materials owning to their excellent redox character and high stability in low pH conditions [6, 7]. Thus, Keggin-type POM-based films have become a kind of promising materials with charming potential applications. POM-based films generally are prepared by methods such as dip coating, Langmuir-Blodgett loading, electrodeposition, doping in conducting polymers, and layer-by-layer (LbL) self-assembly [8 – 10]. The LbL method is based on alternate adsorption of oppositely charged polyelectrolytes or polyions by electrostatic attractions [11], which provides a convenient way to combine various inorganic and organic species into functional inorganic-organic composite film materials [12] and capsules [13]. By using the LbL method, Jang and coworkers obtained photoluminescent thin films based on the lacunary Dawson-type POM $K_{17}[Ln(P_2Mo_{17}O_{61})_2]$ and poly(allylamine hydrochloride) [14]; Cox *et al.* prepared electrochromic films of pentaerythritol-based metallodendrimers with Ru^{II} terpyridine units (RuDen) and a Dawson-type phosphotungstate $[P_2W_{18}O_{62}]^{6-}$ as a bifunctional electrocatalyst [15]; Wang and coworkers fabricated a novel thermochromic multilayer film of $(NaP_5W_{30}/PEI)_n$ which may be of use in the development of thermosensors [16], and finally Xu *et al.* synthesized $[P_2W_{17}/PAH/P_2W_{17}/NR]_n$ multilayer films, showing a potential application in tunable-color electrochromic devices [17].

Dyes are extensively used in the textile industry, as well as in the decoration of materials and in bacteriological and histopathological methods as colorants and staining agents. Recently, cationic dyes have been used in constructing POM-based film materials by the LbL method, including thionine (TH) [18], Methylene Blue (MB), Azure A (AA), Basic Blue 3 (BB3), Brilliant Cresyl Blue (BCB), Nile Blue Chloride (NB) [19], Rhodamine B (RB), and Rhodamine 6G (R6G) [2], *etc.*

FB ($C_{20}H_{20}ClN_3$) is a triphenylmethane based dye, widely found in living organisms, and can be used as a fluorescence probe for the determination of metallic and non-metallic ions, proteins and nucleic acids [21, 22]. Therefore, it is a good candidate to assemble film materials with special fluorescence properties. FB possesses positive charge in neutral and alkaline solutions. With the singly charged FB cation it is difficult to form highly reproducible $\{PEI/(PSS/FB)_n\}$ films, since it is not absorbed firmly on common poly-

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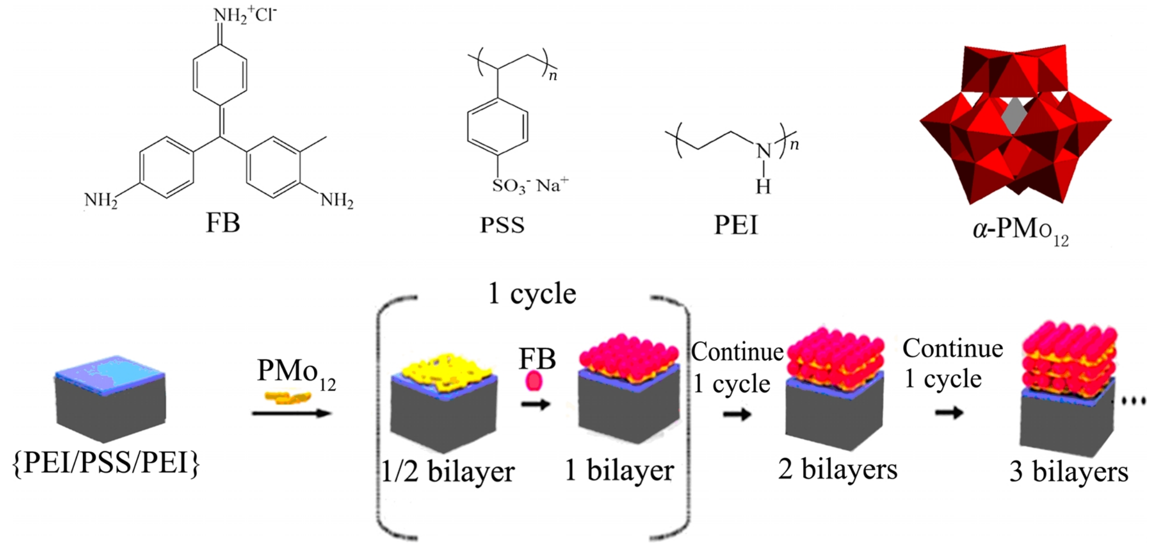

Scheme. 1. The schematic procedure of fabricating (α-PMo$_{12}$/FB)$_n$ multilayer films.

electrolytes such as PSS, and might be eluted into PSS aqueous solution. POMs' strong electrostatic force which arises from the high surface charge makes their combination with the FB firmer than that with the polyelectrolyte PSS. Hence, the FB can be absorbed substantially into the LbL multilayer films. In this work, we have selected Keggin α-PMo$_{12}$ and FB to fabricate an organic-inorganic composite film by the LbL method shown in Scheme 1. The fluorescence and electrocatalytic properties of the obtained film have been studied.

Results and Discussion

UV/Vis absorption spectra

The UV/Vis spectra (Fig. 1) of the {PEI/PSS/PEI/(α-PMo$_{12}$/FB)$_n$} ((α-PMo$_{12}$/FB)$_n$, $n = 1-10$) multilayer film exhibit the characteristic absorption peaks of the polyanions at 207 and 291 nm for α-PMo$_{12}$ in the UV region, attributed to the $O_d \rightarrow Mo$ and $O_{b,c} \rightarrow Mo$ charge transfer transitions, respectively. In the visible region, the absorption band at 552 nm could be assigned to the characteristic peak of the FB. This confirms the incorporation of α-PMo$_{12}$ and FB into the multilayer film. The absorbence values at 207, 291 and 552 nm have a steady linear increase with the increase of the bilayer number of the LbL film built up by an increasing number of dipping cycles (shown in Fig. 1, inset), indicating that each adsorption cycle proffers nearly equal amounts of α-PMo$_{12}$ and FB into the thin film, and the growth of the multilayer film is regular.

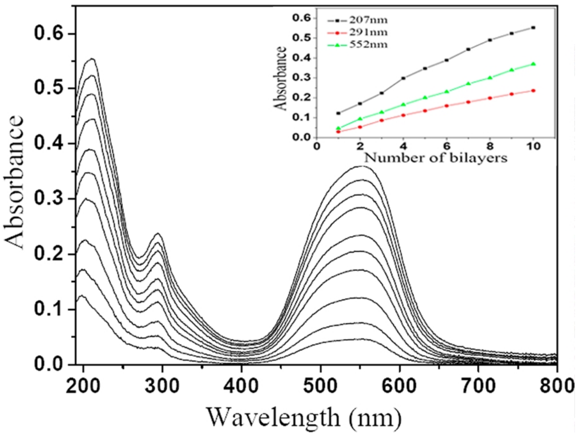

Fig. 1. UV/Vis absorption spectra of an (α-PMo$_{12}$/FB)$_n$ ($n = 1-10$) multilayer film assembled on a quartz substrate. The inset shows plots of the absorbance values at 207, 291 and 552 nm for the number of (α-PMo$_{12}$/FB)$_n$ bilayers.

Atomic force microscopy

The surface morphology of a {PEI/PSS/PEI/(α-PMo$_{12}$/FB)$_3$} thin film fabricated on a silicon substrate was studied by AFM (Fig. 2). The AFM image shows that the surface of the film is flat covered by uniformly distributed round nanoparticles with a mean diameter of *ca.* 52 nm. The thickness of the film has been estimated to be 23.62 nm. The average interface rough-

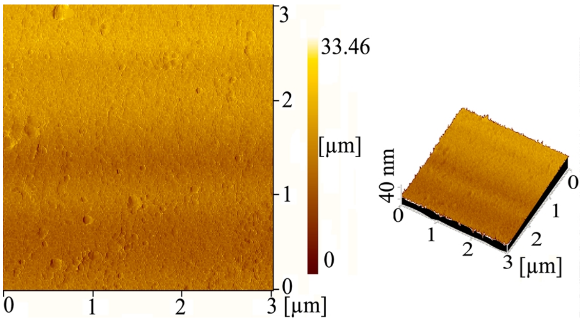

Fig. 2. AFM image of an (α-PMo$_{12}$/FB)$_3$ multilayer film: planar image (left) and three-dimensional image (right).

ness, determined in an area of $3.0 \times 3.0\ \mu m^2$ by AFM is 3.95 nm.

X-Ray photoelectron spectra

XPS spectra were investigated to identify the elemental components of the (α-PMo$_{12}$/FB)$_5$ film deposited on the silicon substrate. XPS measurements were performed to confirm the presence of C, N, P, and Mo. These elemental components of the film were detected by the binding energy (BE) peaks corresponding to C $1s$ (BE = 284.6 eV), N $1s$ (BE = 3989 eV), P $2p$ (BE = 133.4 eV), Mo $3d_{5/2}$ (BE = 232.65 eV), and Mo $3d_{3/2}$ (BE = 235.85 eV) (Fig. 3). XPS results thus confirm the existence of α-PMo$_{12}$ and FB in the multilayer film in conjunction with the results of the UV/Vis spectra.

Electrochemical properties of the multilayer film

Polyoxometalates have good redox activities and are extensively used as electrocatalysts [23, 24]. The (α-PMo$_{12}$/FB)$_5$ multilayer film undergoes three redox processes, which were measured in the range from -400 to 1200 mV in 0.1 mol L^{-1} HAc-NaAc buffer solution. The midpoint potential $E_{\mathrm{mid}} = (E_{\mathrm{pa}} + E_{\mathrm{pc}})/2$ values are -194 (IV–IV′), -31 (III–III′), and 263 (II–II′) mV, respectively, which can be assigned to molybdenum-centered redox processes of α-PMo$_{12}$ [25]. The peak at 1054 mV for (α-PMo$_{12}$/FB)$_5$ is obviously due to an irreversible oxidation of FB (Fig. 4a). The result suggests that the electrochemical properties of α-PMo$_{12}$ and FB are maintained in the LbL film. The redox behavior of the α-PMo$_{12}$ anion in the (α-PMo$_{12}$/FB)$_5$ film is similar to that in solution, but shifts of the corresponding peaks are observed which are perhaps due to the α-PMo$_{12}$ anion in different phases (Fig. 4b).

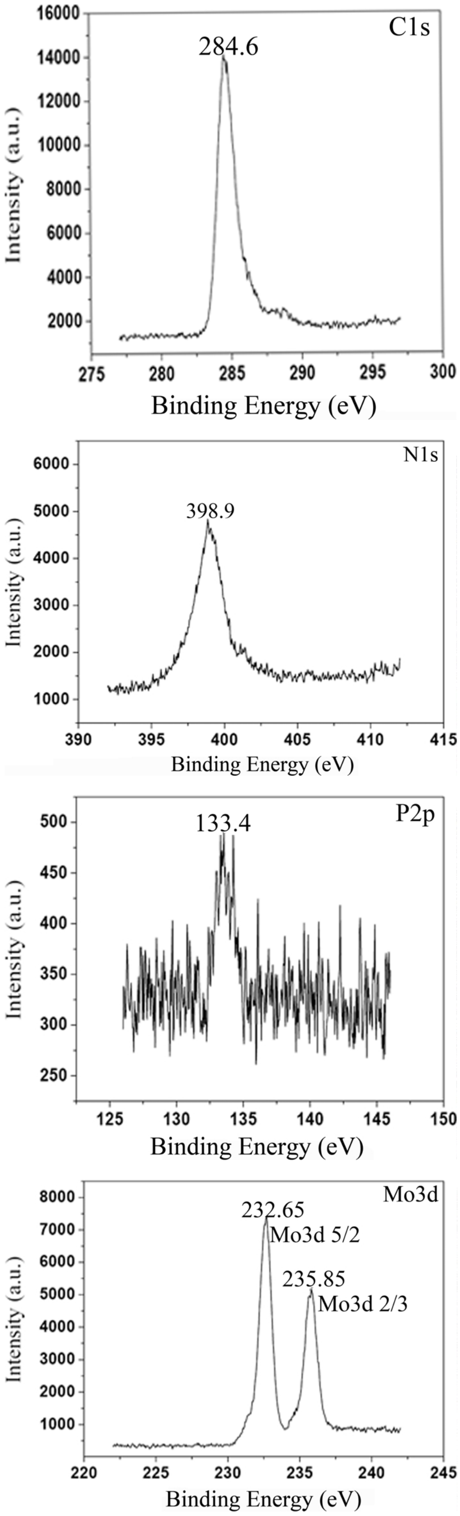

Fig. 3. XPS spectra of an (α-PMo$_{12}$/FB)$_5$ multilayer film.

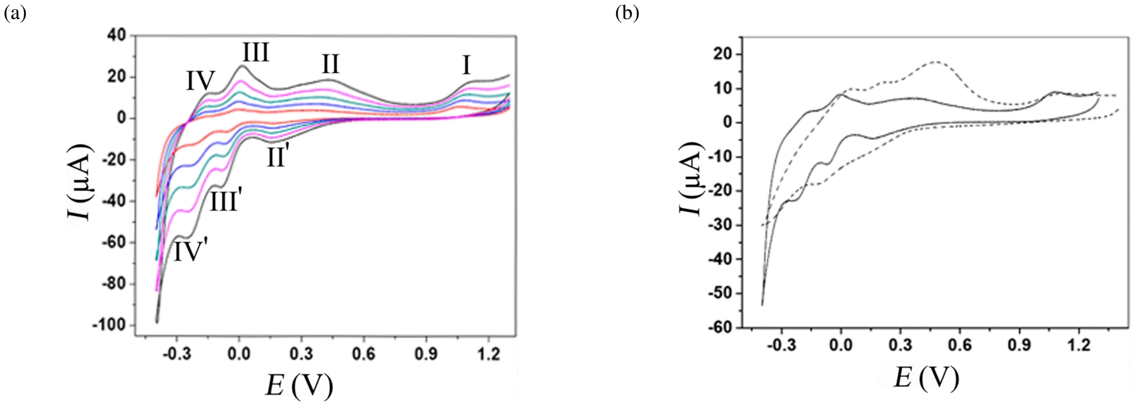

Fig. 4. CV of (a) the (α-PMo$_{12}$/FB)$_5$ film on ITO electrodes in 0.1 mol L^{-1} HAc-NaAc (pH = 4.76) at scan rates of 20, 40, 60, 80, and 100 mV s^{-1}, and (b) a bare ITO electrode in a solution containing 0.5 mmol L^{-1} α-PMo$_{12}$ and FB (dotted line), and an (α-PMo$_{12}$/FB)$_5$ film (solid line) on an ITO electrode in 0.1 mol L^{-1} HAc-NaAc (pH = 4.76), at a scan rate of 200 mV s^{-1}.

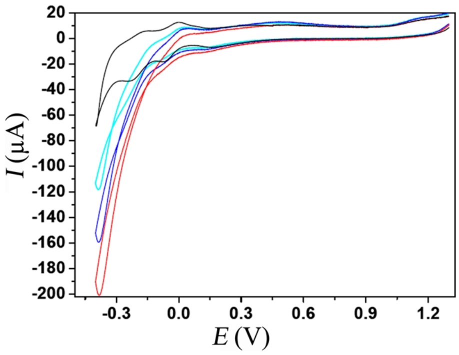

Fig. 5. CV of an (α-PMo$_{12}$/FB)$_5$ film on ITO in 0.1 mol L^{-1} HAc-NaAc (pH = 4.76) containing BrO$_3{}^-$ in various concentrations: 0, 4, 8, 12 mmol L^{-1} (from top to bottom). Scan rate: 200 mV s^{-1}

Electrocatalytic reduction of BrO$_3{}^-$ by the multilayer film

Fig. 5 shows the CV for the electrocatalytic reduction of BrO$_3^-$ by (α-PMo$_{12}$/FB)$_5$ in 0.1 mol L^{-1} HAc-NaAc buffer solution (pH = 4.76). With addition of BrO$_3^-$, the reduction peak current (IV) of Mo$^{\mathrm{VI}}$ substantially increases, while the corresponding oxidation peak current decreases, suggesting that the six-electron reduced species of α-PMo$_{12}$ can electrochemically catalyze the reduction of the BrO$_3{}^-$ [26].

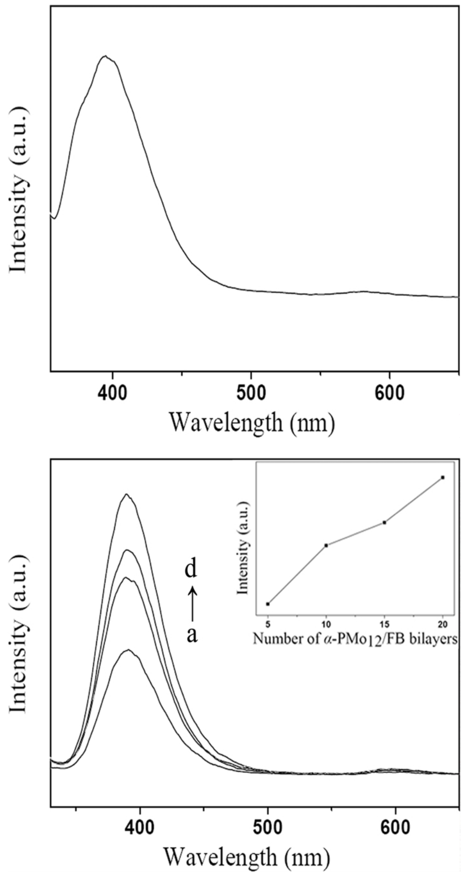

Fig. 6. Fluorescence spectra of FB aqueous solutions (top) and (α-PMo$_{12}$/FB)$_n$, a: n = 5, b: n = 10, c: n = 15, d: n = 20 multilayer films (botom), excited at 245 nm at r. t. The inset shows the plot of the emission intensity *vs.* the number of α-PMo$_{12}$/FB bilayers.

Fluorescence properties of the multilayer film

The fluorescence spectra (Fig. 6) of an FB aqueous solution (10^{-4} mol L^{-1}) and of the (α-PMo$_{12}$/FB)$_n$ (n = 5, 10, 15, and 20) multilayer films were mea-

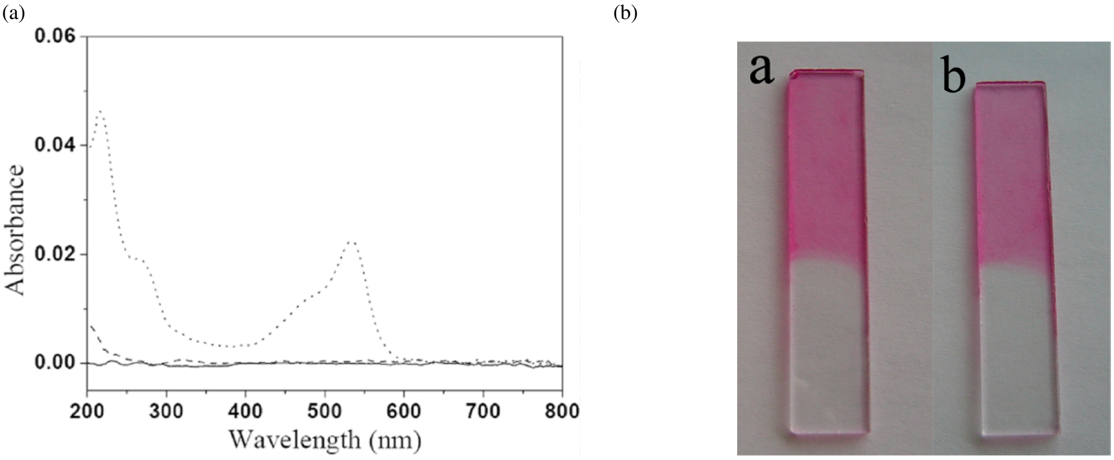

Fig. 7. Left: UV/Vis absorption spectra of the (α-PMo_{12}/FB)$_{10}$ multilayer films after dipping for 1 h (dashed line) and for 12 h (dotted line) into deionized water, and a control experiment (solid line); Right: optical micrographs of the (α-PMo_{12}/FB)$_{10}$ multilayer films before (a) and after (b) dipping into deionized water.

sured by fluorescence emission spectroscopy at r. t. The inset in Fig. 6 indicates the variation of the fluorescence intensity with the number of α-PMo_{12}/FB bilayers. As shown in Fig. 6, all the multilayer films exhibit the characteristic fluorescence of the FB molecule at 390 nm, indicating that the FB cation is firmly fixed in the multilayers. Moreover, the emission intensity tends to increase almost linearly with the number of (α-PMo_{12}/FB)$_n$ bilayers, while the shape and position of these emission bands remain nearly unchanged. This fact also confirms a high reproducibility of the LbL self-assembly technique in fabricating the multilayer films.

The stability of the (α-PMo_{12}/FB)$_n$ multilayer film

Elution experiments were performed to study the stability of the multilayer films. After the (α-PMo_{12}/FB)$_{10}$ films were dipped in deionized water for 1 h and 12 h, respectively, the aqueous solutions were monitored by UV/Vis spectra in order to check if any elution of α-PMo_{12} and/or FB had occurred (Fig. 7, left). The absorption peaks of α-PMo_{12} at 209 and 291 nm and of FB at 552 nm just appeared after dipping for 1 h, and the absorption intensity increased significantly after 12 h, but was much weaker than those of the (α-PMo_{12}/FB)$_1$ film. Therefore the elution of α-PMo_{12} and/or FB was negligible. Optical micrographs of (α-PMo_{12}/FB)$_{10}$ films were taken before and after the elution experiments (Fig. 7, right) and showed that the colors of the (α-PMo_{12}/FB)$_{10}$ multilayer films did not change observably. Similar elution experiments were also carried out in ether, and no characteristic absorptions of α-PMo_{12} and FB were observed in the UV/Vis spectra. These facts indicate that the components are indeed firmly attached, and that the (α-PMo_{12}/FB)$_n$ multilayer films are mildly stable in aqueous solutions and quite stable in ether.

Conclusions

A luminescent multilayer film based on $\alpha[PMo_{12}O_{40}]^{3-}$ and FB was fabricated by the LbL self-assembly method. The mauve film in which close-packed nanoclusters of α-PMo_{12} anions and FB cations are distributed uniformly was smooth and homogeneous. The (α-PMo_{12}/FB)$_n$ films show not only good stability and reproducibility, but also intense fluorescence and electrocatalytic activity for the reduction of BrO_3^-. The films are expected to have potential applications in the field of luminescence sensors, electrotransfer and electrocatalysis devices.

Experimental Section

Chemicals and measurements

Poly(ethylenimine) (PEI; MW. 750 000), Poly(sodium styrenesulfonate) (PSS; MW. 70 000), and Fuchsin Basic (FB; MW. 337.85) were commercially obtained from Aldrich and used without further purification. $H_3PMo_{12}O_{40}$ was synthesized by a published method [27]. The water used in all experiments was deionized. 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 measurements were carried out on a Thermo ESCALAB 250 spectrometer with an AlK_α

(1486.6 eV) achromatic X-ray source. AFM images were obtained by using the 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 controlling the electrochemical measurements and data collection. A conventional three-electrode system was used, with a bare ITO electrode or a $(\alpha\text{-PMo}_{12}/\text{FB})_n$ multilayer film-coated ITO electrode as working electrodes, platinum foil as a counter electrode, and SCE as a reference electrode.

LbL assembly

The fabrication of the multilayer film was carried out as follows: The substrate (silicon or a quartz glass slide) was cleaned according to the literature [28], making its surface become hydrophilic, rinsed with deionized water, and then dried under a nitrogen stream. The hydrophilized substrate was alternately immersed in 1×10^{-3} mol L^{-1} PEI solution (the concentration was calculated based on their repeating units), 1×10^{-3} mol L^{-1} PSS solution and 1×10^{-3} mol L^{-1} PEI solution for 20 min. After washing, a nitrogen stream was blown over the film surface until the adhering water layer was completely removed. The PEI/PSS/PEI-coated substrate then was alternately dipped into 1×10^{-3} mol L^{-1} α-PMo$_{12}$ 1×10^{-4} mol L^{-1} FB for 20 min, also rinsed with deionized water, and dried in a nitrogen stream after each dipping to give a mauve multilayer film $\{$PEI/PSS/PEI/$(\alpha\text{-PMo}_{12}/\text{FB})_n\}$.

The stability of the multilayer film

Elution experiments of α-PMo$_{12}$ and/or FB were performed by dipping the multilayer films $(\alpha\text{-PMo}_{12}/\text{FB})_{10}$ in deionized water and ether for 1 h and 12 h, respectively, and then monitoring the UV/Vis absorption spectra of these solutions.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (21071029) and the Program for Changjiang Scholars and Innovative Research Team in University.

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