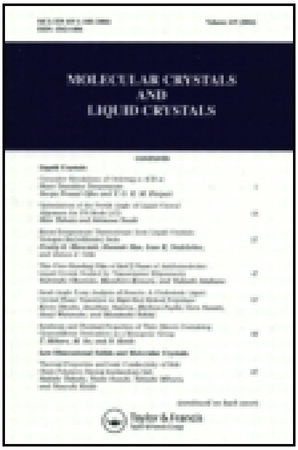

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Layer-by-layer Assembled Molecular Films—I: Organic-Inorganic Hybrid Films and Electrocatalytic Sensing Applications

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Layer-by-layer Assembled Molecular Films – I: Organic-Inorganic Hybrid Films and Electrocatalytic Sensing Applications

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Functional molecular films are prepared by alternatively assembling organic and inorganic molecular units in a layer-by-layer fashion. The building blocks of the films are nanometer-sized species carrying either special catalytic or unique chromic properties. Electrostatic interactions are employed as the driving force for assembling. Such films can be assembled on almost any kind of substrate, making it possible to fully characterize their chemical and physical properties.

Keywords layer-by-layer; organic-inorganic hybrid; electrostatic

INTRODUCTION

The function of a multi-layered molecular film depends not only on the properties of its molecular building blocks, but also on its assembling architecture[1-3]. In principle, a multi-layered molecular film can be constructed from various molecular monolayers by employing one or the combination of several types of chemical linkages as the anchoring forces, including covalent, ionic(electrostatic), coordination, and hydrogen-bonding. Depending on the desired application for a film, each of the above chemical linkages has its advantages as well as limitations. For example, ionic linkage based on electrostatic attraction has a unique advantage that the linkage itself is inert to various harsh reactive environments such as the presence of strong oxidative/ reductive or acidic/basic agents or reactive radicals. Therefore, electrostatic assembling is often suitable for the preparation of catalytic films. In this paper, we report the molecular films prepared by alternatively assembling organic and inorganic layers carrying opposite charges. Either organic or the inorganic layers also carry either catalytic or chromic functionality, so that the as-prepared films show electrocatalytic, photocatalytic, as well as electrochromic properties.

EXPERIMENTAL

All reagents used in this paper, including Ni(II)-tetrakis(N-methyl-4-pyridyl-porphine ($NiTMPyP^{4+}$), Cu(II)-tetrapyridinium-tetramethyl phthalocyanine($CuTPyTMPc^{4+}$), Bis-N-methyl acridinium (BMA^{2+}), methlviologen (MV^{2+}), heteropoly acids were purchased from Aldrich. The nanometer-sized sodalite (~100 nm) and some special heteropoly acids were synthesized in our own lab, and their composition and structures were confirmed by several techniques including X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). Triply-distilled water was used to prepare all the solutions. When electrochemistry was used, the solution was purged by dry N_2 for 20 minutes to remove the dissolved oxygen. The layer-by-layer assembling of each film was achieved by alternatively inserting a substrate in solutions containing either cationic or anionic species. The substrate can be any common electo-conductive materials such as glassy carbon, ITO glass, noble metal plates (Pt, Au, Ag), or any optical-transparent materials such as Pyrex or quartz glass slides. The layer-by-layer growth of our films was monitored by UV-Vis. and FT-IR spectroscopies, and by cyclic voltammetry (CV).

RESULTS AND DISCUSSION

Figure 1 shows two examples of our functional films prepared by alternatively assembling in two solutions, one containing an inorganic anion donor and another containing an organic cation donor. On the left side of Figure 1 are the UV-Vis spectra showing the layer-by-layer growth of a nanometer-sized zeolitic anion donor (Na_m.nSiO2. $mAlO_2^-$ .xH_2O in sodalite structure) and a metalloporphyrin cation donor ([NiTMPyP]Cl_4). On the right side of Figure 1 are the UV-Vis spectra of a film grown from solutions containing $H_3PMo_{12}O_{40}.xH_2O$ (an anion donor) and [CuTPyTMPc]Cl_4 (a cation donor), respectively. The insets of the Figure 1 show the linear increase of the absorption maxima with the increase of the layers, suggesting that the number of species assembled in each layer are roughly the same. Both films show remarkable electrocatalytic activity and electrochromism.

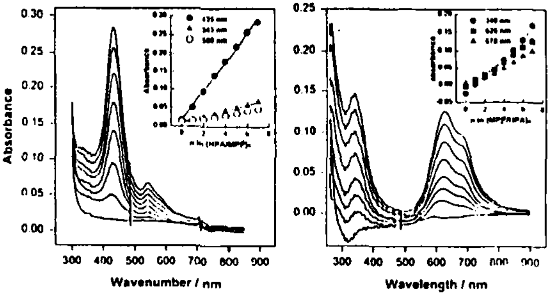

FIGURE 1. UV-Vis spectra of the layer-by-layer assembled {$Sodalite^{x-}$|$NiTMPyP^{4+}$}$_n$ (the left) and {$PMo_{12}O_{40}^{3-}$|$CuTPyTMPc^{4+}$}$_n$ (the right) films on ITO substrates. The insets show the linear increase of the absorption maxima with the increase of layer numbers.

Figure 2 shows the cyclic voltammograms of a film assembled in a layer-by-layer fashion from solutions containing $PMo_{12}O_{40}^{3-}$ and BMA^{2+}, respectively. The inset displays the linear increase of the peak currents for the middle redox pair with the increase of the layer number, suggesting the amount of assembled species in each layer is almost the same. All the films shown here, and many other similar films prepared in our lab, display very interesting electrocatalytic and electrochromic effects[4].

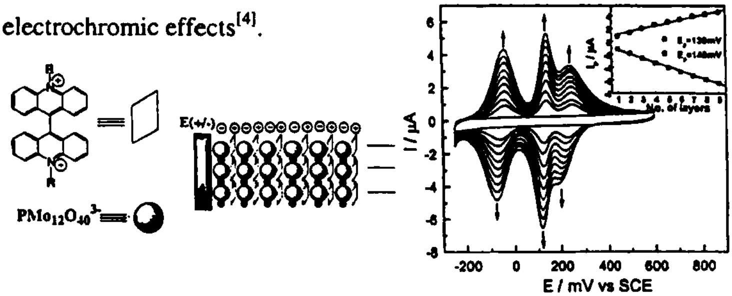

FIGURE 2. The cyclic voltammograms of layer-by-layer assembled $\{PMo_{12}O_{40}^{3-}|BMA^{2+}\}_n$ film.

CONCLUSION

Positively charged derivatives of porphyrins, phthalocyanines and viologens are assembled with the negatively charged HPA and nano-zeolites in a layer-by-layer fashion. The films show very interesting electrocatalytic and electrochromic effects.

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