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Layer-by-layer Assembled Molecular films—III: Electrochemical Assembly and Electropolymerization of Noble Metal Complexes

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Layer-by-layer Assembled Molecular films – III: Electrochemical Assembly and Electropolymerization of Noble Metal Complexes

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A class of inorganic films based on electrochemically assembled Pt(IV/II) and Pd(IV/II) complexes were prepared. The films display very interesting electrocatalytic and electrochromic properties.

Keywords electrochemical assembly; platinum; palladium; complexes

INTRODUCTION

Complexes of Pt(IV/II) and Pd(IV/II) ions are a family of very interesting building blocks for films[1]. Many Pt(IV/II) and Pd(IV/II) complexes readily form ionic crystals consisting of mixed-valence, one-dimensional conductive polymers[2]. These complexes and their polymers show interesting catalytic[3], optical and electronic[4] properties. Here we report the preparation of a class of films based on Pt(IV/II) and Pd(IV/II) complexes by electrochemical assembly and electropolymerization. Normally, three types of one-dimensional structures can be formed by Pt(IV/II) and Pd(IV/II) complexes as illustrated in Figure 1. In Type-I structure, a bridging ligand is required between two neighboring metal ions, while such a bridging ligand does

not exist in Type-II structure. Type-IA structure has a negatively charged backbone and requires the presence of proper metal cations. The backbones of Type-IB and Type-II structures consist of alternatively connected cationic and anionic complexes. The films with all three types of structures are electrochemically assembled or polymerized on various electroconductive substrates in this work.

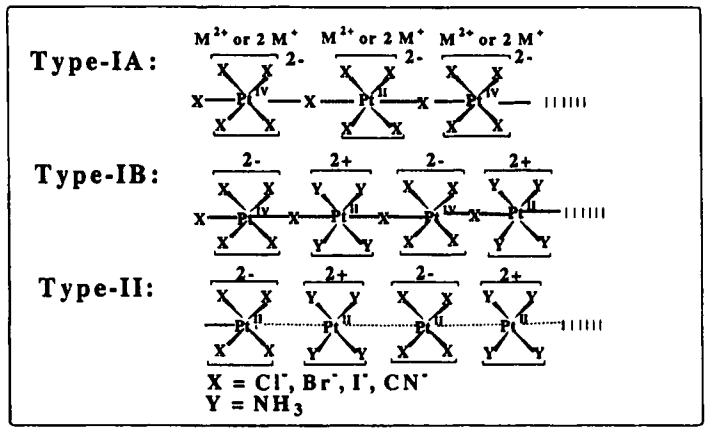

FIGURE 1. The structural types of Pt(IV/II) and Pd(IV/II) complexes.

EXPERIMENTAL

Chemicals used in this study, including K_2MX_4, K_2MX_6 (M = Pt, Pd; X = Cl^-, Br^-, I^-, CN^-), $K_4Ru(CN)_6$, $Pt(NH_3)_4Cl_2$, $Pd(NH_3)_4Cl_2$, $CuCl_2$., $RuCl_3$, were all purchased from Aldrich and used as received. High purity nitric oxide (NO) gas in lecture bottle was purchased from Matheson. All solutions were prepared using triply distilled water. Cyclic voltammetry(CV) was used to assemble the films of Pt(IV/II) and Pd(IV/II) complexes. The range of potential scan and the direction of the initial scan are very important for electrochemical assembly and

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electropolymerization. The preparation of $[CuPtCl_6.CuPtCl_4]_n$ film, for example, was carried out in an aqueous solution containing ~ 3 mM of K_2PtCl_6, 3 mM of $CuCl_2$ and 1 M of KCl. The potential was cyclically scanned from + 0.7 to –0.8 V (*vs.* SCE). X-ray powder diffraction (XRD), scanning electron microscopy (SEM), micro-Raman spectroscopy, and CV behaviors were used to characterize the films.

RESULTS AND DISCUSSION

Figure 2 shows the electrochemical assembly of $[Cu^{2+}(PtCl_6)^{2-}Cu^{2+}(PtCl_4)^{2-}]_n$ film (Type-I structure) on a 10 μ glassy carbon disk (the left) and the electrocatalytic behavior of the assembled film in the oxidation of NO (the right). As can be seen from the CVs, the currents corresponding to both Cu^{2+}/Cu^{+} and Pt^{4+}/Cu^{2+} redox couples increase with the number of scans, indicating the growth of Pt(IV/II) complex layers in the film.

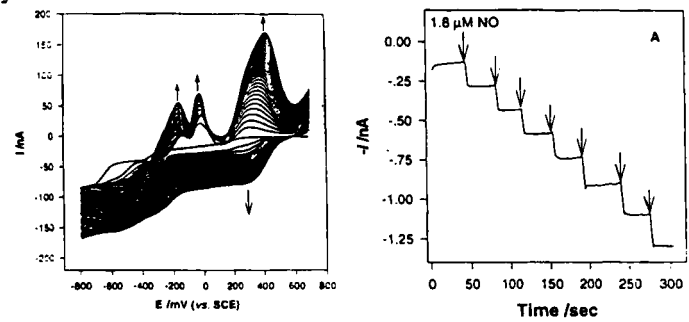

FIGURE 2. CVs showing the electrochemical assembly of $[Cu^{2+}(PtCl_6)\text{-}Cu^{2+}(PtCl_4)^{2-}]_n$ film (the left) and the electrocatalytic oxidation of NO at the film at +0.7 V *vs.* SCE (the right).

The electrocatalytic activity of the film in the oxidation of NO at pH 7 is among the best in all the known electrocatalysts for NO. We have

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prepared a NO sensor based on this film, and its detection limit for NO at pH 7 can reach ~ 2 nM. Using the same electrochemical assembling method, we synthesized a class of films based on Pt(IV/II) and Pd(IV/II) complexes and with all three types of structures (Figure 1). Table 1 lists the films successfully prepared in our lab. Most of these films show both good electrocatalytic and electrochromic properties[1].

TABLE 1. Electrochemically assembled films where M = Pt(IV/II), Pd(IV/II) and X = Cl^-, Br^-, I^-.

STRUCTURE TYPE	ELECTRO-ASSEMBLED FILMS
Type-IA	$[CuMX_6.CuMX_4]_n$
Type-IB	$[M(NH_3)_4.MX_6]_n$
Type-II	$[M(NH_3)_4.MX_4]_n$
Unspecified	$[Ru^{3+/2+}MX_6]_n$, $[CuPt(CN)_6]_n$ $[Cu_2Ru(CN)_6]_n$, $[CuM(CN)_4]_n$

CONCLUSION

A class of inorganic films based on Pt(IV/II) and Pd(IV/II) complexes were assembled electrochemically on various electroconductive substrates. The films show very good electrocatalytic activity in the oxidation of nitric oxide.

Acknowledgement

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