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Modification of electrodes with nanostructured films containing dirhodium-substituted polyoxometalates

Abstract Layer-by-layer (LBL) electrostatic assembly was used to prepare films comprising generation-4 polyamidoamine dendrimers (G4-PAMAM) and dirhodium polyoxometalates (Rh$_2$POMs) on glassy carbon (GC) electrodes. To employ the propensity of P$_2$Mo$_{18}$O$_{62}$$^{6-}$ (PMo) to directly adsorb on glassy carbon, a new compound, Rh$_2$PMo, was synthesized and characterized. The behavior was compared to that of a previously reported Rh$_2$POM prepared from PW$_{12}$O$_{40}$$^{3-}$ (PW). The LBL assembly of (G4-PAMAM, Rh$_2$PW)$_n$ bilayers on GC pretreated by formation of a monolayer of 4-aminobenzoic acid was studied by doing a linear least-squares fit of peak current to n ($n = 5$); the result gave an r^2 of only 0.90. With Rh$_2$PMo, the analogous experiments with $n = 7$ gave an $r^2 = 0.995$. Strong adsorption of Rh$_2$PMo onto GC allowed the assembly of Rh$_2$PMo$_{adsorbed}$|(G4-PAMAM, Rh$_2$PMo)$_n$ on conventional GC and on a 10-μm carbon fiber. The latter was used to demonstrate the bifunctional electrocatalytic property of these films through reduction of nitrite and the oxidation of arsenite.

Keywords Catalysis · Dirhodium · Polyoxometalates · Voltammetry

Introduction

Because polyoxometalates (POMs) undergo reversible, stepwise, multi-electron transfer at a variety of electrodes, they have generated interest in several fields of chemistry, including electrocatalysis and energy storage [1, 2].

Dedicated to the memory of Harry B. Mark, Jr. (28 February 1934–3 March 2003)

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Generally they are used as solutes in aqueous solution; however, the scope of potential applications is extended by their compatibility with single-crystal electrochemical methodology [3, 4], by immobilization in sol-gel materials for solid-state voltammetry [5, 6], and by incorporation in films on electrode surfaces, which is the topic of the present study. Adsorption of POMs on various types of carbon [7, 8, 9, 10, 11], mercury [9, 12], gold [9, 10], and indium tin oxide (ITO) [10] electrodes has been reported. The penchant to adsorb is perhaps strongest for the phosphomolybdates, Keggin-type PMo$_{12}$O$_{40}$$^{3-}$ and Dawson-type P$_2$Mo$_{18}$O$_{62}$$^{6-}$ anions, of the POMs that have been studied. For example, an adsorbed layer of P$_2$Mo$_{18}$O$_{62}$$^{6-}$ (PMo) on glassy carbon survived sonication for several minutes in water, and a voltammetric signal was observed even after the modified surface was polished briefly with alumina [10]. Evidence for film formation was observed by reducing PMo to the heteropoly blue form on ITO and recording the visible absorption spectrum. From the absorbance at 700 nm and the molar absorptivity, a surface coverage of 5×10^{-11} mol PMo cm^{-2} was estimated. Kulesza et al. [13] obtained a higher value, 1.5×10^{-10} mol PMo cm^{-2}, by determining the charge from the voltammetry of an adsorbed layer of that species on a glassy carbon electrode.

The present investigation was on the fabrication of nanostructured assemblies of POMs by layer-by-layer (LBL) deposition of oppositely charged species. A detailed description of the development of the LBL method has been published [14]. That the LBL method can be used to deposit POM-containing multilayers has been reported. Kuhn and Anson [10] and Ingersoll et al. [15] fabricated such multilayers on surfaces that had the adsorbed POM as the initial layer. Using Os(bpy)$_3$$^{2+}$ as the cationic counter-layer, the former study found that films with up to 20 layers were achieved. The layer comprising PMo directly adsorbed to the surface contained about twice the quantity of that anion as those which were subsequently deposited. We fabricated LBL assemblies of PMo$_{12}$O$_{40}$$^{3-}$ and a cation, a generation-4 polyamidoamine dendrimer (G4-PAMAM), on gold

that was pretreated by deposition of a monolayer of 4-aminothiophenol (4-ATP) [16]. With deposits of up to 12 bilayers, 3.6×10^{-11} mol $PMo_{12}O_{40}^{3-}$ cm^{-2} was found in each, including the initial layer of $PMo_{12}O_{40}^{3-}$. Apparently the 4-ATP provides a smooth platform with no significant pinholes upon which to deposit the assembly. Quartz that was treated with poly(diallyl-dimethylammonium) chloride was suited as a platform on which LBL assemblies of either a Keggin-structured POM, $PMo_{12}O_{40}^{3-}$, or a Dawson-structured POM, $P_2W_{18}O_{62}^{6-}$, were fabricated [17]. The study was extended by using a redox-active cation, a pentaerythritol-based metallodendrimer with Ru^{II} pyridine subunits (RuDen), as the spacer [18]. In this manner, a bifunctional film was assembled; that is, the RuDen mediated the oxidation of arsenite whereas the $P_2W_{18}O_{62}^{6-}$ mediated the reduction of iodate.

An alternative approach to fabricating bifunctional assemblies is to include centers that can mediate either oxidations or reductions. Candidates for these centers include transition-metal substituted POMs (TMSPs). The present study is focused on dirhodium TMSPs. The synthesis of these species is achieved by replacing tungsten and its terminally bonded oxygen atoms of a POM with a transition metal center [19]. We are particularly interested in dirhodium centers because of the ability of dirhodium acetate to mediate the electrochemical oxidation of sulfur-containing amino acids in homogeneous solution [20]. Wei et al. [21] reported the synthesis of bis(acetato)dirhodium-11-tungstophosphate, Rh$_2$PW, by a stepwise process in which the lucunary form of phosphotungstic acid was an intermediate that was reacted with dirhodium acetate during a high-temperature (120 °C) acid digestion. We immobilized Rh$_2$PW in a conducting sol-gel composite and used this material as an electrode for the amperometric determination of amino acids after separation by high performance liquid chromatography [22]. An advantage of Rh$_2$PW over similar electrochemical oxidation catalysts such as RuDen was that it was effective over the range pH 2–10, rather being restricted to acidic media [20, 22].

A potentially important application of electrode-modified oxidation catalysts is to monitor biochemical compounds in cells [23]. A need is to immobilize catalysts on electrodes with dimensions on the micrometer scale or lower without compromising the dimension of the surface or the mass transport characteristics. Neither sol-gel composites nor any film of micrometer-range thicknesses are suited in this regard. The present study was initiated to determine whether the LBL method allowed immobilization of bifunctional TMSPs, in which dirhodium was the metal center, on electrodes, particularly those with micron-scale diameters.

Experimental

Unless otherwise stated, all chemicals were ACS Reagent Grade. Phosphotungstic acid (PW) as $H_3PW_{12}O_{40}$, rhodium acetate dimer

(Rh$_2$ac), 4-aminobenzoic acid (4-ABA), Starburst dendrimer generation-4-polyamidoamine (G4-PAMAM), cesium chloride, L-methionine (Met), and lithium perchlorate were from Aldrich (Milwaukee, Wis.). The phosphomolybdic acid (PMo) as $H_6P_2Mo_{18}O_{62}$ hydrate, acetic acid, sodium acetate, and phosphate buffer salts were from Fisher (Fair Lawn, NJ), and the lithium carbonate was from Mallinckrodt (St. Louis, Mo.). The absolute ethanol was USP Grade from Pharmco (Brookfield, Conn.). The water was house-distilled that was further purified with a Barnstead NANOpure II system. For voltammetric experiments with potential excursions negative of ca. −0.2 V vs. Ag|AgCl, solutions were deaerated with water-saturated nitrogen gas for at least 10 min.

Voltammetric experiments were performed with a CH Instruments (Austin, Tex.) model 750 electrochemical workstation. Except where noted, a conventional cell with a Ag|AgCl, 3 M NaCl reference (Bioanalytical Systems, West Lafayette, Ind.), Pt counter, and a glassy carbon (3 mm diameter) working electrode (Bioanalytical Systems) with or without modification, was used. The glassy carbon was pretreated by polishing successively with 1.0, 0.3, and 0.05 μm alumina (Mark V Laboratory, East Granby, Conn.) and sonicating in water. In some cases a carbon fiber electrode, 10 μm diameter, from Bioanalytical Systems was used.

The synthesis of the Cs$^+$ salt of Rh$_2$PW was by a previously described method [21]. Briefly, equal molar amounts of phosphotungstic acid and dirhodium acetate were reacted in a Teflon-lined acid digestion bomb at 120 °C for 16 h. After cooling, CsCl was added to precipitate the product. The yield was 85%. We used this procedure in an attempt to prepare Rh$_2$PMo, a previously unreported compound. As in the case of Rh$_2$PW, a brown precipitate was obtained at an apparent yield of 80%. The identity was verified by voltammetry, as described in the Results and discussion section.

The glassy carbon (GC) electrodes were modified by the LBL method or by direct adsorption. Except where noted, the LBL assemblies were prepared on a surface that was initially pretreated by formation of a covalently bound monolayer of 4-ABA using the amine cation radical method [24]. A freshly polished electrode was sonicated for 5 min in ethanol, introduced to an ethanolic solution of 3.0 mM 4-ABA and 0.1 M LiClO$_4$, and scanned over the range 0.4–0.96 V at 10 mV s^{-1} for 5 min. A decrease in the irreversible anodic peak current at 0.89 V monitored the formation of the coating. Deprotonation of the 4-ABA (surface pK_A = 3.1) provided a negative surface onto which a counter monolayer of G4-PAMAM was adsorbed. Specifically, after rinsing sequentially in ethanol and water, the GC|4-ABA was dipped in 0.7 wt% G4-PAMAM at pH 3.85 for 60 min. The GC|4-ABA|G4-PAMAM was rinsed in water and immersed in 3.5 mM Rh$_2$POM at pH 3.85 for 60 min. By repeating the last two steps n times, the surface GC|4-ABA|(G4-PAMAM|Rh$_2$POM)$_n$ was prepared, as verified by the data in the Results and discussion section.

For experiments where the GC and the carbon fiber electrodes were modified by direct adsorption, 5.0 mM Rh$_2$PMo in a 0.05 M phosphate buffer at pH 1.1 was used. The procedure was based on the report by Rong and Anson [12] on the direct adsorption of PMo. The immersion time for the freshly pretreated surfaces was 30 min. Next, the electrode was rinsed with water and transferred to a 1% (wt) G4-PAMAM solution of 0.1 M HCl. After 30 min, the immersion cycles in Rh$_2$PMo and G4-PAMAM were repeated. The adsorption process was monitored by cyclic voltammetry at 50 mV s^{-1} in 0.5 M H$_2$SO$_4$. Carbon fiber electrodes also were modified by this method.

Results and discussion

Our interest in modified electrodes with dirhodium centers stems from their ability to mediate oxidations at physiological pH. That this property extends to Rh$_2$PW was verified by cyclic voltammetry of 3.7 mM Met in the presence of 3.5 mM Rh$_2$PW in a pH 7.4 phosphate buffer (Fig. 1). The augmentation of the current for the
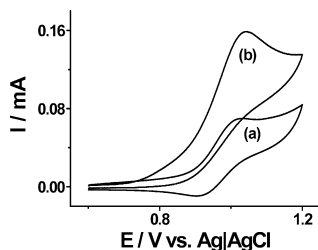
Fig. 1 Cyclic voltammetry of 3.5 mM Rh$_2$PW in the absence (*a*) and the presence (*b*) of 3.7 mM L-methionine in 0.08 M phosphate buffer at pH 7.4. Scan rate, 25 mV s^{-1}

oxidation of Rh^{II} at ca. 1.0 V in conjunction with the attenuation of the current for the reduction of Rh^{III} is consistent with a mediated oxidation pathway. The voltammogram in the absence of Met (Fig. 1) yielded a formal potential for the Rh^{II,III} couple, 0.95 V, that is in agreement with an earlier reported value, 0.97 V [20].

A limitation of our earlier work was that electrodes modified with Rh$_2$PW employed sol-gel matrices, which are not compatible with our intended applications. A general approach to modifying carbon electrodes with thin films is LBL electrostatic assembly. Here, the first step is to form a monolayer of a charged species (4-ABA); subsequently, alternating layers of spacer (G4-PAMAM) and targeted species (Rh$_2$POM catalysts of appropriate charge sign) are assembled (Fig. 2). Our initial experiments used this approach with a carbon electrode of conventional size that was modified by deposition of a monolayer of 4-ABA. When the spacer and the electrocatalyst are G4-PAMAM and Rh$_2$PW, respectively, the LBL method did not provide a linear relationship between bilayer number, n, and the amount of electrocatalyst on the surface, and the voltammetric features for the redox of the phosphotungstate were not well defined (Fig. 3). Therefore, we explored whether
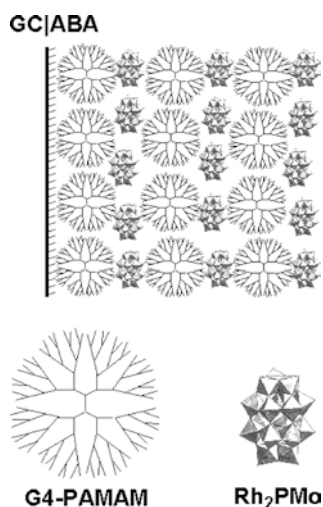

Fig. 2 Schematic representative of the layer-by-layer assembly of G4-PAMAM and Rh$_2$PMo on glassy carbon (GC) pretreated by deposition of a monolayer of 4-aminobenzoic acid (ABA). The relationship between the number of G4-PAMAM and Rh$_2$PMo centers in each layer is not scaled
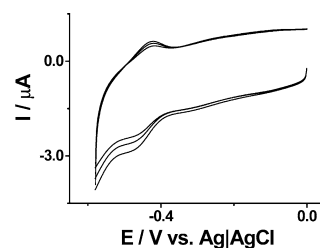

Fig. 3 Cyclic voltammetry at 50 mV s^{-1} of GC|4-ABA|(G4-PAMAM, Rh$_2$PW)$_n$ for $n = 3$–5 at pH 3.85. The inner trace is for $n = 3$

Rh$_2$POM can be synthesized from P$_2$Mo$_{18}$O$_{62}$$^{6-}$. We predicted that by attaining a more highly charged and physically larger TMSP from a Dawson anion, more facile LBL assembly will be achieved. Moreover, the facile adsorption of phosphomolybdates on carbon [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13] suggested that the dirhodium analogue may be assembled on these electrodes without the need to pretreat the surface with 4-ABA.

We modified the method reported for the synthesis of Rh$_2$PW, which is detailed in the Experimental section, in an attempt to obtain Rh$_2$PMo. Evidence that Rh$_2$PMo was the product was obtained by cyclic voltammetry of a 3.7 mM solution at a glassy carbon electrode at 50 mV s^{-1}. The experiment was performed immediately upon immersion of the electrode in order to minimize adsorption of the Rh$_2$PMo (although some certainly occurred). Formal potentials of 0.33, 0.10, and −0.07 V for the redox processes of the PMo moiety and 1.05 V for the Rh^{II,III} couple were obtained. The former set is lowered than those shown by Rong and Anson [12] for PMo, namely ca. 0.45, 0.3, and 0.1 V, but given the pH difference (pH 1.0 vs. pH 3.85 in this study) and the presence of Rh$_2$ in the present system, a shift in formal potential was expected. In addition, as detailed later, the product of the synthesis retained the strong tendency to adsorb to carbon as that of the phosphomolybdate Keggin and Dawson anions.

The experiment in Fig. 3 was repeated except that Rh$_2$PMo was used rather than Rh$_2$PW. The results obtained for GC|4-ABA|(G4-PAMAM, Rh$_2$PMo)$_n$ (Fig. 4) showed a systematic increase in the quantity of this species with n. The experiment was terminated with
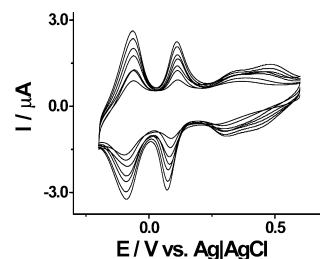

Fig. 4 Cyclic voltammetry of GC|4-ABA|(G4-PAMAM, Rh$_2$PMo)$_n$ for $n = 1$–7. The conditions are those in Fig. 2. The inner trace is for $n = 1$

$n = 7$. A linear least-squares fit of the second redox peak current for the PMo moiety, i_{p2}, vs. n yielded the following: slope, 3.0 ± 0.4 µA n^{-1}; intercept, 2.4 µA; and r^2, 0.995. The intercept reflects the background current from the onset of the reduction of dioxygen. Because of the length of this experiment (several hours), no attempt to remove dioxygen was made; instead, the negative potential excursion was limited to minimize its reduction. The more facile deposition of Rh$_2$PMo than of Rh$_2$PW is perhaps a result of the greater charge of the former (6− vs. 3−) and/or the better match to the size of G4-PAMAM. This dendrimer has a calculated diameter of 4.5 nm. A reported size of PMo (Dawson-type), 1.45 nm [25], is significantly greater than that reported for the Keggin anion, PW, 1.1 nm [26].

Current limitation with the GC|4-ABA|(G4-PA-MAM, Rh$_2$PMo)$_n$ electrodes was studied by cyclic voltammetry in 0.5 M H$_2$SO$_4$. Specifically, the current, i_{p2}, was measured as a function of scan rate, v, over the range 10–500 mV s^{-1} using electrodes with n-values of 1 and 5. A plot of log i_{p2} vs. log v yielded a slope of 1.05 ± 0.07 when $n = 1$, which denotes a surface process. When $n = 5$, the slope was 0.487 ± 0.005, which suggests a diffusion-limited process. In the latter case, diffusion of the counterion from the supporting electrolyte apparently limits the current.

The LBL assembly of multilayers on electrodes first modified with direct adsorption of PMo has been reported [10, 13, 15]. Here, we applied that approach to modification with the TMSP, Rh$_2$PMo. Initially, a GC electrode of conventional size (3 mm diameter), was used. The electrode was polished, sonicated, and modified by adsorption of Rh$_2$PMo as described in the Experimental section. The assembly GC|Rh$_2$PMo$_{adsorbed}$|(G4-PAMAM, Rh$_2$PMo)$_n$ was fabrication by the above-described alternating immersions in G4-PAMAM and Rh$_2$PMo. After each bilayer was deposited, a cyclic voltammogram was obtained at 50 mV s^{-1}. A systematic increase in the voltammetric current was observed; however, the average quantity ($n = 5$) of Rh$_2$PMo in the layers, 7.4×10^{-11} mol cm^{-2}, was somewhat lower that that expected compared to the monolayer coverage reported by Kulesza et al. [13] for PMo on glassy carbon, 1.5×10^{-10} mol cm^{-2}. Two factors were probably responsible for this difference in surface coverage. First, Rh$_2$PMo is larger than PMo. More important, the molecular size of G4-PAMAM is three times that reported for PMo [25], which may, in turn, decrease the quantity of bound Rh$_2$PMo except in the primary layer.

When this modification was repeated with a 10-µm carbon fiber, the results in Fig. 5 were obtained. The plot of i_{p2} vs. n for n values of 1–5 was linear. The linear least-squares fit of the data yielded the following: slope, 0.10 ± 0.03 nA n^{-1}; intercept, 0.55 ± 0.03 nA; and r^2, 0.98. The greater r^2 value than with the 3-mm GC may reflect a difference in the nature of the carbon surfaces with these electrodes. The surface coverage by the first layer, 3×10^{-11} mol Rh$_2$PMo cm^{-2}, was lower than that at GC; hence, the values in layers 2–5, which are

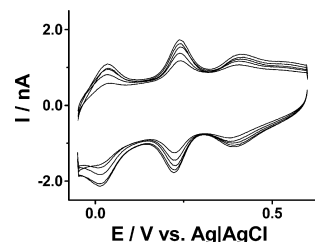**Fig. 5** Cyclic voltammetry of a 10-µm carbon fiber with an adsorbed layer of Rh$_2$PMo (*inner trace*) and bilayers of (G4-PAMAM, Rh$_2$PMo)$_n$ with $n = 1$–4. The *outer trace* is for $n = 4$ (total of 5 layers of Rh$_2$PMo). The electrolyte is pH 1.1 phosphate buffer, and the scan rate is 50 mV s^{-1}

presumably limited by the G4-PAMAM as discussed above, are closer to that of the primary adsorbed layer, thereby resulting in a more linear fit of i_{p2} to n.

Applications of electrodes with Rh$_2$POM-containing bilayers were restricted to a proof-of-concept that they serve as bifunctional catalysts. The mediated reduction of nitrite was observed by cyclic voltammetry at 50 mV s^{-1} at both a carbon fiber and a conventional GC electrode after modification by adsorption of Rh$_2$PMo and LBL assembly thereon of (G4-PAMAM, Rh$_2$PMo)$_4$. When 5 mM NO$_2^-$ was included in a 0.5 M H$_2$SO$_4$ solution, the cathodic current, i_{p2}, increased from 1.0 to 11.5 µA at the modified 3-mm GC electrode because of the chemical reduction of NO$_2^-$ by electrochemically generated Rh^{II}. Consistent with this mediated reduction of NO$_2^-$, the anodic current corresponding to i_{p2} is attenuated because of the consumption of Rh^{II} by this chemical reaction. With the 10-µm carbon fiber, the analogous experiment showed an increase by the same factor (from 0.67 to 7.7 nA). The test system for mediated oxidation was 10 mM AsO$_2^-$ at pH 2.2. Cyclic voltammetry at 50 mV s^{-1} was used; the current for the oxidation of Rh^{II} at 1.0 V was monitored. When the electrode was GC|(Rh$_2$PMo)$_{adsorbed}$, the current increased from 1.7 (blank) to 5.1 µA, whereas with $n = 5$ the analogous change was from 5.4 to 170 µA. These data not only demonstrate bifunctionality of this modified electrode but also that the catalytic efficiency increases with the number of bilayers. Comparable results were obtained with modified carbon fiber electrodes.

Conclusions

This study demonstrates that the TMSP, Rh$_2$PMo, shares the ability of PMo to strongly adsorb to carbon surfaces, thereby providing not only an electrocatalytic modified electrode but also a platform for LBL electrostatic assembly of bilayers. A greater linearity of the relationship between bilayer number and the quantity of the TMSP immobilized is achieved when a GC surface is first treated by deposition of a monolayer of 4-ABA. With a carbon fiber rather than 3-mm GC as the electrode, direct adsorption of Rh$_2$PMo provides linearity in this relationship, obviating the need to do an initial

modification of the carbon fiber with 4-ABA. Whether the factor was a difference between the types of carbon used or more facile diffusion to the fiber is unknown at this time.

That LBL assembly of TMSPs on fiber electrodes was accomplished has intrinsic merit in extending the range of potential applications of this fabrication process. The applicability is enhanced by the demonstration that electrodes modified with bilayers that contain Rh_2PMo serve as bifunctional catalysts.

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