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Preparation and Electrocatalytic Application of Composites Containing Gold Nanoparticles Protected with Rhodium-Substituted Polyoxometalates

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Abstract

Substitution of a metal center of phosphomolybdate, $\text{PMo}_{12}\text{O}_{40}^{3-}$ (PMo_{12}), or its tungsten analogue with dirhodium(II) and subsequent stabilization of gold nanoparticles, AuNPs, with $\text{Rh}_2\text{PMo}_{11}$ is demonstrated. The AuNP- $\text{Rh}_2\text{PMo}_{11}$ mediates oxidations but adsorbs too weakly for direct modification of electrode materials. Stability in quiescent solution was achieved by modifying glassy carbon (GC) with 3-aminopropyltriethoxysilane (APTES) and then electrostatically assembling AuNP- $\text{Rh}_2\text{PMo}_{11}$. At GC|APTES|AuNP- $\text{Rh}_2\text{PMo}_{11}$, cyclic voltammetry showed the expected set of three reversible peak-pairs for PMo_{11} in the range -0.2 to 0.6 vs (Ag/AgCl)/V and the reversible $\text{Rh}^{\text{II,III}}$ couple at 1.0 vs (Ag/AgCl)/V. The presence of AuNPs increased the current for the reduction of bromate by a factor of 2.5 relative to that at GC| $\text{Rh}_2\text{PMo}_{11}$, and the electrocatalytic oxidation of methionine displayed characteristics of synergism between the AuNP and Rh^{II} . To stabilize AuNP- $\text{Rh}_2\text{PMo}_{11}$ on a surface in a flow system, GC was modified by electrochemically assisted deposition of a sol-gel with templated 10-nm pores prior to immobilizing the catalyst in the pores. The resulting electrode permitted determination of bromate by flow-injection amperometry with a detection limit of $4.0 \times 10^{-8} \text{ mol dm}^{-3}$.

Keywords

electrocatalysis; metal nanoparticles; polyoxometalates; sol-gels; dirhodium

1. Introduction

Polyoxometalates, POMs, such as phosphotungstate and phosphomolybdate have been established as an important class of compound in chemistry [1,2]. Expanding on early reports [3,4], numerous applications in electrochemistry have been devised, the bases of which primarily relate to their favorable electron-transfer kinetics and ability to strongly adsorb to a wide range of electrode materials. In concert, these properties have led to fabrication of surface-modified electrodes that are capable of mediating numerous electrochemical reductions [5]. The surface activity of POMs has been employed in the formation [6,7] and stabilization [8-11] of nanoparticles. Indeed, the interaction of Keggin-

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type lacunary $\text{PW}_{11}\text{O}_{39}^{7-}$ with silver is sufficient to displace the ligand from citrate-protected silver nanoparticles [8], and PMo_{12} displaces the alkanethiol (RSH) from gold nanoparticles in a place-exchange reaction that facilitates a phase transfer of AnNP centers from non-polar solvent into aqueous solution [5]. Adsorption of PMo_{12} is the driving force that converts aggregates of a conventional carbon black suspension into anionic monolayer-protected nanoparticles [6] and of a suspension of platinum black into PtNPs in the 5 - 10 nm domain [7].

Substitution of a transition metal into the polyoxometalate has been explored as a route to increasing the range of application of these compounds [12-17]. Because it has the characteristics necessary for mediating electrochemical oxidations, thereby complementing the ability of polyoxometalates to catalyze electrochemical reductions, the incorporation of Rh^{II} into these compounds is of interest. The synthesis of Rh^{II} -substituted polyoxometalates by first forming the lacunary structure by removing a metal and its terminal oxygen from phosphotungstic acid and then substituting dirhodium acetate to yield $[(\text{PO}_4)_7\text{W}_{11}\text{O}_{35}\{\text{Rh}_2(\text{OAc})_2\}]^{5-}$, $\text{Rh}_2\text{PW}_{11}$, has been described [18]. The $\text{Rh}_2\text{PW}_{11}$ formed from this Keggin anion or the analogous molybdenum compound, $\text{Rh}_2\text{PMo}_{11}$, was demonstrated to catalyze the electrochemical oxidation of methionine and cystine [19], phosphatidylcholine [20], and various peptides [21].

A convenient means of employing these compounds as electrochemical catalysts is to immobilize them on an electrode surface. An early study in this regard was by Shiu and Anson [17] who used $\text{FeSiW}_{11}\text{O}_{39}^{5-}$ as the test species and glassy carbon, GC, as the electrode. Three methods of immobilization were studied, namely anion exchange onto an electrode coated with polyvinylpyridine, PVP (quaternized or protonated); trapping as a composite with an electropolymerized film of polypyrrole (PPY); and co-depositing on the electrode surface with positively charged tetrakis(4-*N*-methylpyridyl)porphine (TMPyP). These methods did not yield stable films, particularly when tested for the electrocatalytic reduction of hydrogen peroxide. The studies on GC | PVP indicated that the instability resulted from conversion of the lacunary anion to $\text{SiW}_{12}\text{O}_{40}^{4-}$ with loss of the iron center along with subsequent hydrolytic decomposition to tungstate and silicate, a process previously described as important in the presence of PVP [22]. The instability of the composite of $\text{FeSiW}_{11}\text{O}_{39}^{5-}$ and PPY occurred during the reduction of H_2O_2 because of localized formation of ferryl ions and hydroxyl radicals that decompose the PPY. With PMPyP, continuous cycling of the potential gave a gradual decrease of the $\text{Fe}^{\text{II,III}}$ signal, suggesting a gradual loss of the iron centers, which was reversed by immersion of this composite in Fe^{3+} solution.

As suggested by the above study, immobilizing transition-metal substituted polyoxometalates (TMSPs) on electrodes is a challenging problem. Unlike many combinations of electrode materials and polyoxometalates, direct adsorption of TMSPs often does not provide a stable modified surface. Layer-by-layer (LbL) electrostatic assembly, a method described initially by Decher [23], has been applied to the immobilization of ionic species, including polyoxometalates [24-26] and TMSPs [27,28], on electrodes. Dong and co-workers [27] applied electrostatic assembly to the immobilization of a series of TMSPs with the general formula, $\text{ZnW}_{11}\text{M}(\text{H}_2\text{O})\text{O}_{39}^{n-}$ ($\text{M} = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{or Zn}$) on a GC electrode modified with a monolayer of aminobenzoic acid (ABA); the LbL assembly thereon comprised alternating layers of the TMSP and a quaternized PVP - $[\text{Os}(\text{bpy})_2\text{Cl}]^{1+/2+}$ complex. We employed LbL electrostatic assembly to immobilized multilayers of $\text{Rh}_2\text{PW}_{11}$ and $\text{Rh}_2\text{PMo}_{11}$ on GC that was modified with a monolayer of ABA [28]. Generation-4 poly(amidoamine) dendrimer, PAMAM, was used as the counter-layer. The quantity of $\text{Rh}_2\text{PW}_{11}$ assembled per bilayer, n , was non-linear, whereas with $\text{Rh}_2\text{PMo}_{11}$, a linear correlation ($R^2 = 0.995$) with n was observed (up to $n = 7$). The

Rh₂PMo₁₁ was demonstrated to be a bifunctional electrochemical catalyst; both the reduction of nitrite and the oxidation of arsenite were promoted. When the assembly GC | ABA | (Rh₂PMo₁₁, PAMAM)_n was further modified with an outer layer of a cyclophane derivative, 1,4-xylylene-1,4-phenylene diacetate (CP), the oxidation of a phospholipid, phosphatidylcholine and its electrochemical determination were accomplished [20]. The CP served as a trapping agent that allowed preconcentration of the phosphatidylcholine at the electrode surface. Because of the weaker electrostatic interaction of Rh₂PW₁₁ than of Rh₂PMo₁₁ with cationic counter- layers, the former species was immobilized on electrodes as a component of a composite with a silica sol-gel [19,21].

In the present study, the synthesis and application of gold nanoparticles (AuNPs) that are stabilized with an adsorbed layer of Rh₂PMo₁₁ is investigated. The objective is to determine whether the inclusion of AuNPs enhances the electrocatalytic activity of Rh₂PMo₁₁ and/or increases the sensitivity of electroanalytical methodology based on electrocatalysis with this TMSP. An important aspect of the study is the development of a method to stabilize the resulting modified electrodes when applied in hydrodynamic experiments such as in a flowing electrolyte.

2. Experimental

2.1. Reagents and materials

Unless otherwise stated, the chemicals were ACS Reagent Grade and used as received from Sigma-Aldrich (St. Louis, MO). In the synthesis of the nanoparticles and of the Rh₂PMo the following were used : hydrogen tetrachloroaurate trihydrate (>99.9%); tetraoctylammonium bromide (98%); 1-hexanethiol (95%); sodium borohydride (powder, 98%) ; phosphomolybdic acid hydrate (powder, 99.99%) ; rhodium(II) acetate dimer (powder) ; cesium chloride (99.9%) ; PAMAM dendrimer (generation-4, 10 wt % solution in methanol); and 3-aminopropyltriethoxysilane, APTES (99%). The counter electrode was platinum gauze, and the reference electrode was Ag/AgCl, 3.0 mol dm⁻³ KCl (Bioanalytical Systems, BAS, West Lafayette, IN). The working electrodes were glassy carbon, GC (6.2 mm²) from BAS and indium tin oxide, ITO (20 mm²) from Delta Technologies, Limited (Stillwater, MN). Distilled water that was further purified with a NANOpure II system (Boston, MA) was used.

2.2. Instrumentation

The electrochemical measurements were performed with a CH Instruments (CHI, Austin, TX) Model 660B electrochemical workstation. A Varian Cary 50 Scan UV-Visible Spectrometer (Walnut Creek, CA) was used for spectrophotometry experiments. The instrumentation for the infrared spectroscopy and the transmission electron microscopy measurements was a Perkin Elmer FT-IR Model 2000 Spectrometer (Waltham, MA) and a JEOL JEM-2100 LaB₆ 200 KV TEM/STEM (Westbury, NY) system, respectively. Scanning electron microscopy was performed with a variable pressure field emission scanning electron microscope, Zeiss Supra 35VP FEG (Oberkochen, Germany).

A Heidolph® LABOROTA 4003 Evaporator equipped with ROTACOOl Chiller (Heidolph Instruments GmbH & Co, Schwabach, Germany) was used to reduce solvent volumes. Flow injection analysis were performed using NE-300 syringe pump (New Era Pump Systems, Inc, Wantagh, NY) combined with a center-flow electrochemical cell model CC-5e from BAS (West Lafayette, IN) and electrochemical detector, CHI 800, from CH Instruments (Austin, TX).

2.3. Syntheses

The bis(aceto)dirhodium -11-tungstophosphate ($\text{Rh}_2\text{PW}_{11}$) and its molybdenum analogue, $\text{Rh}_2\text{PMo}_{11}$ were synthesized in accord with prior reports [18,19]. In summary, Li_2CO_3 was added to 10 mL of $1.13 \times 10^{-3} \text{ mol dm}^{-3} \text{ PW}_{12}$ (or PMo_{12}) in a quantity to give a pH of 4.8. The pH was adjusted subsequently to 3.0 with HCl. 50 mg of dirhodium acetate was added, and the solution was heated at 120 °C for 16 h in a Teflon-lined Parr acid digestion bomb. The product of the hydrothermal reaction was precipitated by addition of a 5:1 mole ratio of CsCl_2 , filtered, rinsed with a 2:1 (vol) water:ethanol solution, and air-dried overnight.

Analogous to our procedure for preparing polyoxometalate-protected AuNPs [5], the TMSP-protected gold nanoparticles were synthesized by a combination of the Brust-Schiffrin method [29] and a ligand place-exchange reaction [30] by which a hexanethiol (RSH) monolayer on the AuNP core was replaced by the TMSP. The AuNP-SR nanoparticles were synthesized by reduction of HAuCl_4 with NaBH_4 in aqueous solution in contact with toluene, into which AuNP-SR was extracted. These NPs were collected and re-dissolved in hexane (10 mg of AuNP-SR in 4 mL of hexane). Upon contacting this hexane solution with an acidified aqueous solution of $\text{Rh}_2\text{PMo}_{11}$ (4 mL of $3.5 \times 10^{-3} \text{ mol dm}^{-3} \text{ Rh}_2\text{PMo}$ in 0.05 $\text{mol dm}^{-3} \text{ H}_2\text{SO}_4$), the TMSP exchanged with the hexanethiolate, and the AuNP- $\text{Rh}_2\text{PMo}_{11}$ partitioned into the aqueous phase. It was purified by multiple dialyses (water changed every 60 min for the first four hours followed by an overnight dialysis) with a 3500 molecular mass cut-off tube.

2.4. Procedures

For voltammetry in quiescent solution, the working electrodes were ITO or GC, which were polished with 1- μm and 0.3- μm alumina. Prior to modification, the electrodes were scanned 20 times between -0.5 V and 1.2 V in 0.5 $\text{mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 100 mV s^{-1} . The treated electrodes were rinsed with methanol, immersed in 0.06 mol dm^{-3} APTES in methanol for 60 min, rinsed with water, and immersed in the purified $\text{Rh}_2\text{PMo}_{11}$ (or $\text{Rh}_2\text{PW}_{11}$) solution, which is described above. All measurements were made and reported vs a Ag/AgCl, 3.0 mol dm^{-3} KCl reference electrode.

The GC electrodes used in flow-injection amperometry measurements were modified by electrochemically assisted deposition of a ca. 100-nm film of silica sol-gel with templated pores [31]. The procedure was based on that reported by Mandler and coworkers [32] except that the precursor solution contained PAMAM to template pores [31]. In accord with Mandler and coworkers [32], the sol-gel precursor solution contained 7.5 mL of anhydrous 2-propanol that was mixed with 0.15 $\text{mol dm}^{-3} \text{ LiClO}_4$, and 2.5 mL of TEOS; the quantity of templating agent that was added was 175 μL of 10% PAMAM. The GC electrodes were immersed into the plating solution for 30 min, after which 2.35 V vs a platinum quasi-reference electrode was applied. The electrode was then withdrawn from the plating solution at 50 $\mu\text{m min}^{-1}$; during the withdrawal, the potential was maintained. Electrodes were rinsed and dried for 60 min. Next, 100 μL of purified $\text{Rh}_2\text{PMo}_{11}$ (or $\text{Rh}_2\text{PW}_{11}$) solution was applied to the surface, and the electrodes were further dried overnight.

3. Results and discussion

3.1. Fabrication and characterization of ITO | APTES |AuNP- $\text{Rh}_2\text{PMo}_{11}$

The $\text{Rh}_2\text{PW}_{11}$ and AuNP- $\text{Rh}_2\text{PW}_{11}$ (and their molybdenum analogues) were prepared as described in Section 2.3. Evidence for the displacement of the hexanethiol by $\text{Rh}_2\text{PW}_{11}$ and the transfer of the AuNP core into the aqueous phase was obtained by infrared spectroscopy. A 0.5 mL aliquot of the purified aqueous solution of AuNP- $\text{Rh}_2\text{PW}_{11}$ was dried, the powder was transferred onto a silica crystal, and the reflectance spectrum was obtained (Fig. 1). The

thiolate peaks that were observed in the range 2852 – 2925 cm⁻¹ with the AuNP-SR samples (Fig. 1B) were not seen after reaction with Rh₂PW₁₁ (Fig. 1A), a result consistent with our reported synthesis of AuNP-PW₁₂ by the analogous place-exchange and phase-transfer reactions [5]. The TEM samples were prepared by placing 5 μL of the purified AuNP-Rh₂PW₁₁ onto collodion-supported, carbon-coated copper grids. After vacuum drying, images were obtained using a 200 kV accelerating voltage (Fig. 2). A comparison of the particle sizes for AuNP-SR (Fig. 2A) and the presumed AuNP-Rh₂PW₁₁ (Fig. 2B) are consistent with the ca. 2-nm increase in particle diameter when the polyoxometalate replaces the hexanethiol as the protecting group [5]. The estimated size of AuNP-Rh₂PW₁₁ from TEM data, 5.0 ± 1.5 nm, was consistent with that from spectrophotometric measurements (Fig. 3). From the surface plasmon resonance peak, λ_{max}, at 512 nm, a diameter, d, of 4.6 nm was estimated from the relationship: $d = 3 + 7.5 \times 10^{-5} \cdot X^4$ for $X < 23$ where $X = \lambda_{\text{max}} - 500$ [33].

The ligand place-exchange reactions were complicated somewhat by a lower affinity of these TMSPs for the AuNPs than that observed with PMo₁₂ and PW₁₂. The phase-transfer reaction time was increased from 1 h to 2 h under sonication when the aqueous phase was Rh₂PW₁₁ rather than PW₁₂ (or the molybdenum analogues). The apparent lowering of the free energy of adsorption precluded modification of GC and ITO electrodes by direct adsorption of AuNP-Rh₂PW₁₁ and AuNP-Rh₂PMo₁₁. Cyclic voltammetry of electrodes modified by direct adsorption of these TMSPs showed a complete loss of the characteristic peak currents after three trials at 50 mV s⁻¹ in supporting electrolyte. Instead, the electrodes were first modified with a monolayer of APTES (Section 2.4). After immersion for 12 h in the purified AuNP-Rh₂Mo₁₁ solution and rinsing, the voltammograms shown in Fig. 4 were obtained. The electrode processes at potentials negative of 0.8 V relate to PMo₁₂, whereas the peaks near 1.0 V are from the Rh^{II,III} couple [18,28].

The initial application was to the oxidation of methionine mediated by the Rh^{II,III} couple at the GC | APTES | AuNP-Rh₂PMo₁₁ electrode. The questions were whether the presence of the AuNP increased the current over that obtained with Rh₂PMo₁₁ alone and whether the overpotential for the oxidation was lowered when AuNPs were included in the film. The voltammograms in Fig. 5 demonstrates that a catalytic oxidation occurred at both GC | APTES | Rh₂PMo₁₁ (Fig. 5A) and GC | APTES | AuNP-Rh₂PMo₁₁ (Fig. 5B); the former is consistent with the constant potential amperometry of methionine at a sol-gel composite doped with Rh₂PW₁₁ [21]. The effect of the AuNPs was to increase the current by a factor of 3.5 (Fig. 5B) relative to that in Fig. 5A and to lower the overpotential for the oxidation of methionine by 50 mV. In both Fig. 5A and Fig. 5B, voltammograms labeled as “a” and “b” refer to methionine-containing and blank solutions, respectively. The increased current can be related in part to an increase in the effective area of the electrode; however, the latter permits a hypothesis of synergism between the AuNPs and the Rh₂PMo₁₁ in the catalysis of the electron-transfer reaction. To test this hypothesis, the influence of scan rate on the peak current for the oxidation of methionine was studied. If the electrode processes were diffusion limited both in the presence and absence of AuNPs, synergism would be precluded. When the outer layer of the assembly was Rh₂PMo₁₁, a least square fit of log I_p vs. log v (I_p, peak current; v, scan rate) yielded a slope of 0.41 (R² = 0.999), and when this layer was AuNP-Rh₂PMo₁₁, the slope was 0.51 (R² = 0.994). The latter agrees with the theoretical value, 0.50, for a diffusion-limited process, whereas the former slope is indicative of partial control of the peak current by electron-transfer kinetics. Hence, it is concluded that there is synergism between the AuNPs and the Rh₂PMo₁₁ because in combination they increase the rate of the electron-transfer rate relative to that with Rh₂PMo₁₁ alone. In this regard, metal nanoparticles are known to increase the rates of electron transfer, possibly by influencing the electronic structure of species they contact directly [34,35].

Bifunctional catalysis of GC | APTES | AuNP-Rh₂PMo₁₁ was demonstrated in that the phosphomolybdate moiety retained is ability to promote electrochemical reductions such as the catalysis of bromate reduction. Here, the possibility of synergism by the AuNP also was considered. The voltammetry of bromate at an electrode modified with AuNP-Rh₂PMo₁₁ and with Rh₂PMo₁₁ is shown in Fig. 6. Compared to the same experiment but in the absence of AuNPs, the current for the reduction of bromate at the peak potentials for the second reduction step is amplified by a factor of 2.5 by the presence of AuNPs; however, a significant shift in the reduction potential was not observed; the average shift of the first and second reduction peak when AuNPs were present was +5 mV. Moreover, the reduction of bromate was diffusion limited with both Rh₂PMo₁₁ and AuNP-Rh₂PMo₁₁ as catalysts. In this regard, plots of log I_{p2} vs. log ν (I_{p2}, increase in current of the second reduction peak when bromate is present) over the ν -range, 50 - 250 mV s⁻¹ had slopes of 0.47 and 0.52 in the presence and absence of AuNP, respectively, when the bromate was 1.2 × 10⁻³ mol dm⁻³ in 0.5 mol dm⁻³ H₂SO₄. The respective R² values were 0.998 and 0.995. As a result, the amplification factor of 2.5 was attributed solely to an increase in the effective area of the electrode by AuNPs in that synergism is precluded when the electrode processes are diffusion limited in both cases. This increase in effective area of the electrode also was seen in an investigation of the oxidation of 1.0 × 10⁻³ mol dm⁻³ HAsO₂ in 0.1 mol dm⁻³ KCl at pH 2.0 (added HCl) at ITO | APTES | AuNP-Rh₂PMo₁₁ and ITO | APTES | Rh₂PMo₁₁ electrodes. Plots of log I_{pa} vs. log ν (I_{pa}, anodic peak current near 1.0 V) had slopes of 0.50 and 0.48, respectively, when the ν -range was 25 - 250 mV s⁻¹. Therefore, I_{pa} was diffusion limited in both cases. The amplification factor from the presence of AuNP was 2.2, but there was uncertainty in measuring the anodic peak at 1.05 V, which is at the onset of the oxidation of water, when AuNPs were present, so the amplification factor due to the increased effective area of the electrode was taken as 2.5, the value from the bromate study.

A comparison of the effect of AuNPs on the reduction of bromate and on the oxidation of methionine illustrated the importance of synergism on the amplification of the current for the oxidation of methionine. Given that the oxidation of methionine was kinetically limited in the absence of AuNPs but diffusion limited in presence of AuNPs and that with a diffusion-limited system (bromate reduction) the electrode reaction was amplified by a factor of 2.5 due to increased effective area of the electrode, the enhancement of the electron transfer rate by AuNPs in the oxidation of methionine caused an increase in I_p of about 40%.

An important factor in the use of AuNP-Rh₂PMo₁₁ rather than either Rh₂PMo₁₁ or PMo₁₂ is that the fabrication of stable modified electrodes cannot be done by direct adsorption onto the surface. Moreover, the use of hydrodynamic rather than quiescent solution conditions complicates the stability issue, even when the base electrode is modified with a charged self-assembled monolayer. For example, The GC | APTES | AuNP-Rh₂PMo₁₁ electrode was stable under the quiescent conditions used in cyclic voltammetry. After 50 voltammetric experiments at 50 mV s⁻¹ in supporting electrolyte, an electrode showed a decrease in peak currents of only 10% from the initial value. A given electrode was not used for more than 1-2 days, so long term stability during experiments was not demonstrated; however, this modified electrode was shown to be stable when stored for several days. In contrast, under hydrodynamic conditions such as in flow-injection amperometry, a loss of the catalyst was apparent. With a flow rate of 0.5 mL min⁻¹ the current at 1.0 V for 100- μ L injections of 1.0 × 10⁻⁵ methionine decreased rapidly; after 5 min in the flowing electrolyte, a current for the oxidation of methionine was not observed. Apparently, under the conditions employed the Reynolds number is exceeded so that turbulent rather than laminar flow conditions are operative, leading to a loss of the catalyst. The same effect was seen when ITO was used rather than GC as the base electrode

To mitigate the loss of catalyst under hydrodynamic conditions, we investigated the modification of a GC electrode with a sol-gel film that contained templated pores that served as sites for immobilization of the catalyst and conductance networks connecting the GC to the bulk solution. As in our previous work with pores templated with β -cyclodextrin [20], an electrochemically assisted deposition of a silica sol-gel film was employed but in this case PAMAM was the templating agent [31]. The general procedure for fabricating the nanoporous sol-gel film on GC, which is designated as GC | npSG, was similar to that reported by Mandler and coworkers [32] except for the inclusion of PAMAM to template pores. The pores maintain conductivity of the otherwise-insulating sol-gel. The PAMAM (generation 4) has a calculated diameter of 4.5 nm [36], but analysis of scanning electron microscopy images yielded a pore size of 10 ± 5 nm diameter. This increase in size over the calculated diameter is probably the result of some clustering of the PAMAM, a phenomenon that has been reported previously [37]. In that study, atomic force microscopy yielded a relationship of measured size vs. generation number (G5 - G10) that agreed with the predicted diameter at low PAMAM concentration, but even generation-4 PAMAM formed clusters on mica at a concentration of 0.1% w/w [37]. Under the deposition conditions used herein, the pore size in the templated sol-gel film accommodated subsequent introduction of AuNP-Rh₂PMo₁₁, which has a diameter of about 5 nm (Fig. 2) when synthesized by the procedure described in Section 2.4.

The stability and electroanalytical utility of GC | npSG/AuNP-Rh₂PMo₁₁ was studied by flow-injection amperometry. The following conditions were used: methionine concentrations, $5.0 - 50 \times 10^{-6}$ mol dm⁻³; flow rate, 2.0 mL min⁻¹; injection loop, 100 μ L; carrier solution, 0.1 mol dm⁻³ H₂SO₄; and applied potential, 1.0 V. No attempt to optimize the analytical figures-of-merit was made; however, this result demonstrated linearity of peak current vs. concentration ($R^2 = 0.999$). The detection limit based was estimated as the concentration yielding a current that was three-times the standard deviation of five trials on a blank ($k = 3$ criterion); the value was 2.5×10^{-7} mol dm⁻³ methionine. The more important result was that a single electrode preparation was used for at least 100 injections over a period of several hours without measurable loss of sensitivity. Application of a single electrode for more than one day was not studied, but the electrodes were stable under storage. The introduction of the AuNP-Rh₂PMo₁₁ into the npSG was undoubtedly aided by the presence of positively charged PAMAM in the pores. In this regard, layer-by-layer electrostatic assembly of PAMAM and Rh₂PMo₁₁ has been reported [28]. However, the stability is not a result of substituting APTES with PAMAM; flow-injection amperometric experiments on GC | PAMAM | AuNP-Rh₂PMo₁₁ were characterized by a similar loss of the catalyst as the measurements on GC | APTES | AuNP-Rh₂PMo₁₁.

The same electrode was used for the flow-injection amperometry of bromate (Fig. 7). The calibration curve was linear ($R^2 = 0.995$). The detection limit ($k = 3$ criterion) based on five trials on with a blank injection was 4.0×10^{-8} mol dm⁻³. With further work involving optimization of the sol-gel thickness and the three-electrode flow cell design, this method may possibly yield a detection limit and linear dynamic calibration range for bromate and related oxyanions that competes favorably with presently reported methods for these analytes. In contrast to most electrocatalytic modified electrodes, the present design is applicable to both electrochemical oxidations and reductions.

4. Conclusions

Chemical modification of polyoxometalates to include the dirhodium moiety extends their use to include catalysis of electrochemical oxidations [19-21]. Here, these studies were further expanded to the synthesis and application to electrocatalysis of gold nanoparticles protected by Rh₂PMo₁₁. One consequence of using AuNP-Rh₂PMo₁₁ rather than the TMSP

alone was that modification of GC and ITO electrodes by direct adsorption did not yield a stable film. Instead, the base electrode was modified with APTES, which, when in its protonated state, electrostatically assembled a monolayer of the negatively charged TMSP. The resulting electrode, GC | APTES | Rh₂PMo₁₁, was stable in quiescent solution but not under hydrodynamic conditions. With a flow rate of 0.5 mL min⁻¹, after a few minutes catalysis of the oxidation of methionine was not observed, suggesting a loss of the AuNP-Rh₂PMo₁₁. This observation was confirmed by cyclic voltammetry. To alleviate this instability, the GC electrode was initially modified with a film of silica sol-gel that was formed in the presence of PAMAM so that it contained a distribution of “nanowells”. The AuNP-Rh₂PMo₁₁ was then immobilized therein by electrostatic interaction with the PAMAM. This electrode was stable for at least one day in a flowing solution; a study of long term stability is presently underway. Although attachment of the Rh₂PMo₁₁ to a nanoparticle complicates the fabrication of a modified electrode with this catalyst, the incorporation of AuNPs has advantages over the use of the TMSP alone. First, the sensitivity of electroanalytical measurements is increased. Under conditions employed herein, the current density for a diffusion-limited process that was based on geometric area of the electrode was greater by a factor of 2.5 when the Rh₂PMo₁₁ was attached to AuNPs rather than used alone. As a result, the detection limit ($k = 3$ criterion) for the flow-injection amperometric determination of bromate based on its reduction was 4.0×10^{-8} mol dm⁻³. Perhaps more important, the inclusion of AuNPs can act synergistically with Rh₂PMo₁₁. For example, the rate of electron transfer in the mediated oxidation of methionine was increased by the AuNPs, and the overpotential for the oxidation was lowered by 50 mV. With Rh₂PMo₁₁ alone, the oxidation of methionine by cyclic voltammetry is kinetically limited, but with AuNP-Rh₂PMo₁₁ the current is diffusion limited. The combination of the increase in effective electrode area and in the rate of electron transfer resulted in an increase of sensitivity by a factor of 3.5 when AuNP-Rh₂PMo₁₁ was used as the catalyst of the oxidation of methionine. Future studies with these catalysts will focus on investigation of systems where the nanoparticle lowers the overpotential of electron-transfer reactions.

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References

1. Hill CL. Chem Rev. 1998; 98:1. [PubMed: 11851497]
2. Hill CL, Prosser-McCartha CM. Coord Chem Rev. 1995; 143:407.
3. Pope, MT. Heteropoly and Isopoly Oxometalates. Springer-Verlag; New York: 1983.
4. Keita B, Nadjro L. J Electroanal Chem. 1985; 191:441.
5. Ernst AZ, Sun L, Wiaderek K, Kolary A, Zoladek S, Kulesza PJ, Cox JA. Electroanalysis. 2007; 19:2103. and references therein.
6. Garrigue P, Delville M-H, Labrugere C, Cloutet E, Kulesza PJ, Kuhn A. Chem Mater. 2004; 16:2984.
7. Kulesza PJ, Chojak M, Karnicka k, Miecznikowski K, Palys B, Lewera A, Wieckowski A. Chem Mater. 2004; 16:4128.
8. Lica GC, Browne KP, Tong YY. J Clust Sci. 2006; 17:349.
9. Ernst AZ, Zoladek S, Wiaderek K, Cox JA, Kolary-Zurowska A, Miecznikowski K, Kulesza PJ. Electrochim Acta. 2008; 53:3924.
10. Keita B, Zhang G, Dolbecq A, Mialane P, Secheresse F, Miserque F, Nadjro L. J Phys Chem C. 2007; 111:8145.

11. Wang Y, Neyman A, Arkhangelsky E, Gitis V, Meshi L, Weinstock IA. *J Am Chem Soc.* 2009; 131:17412. [PubMed: 19902946]
12. Hill CL, Brown RB. *J Am Chem Soc.* 1986; 108:536.
13. Toth JE, Melton JD, Cabelli D, Bielski BHJ, Anson FC. *Inorg Chem.* 1990; 29:1952.
14. Rong C, Anson FC. *Inorg Chem.* 1994; 33:1064.
15. Keita B, Belhourari A, Nadjio L, Content R. *J Electroanal Chem.* 1998; 442:49.
16. Müller A, Dloczik L, Dittman E, Pope MT. *Inorg Chem Acta.* 1997; 257:231.
17. Shiu K-K, Anson FC. *J Electroanal Chem.* 1991; 309:115–129.
18. Wei X, Dickman MH, Pope MT. *Inorg Chem.* 1997; 36:130.
19. Tess ME, Cox JA. *Electroanalysis.* 1998; 10:1237.
20. Wandstrat MM, Cox JA. *Electroanalysis.* 2007; 19:49.
21. Cox JA, Holmstrom SD, Tess ME. *Talanta.* 2000; 52:1081. [PubMed: 18968070]
22. Keita B, Bouaziz D, Nadjio L. *J Electroanal Chem.* 1990; 284:431.
23. Decher G. *Science.* 277:1232.
24. Ingersoll D, Kulesza PJ, Faulkner RF. *J Electrochem Soc.* 1994; 141:140.
25. Kuhn A, Anson FC. *Langmuir.* 1996; 12:5481.
26. Liu S, Volkmer D, Kurth DG. *J Clust Sci.* 2003; 14:405. and references therein.
27. Liu J, Cheng L, Dong S. *Electroanalysis.* 2002; 14:569.
28. Kijak AM, Perdue RK, Cox JA. *J Solid State Electrochem.* 2004; 8:376.
29. Brust M, Walker M, Bethell D, Schiffrin DJ, Whyman R. *J Chem Soc Chem Comm.* 1994:801.
30. Hostetler MJ, Wingate JE, Zhong CJ, Harris JE, Vachet RW, Clark MR, Londono JD, Green SJ, Stokes JJ, Wignall JD, Glish GL, Porter MD, Evans ND, Murray RW. *Langmuir.* 1998; 14:17.
31. Ranganathan D, Zamponi S, Berrettoni M, Mehdi BL, Cox JA. *Talanta.* 2010; 82:1149. [PubMed: 20801311]
32. Shacham R, Avnir D, Mandler D. *Adv Mater.* 1999; 11:384.
33. Khlebtsov NG. *Anal Chem.* 2008; 80:6620. [PubMed: 18642876]
34. Schmid G, Corain B. *Eur J Inorg Chem.* 2003:3081.
35. Cox, JA.; Zou, S.; Pierce, DT.; Zhao, JX. *Trace Analysis with Nanomaterials.* WILEY-VCH Verlag GmbH & Co; Weinheim, Germany: 2010.
36. Hierlemann A, Campbell JK, Baker LA, Crooks RM, Ricco AJ. *J Am Chem Soc.* 1998; 120:5323.
37. Li J, Piehler T, Qin D, Baker JR Jr, Tomalia DA. *Langmuir.* 2000; 16:5613.

Figure 1. FTIR spectra of (left) hexanethiol-gold nanoparticles and (right) AuNP-Rh₂PW₁₁. Both traces were obtained in the reflectance mode.

Figure 2.
TEM images of (A) hexanethiol-protected AuNPs and (B) Rh₂PW₁₁-protected AuNPs obtained at 200 kV.

Figure 3. UV – visible spectrophotometry of $8.0 \times 10^{-4} \text{ mol dm}^{-3}$ AuNP-Rh₂PMo₁₁ obtained vs that for $8.0 \times 10^{-4} \text{ mol dm}^{-3}$ Rh₂PMo₁₁.

Figure 4. Cyclic voltammetry of GC | AuNP-Rh₂PMo₁₁ in 0.05 mol dm⁻³ H₂SO₄ at 50 mV s⁻¹.

Figure 5. Cyclic voltammetry of (a) $4.5 \times 10^{-3} \text{ mol dm}^{-3}$ methionine in $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ and (b) $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ blank solution. Electrodes: A) GC | APTES | $\text{Rh}_2\text{PMo}_{11}$ and B) GC | APTES | $\text{AuNP-Rh}_2\text{PMo}_{11}$. v , 50 mV s^{-1} .

Figure 6. Cyclic voltammetry of (A) $3.3 \times 10^{-3} \text{ mol dm}^{-3} \text{ BrO}_3^-$ in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ and (B) a $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ blank solution at an GC | APTES | AuNP-Rh₂PMo₁₁ electrode. $v, 50 \text{ mV s}^{-1}$.

Figure 7.

Flow-injection amperometry of bromate at GC | npSG/AuNP-Rh₂PMo₁₁. Bromate concentrations 5, 10, 25, 50, 75, and 100 $\times 10^{-6}$ mol dm⁻³; flow rate, 2 mL min⁻¹, injection volume, 100 μL ; carrier solution, 0.1 mol dm⁻³ H₂SO₄; applied potential, -0.07 V.