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# Nanocomposite Multilayer Film of a Ruthenium Metallodendrimer and a Dawson-Type Polyoxometalate as a Bifunctional Electrocatalyst

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Highly ordered, ultrathin assemblies with molecularly controllable surface properties are well-suited for application as electrocatalysts. A challenge is to develop bifunctional electrocatalysts, particularly systems that can catalyze both reductions and oxidations.[1−4] A single chemical species can serve this purpose for a limited number of reactions;[1,2] however, a more general approach is to use a bifunctional composite. Previous systems include Pt deposits in tungsten oxide[3] and a mixture of an osmium complex with a polyoxometalate.[4] In the present study, the layer-by-layer (LBL) deposition of oppositely charged species[5−16] is explored as a means of preparing a two-species, bifunctional electrocatalyst in the form of an organized structure on the electrode. Multiple layers of each functionality are deposited because previous studies correlated electrocatalytic activity, stability, and response time of analogous monofunctional systems with layer number.[11−16]

To evaluate this approach, we selected a pentaerythritol-based metallodendrimer with Ru$^{II}$ terpyridine units (RuDen) and a Dawson-type phosphotungstate, $P_2W_{18}O_{62}{}^{6-}$ ($P_2W_{18}$), as the electron-transfer promoters. The regularly branched molecular structures of dendrimers provide well-defined surface functionality and specific geometrical sizes, which results in unique properties compared to conventional polymers.[17−20] Moreover, poly(amidoamine), PAMAM, dendrimers have been demonstrated as suited to LBL formation of organized layers in studies of gold nanoclusters[9] and of single-functional catalysts on gold electrodes.[10] RuDen rather than PAMAM was used in our study to provide centers for mediation of electron transfer.[20]

A polyoxometalate (POM) is the second catalytic component. These rigid inorganic metal−oxygen cluster compounds undergo reversible, stepwise, multielectron-transfer reactions that make them attractive in areas such as catalysis, energy storage, and materials science.[21−23] They are anionic over a wide pH range; hence, POMs are amenable to LBL electrostatic interaction with the positively charged RuDen.

The RuDen[24] and $P_2W_{18}$[25] were prepared by published methods. Glassy carbon was the base electrode material because it has a potential window that accommodates both the high oxidation potential of the RuDen and the low reduction potential of the $P_2W_{18}$. The electrode modification procedures were similar to those reported previously.[10,11] In summary, glassy carbon was first immersed for 20 min in 3.4 mM $P_2W_{18}$ to adsorb a negatively charged $P_2W_{18}$ monolayer.[22,23] After washing with water and drying with $N_2$, the $P_2W_{18}$-coated electrode was placed for 20 min in 0.2 mM RuDen in acetonitrile. Repetition of the above two steps yielded, as shown in Scheme 1, ($P_2W_{18}$|RuDen)*n* multilayers, where the number of deposition cycles (a sequential immersion in $P_2W_{18}$ and in RuDen comprises a deposition cycle) corresponds to the number of bilayers, *n*, on the electrode.

The formation of ($P_2W_{18}$|RuDen)*n* was investigated by spectrophotometry (Figure 1). A quartz slide was first modified with a layer of cationic polymer, poly(diallyldimethylammonium chloride), PDDA. Subsequently, alternating layers of $P_2W_{18}$ and RuDen were deposited. The absorption spectra showed peaks at 273, 313, and 487 nm, which corresponded to maxima obtained at 272, 306, and 482 nm when the sample was 3 $\mu$M RuDen in ethanol. Over the investigated wavelength range, the $P_2W_{18}$ spectrum was featureless absorption except for a shoulder between 240 and 350 nm. The absorbances at 273 and at 313 nm, which includes contributions from both RuDen and $P_2W_{18}$, increased linearly with the number of deposition cycles (Figure 1 inset), suggesting that the quantity of these species deposited per cycle was constant up to at least an *n* value of 10.

The deposition of $P_2W_{18}$ and RuDen was quantified by cyclic voltammetry. When $P_2W_{18}$ is the outer layer, reversible peaks appear at −0.146 and −0.328 V (Figure 2A), which correspond to two-electron processes attributed to a pair of W$^{V/VI}$ reactions at each potential.[21−23] A third redox couple of $P_2W_{18}$, not shown in this figure, appears at −0.564 V (Supporting Information). The

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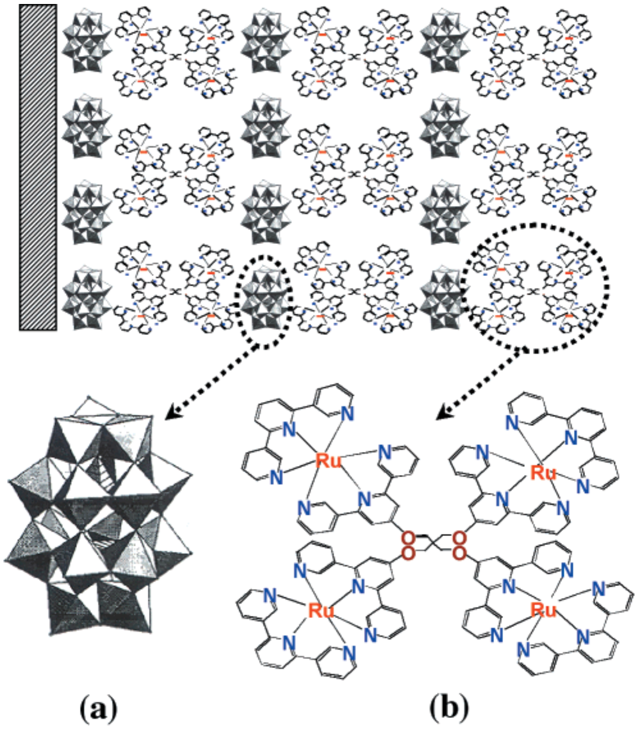
**Scheme 1. Schematic Illustration of the Multilayer Assembly, GCE|$P_2W_{18}O_{62}^{6-}$|RuDen)*n*, $n = 3$**[a]



[a] Note: the sizes of $P_2W_{18}O_{62}^{6-}$(a) and RuDen (b) are not drawn to scale.

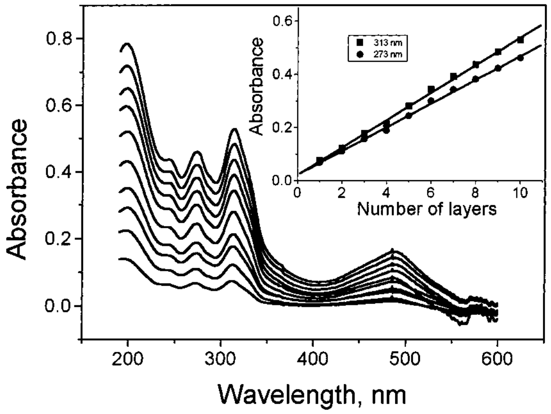


**Figure 1.** UV–visible absorption spectra of $nP_2W_{18}|n$RuDen on PDDA-coated quartz *n* varied from 1 to 10. Each *n* denotes a treatment in $P_2W_{18}$ solution followed by immersion in RuDen solution. The inset shows a linear dependence of absorbance at 273 and 313 nm on *n*.

analogous experiment but with RuDen as the outer layer exhibits a reversible peak at 1.01 V (Figure 2B), corresponding to the $Ru^{II/III}$ redox reaction.[20] With GCE|$nP_2W_{18}|n$RuDen, a scan between −0.66 and 1.2 V yields the combination of parts A and B, Figure 2 (see the Supporting Information for an example with $n = 6$). The voltammetric peak currents for both the W- and Ru-based redox processes are directly proportional to the scan rate up to 1 V $s^{-1}$, which is indicative of surface-confined reactions (Supporting Information).

Coulombic charges determined by integration of the voltammetric peaks increased linearly with the number of deposition cycles for the redox of both $P_2W_{18}$ and RuDen. For example, linear regression analysis (1−10 deposition cycles) of the areas of the oxidation peaks of RuDen ($P_2W_{18}$) at 1.03 V (−0.32 V) vs cycle number yielded the following: slope, 2.23 $\mu$C $n^{-1}$ (1.23 $\mu$C $n^{-1}$) and *r*, 0.9987 (0.9986). From these slopes, the electrode area (0.07 cm$^2$), and the number of electrons transferred, the mean surface coverage, Γ, was calculated. Assuming that each of the four ruthenium centers undergoes a one-electron reaction at 1.0 V and that the redox of $P_2W_{18}$ is a two-electron process, the respective Γ values for RuDen and $P_2W_{18}$ were $8.26 \times 10^{-11}$ and $9.13 \times 10^{-11}$ mol cm$^{-2}$. The charges of $P_2W_{18}$ and of RuDen are formally −6 and +8, respectively. Thus, the Γ ratio, 1.11, and the charge ratio, 1.33, are similar, which signifies that the LBL process occurs stoichiometrically for at least 10 deposition cycles.

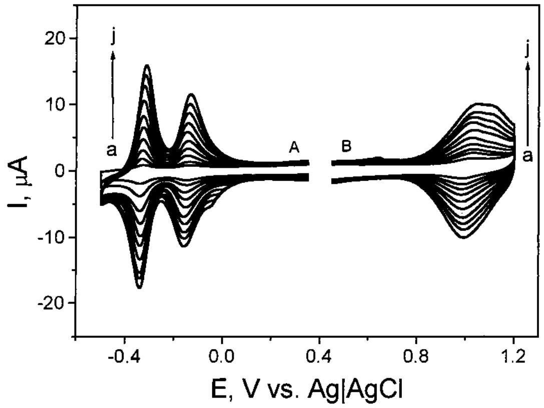


**Figure 2.** Cyclic voltammetry of a glassy carbon electrode modified with $P_2W_{18}$ and RuDen multilayers: (A) GCE|$nP_2W_{18}$|-($n$−1)RuDen and (B) GCE|$nP_2W_{18}|n$RuDen, with *n* from 1(inside, a) to 10 (outside, j). The outer layers were $P_2W_{18}$ for curves in panel (A) and RuDen in panel (B). Electrolyte, 1.0 M $H_2SO_4$. Scan rate, 0.1 V $s^{-1}$.

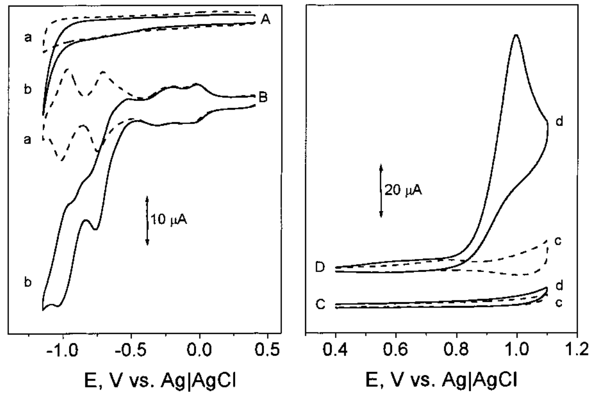


**Figure 3.** Reduction of iodate and oxidation of arsenite at a bifunctional electrocatalytic electrode. (A,C): bare glassy carbon electrode; (B,D): electrode modified with 10 bilayers of $P_2W_{18}$ and RuDen. (a and c, dashed lines): 0.1 M $Na_2HPO_4$ at pH 7.0; (b, solid lines): 5.2 mM iodate in 0.1 M $Na_2HPO_4$ at pH 7.0; (d, solid lines): 2.6 mM $As^{III}$ in 0.1 M $Na_2HPO_4$ at pH 7.0. Scan rate, 0.1 V $s^{-1}$.

Because $P_2W_{18}$ and RuDen promote electrochemical reductions[21,23] and oxidations,[14] respectively, the multilayer electrode is predicted to provide heterogeneous bifunctional electrocatalysis. Here, GCE|*10*$P_2W_{18}$|*10*-RuDen is the electrode, and iodate and arsenite, which are not electroactive under the conditions employed at a bare GCE, are the test systems. The voltammetry of iodate at the multilayer electrode is shown in Figure 3. The peak currents for the third and fourth reduction

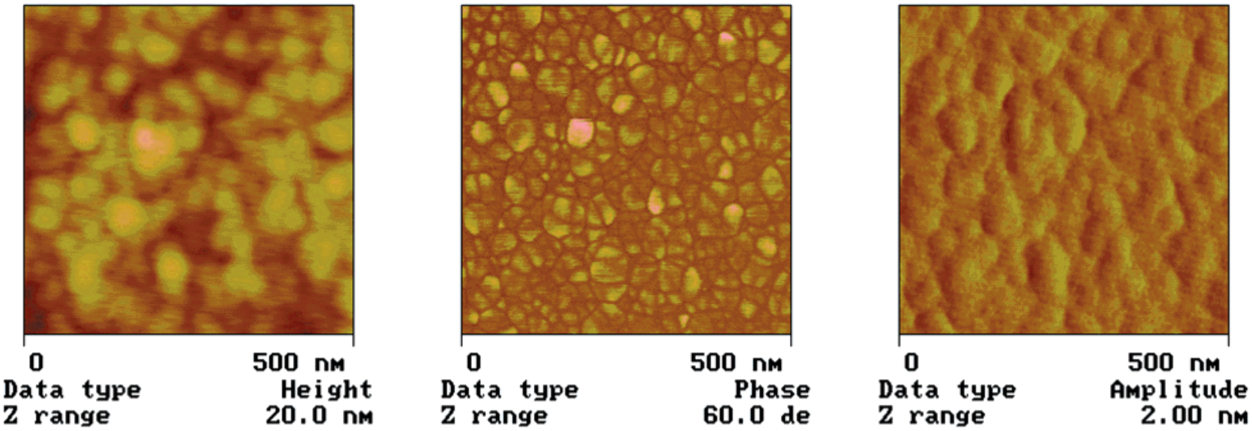


**Figure 4.** AFM images of ($P_2W_{18}$|RuDen)*n* on a PDDA-coated quartz substrate over a 500 × 500 $nm^2$ area. Left, middle, and right are height, phase, and amplitude profiles, respectively.

steps are amplified, signifying the mediated reduction of iodate by $P_2W_{18}$ after 4- and 6-electron reductions. The mediated oxidation of arsenite by RuDen is demonstrated by the criterion of amplification of the peak current for the oxidation of $Ru^{II}$ (Figure 3).

Topographical characterization was conducted by TappingMode atomic force microscopy (AFM) on a bare quartz substrate, quartz|PDDA, quartz|PDDA|$P_2W_{18}$, and quartz|PDDA|*10*$P_2W_{18}$|*10*RuDen. (See Supporting Information for images.) Their rms roughness values were 0.929, 0.659, 1.098, and 2.936 nm, respectively. The smoothing of the bare quartz surface by the PDDA layer is consistent with previously reported results.[26,27] However, the minor difference in surface morphology between the bare quartz and the PDDA film indicated the deposition of PDDA film follows the topographical features of the quartz substrate. In contrast to the PDDA film, the $P_2W_{18}$ monolayer deposited on top of the PDDA film showed a rough granular surface, which can be rationalized by the ellipsoidal structure of $P_2W_{18}$ entrapped or surrounded by PDDA. It is also likely that $P_2W_{18}$ aggregated to a certain level, as reflected by the grain size (≈20−40 nm); the size of a single $P_2W_{18}$ ion is ≈2 nm. In this regard, the cationic polymer PDDA may have reduced the Coulombic repulsion of adjacent $P_2W_{18}$ centers. A similar phenomenon was recently reported for a multilayer self-assembly consisting of glucose oxidase and a redox polymer.[28] AFM images of the quartz|PDDA|*10*$P_2W_{18}$|*10*RuDen over an area of 500 × 500 $nm^2$ were obtained (Figure 4). The height (left), phase (middle), and amplitude (right) profiles showed a granular feature with closely packed particles ranging from 30 to 50 nm in size. Thus, the ($P_2W_{18}$|RuDen) multilayer had a significantly rougher surface than the $P_2W_{18}$ monolayer, which was expected because of the large diameter, ≈3.2 nm, of the monodispersed spacer, RuDen.

The stability was investigated by measuring voltammetric currents of $P_2W_{18}$ and RuDen. A negligible decrease was observed after storage in air for up to 1 month. Also, the decrease in steady-state current over a period of 1 h at 0.1 V $s^{-1}$ in 1.0 M $H_2SO_4$ was only 6%. Thus, ($P_2W_{18}$|RuDen) multilayers formed by the LBL method were highly organized, bifunctional catalytic systems with the stability needed for practical application.

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**Supporting Information Available:** Cyclic voltammograms of the multilayer electrodes and TappingMode AFM images of a bare quartz substrate, quartz|PDDA, quartz|PDDA|$P_2W_{18}$, and quartz|PDDA|*10*$P_2W_{18}$|*10*RuDen (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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