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Polyoxometalates as pH-sensitive probes in self-assembled multilayers

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Received (in Cambridge, UK) 24th January 2002, Accepted 18th March 2002
First published as an Advance Article on the web 8th April 2002

DOI: 10.1039/b200942k

The polyoxometalate cluster $[Co^{II}_4(H_2O)_2P_4W_{30}O_{112}]^{16-}$ (Co-POM) embedded in a self-assembled polyelectrolyte matrix shows a remarkable pH dependence of its electrochemical response, opening a route to use Co-POM as a molecular probe or to fabricate pH microelectrodes.

Layer-by-layer (LbL) assembly of oppositely charged species has become a widespread method to fabricate multicomponent thin films onto various supports.[1] The popularity of the method is due to the ability to tailor the structure and properties of thin films. A nearly unlimited range of functional components awaits to be implemented in thin layered films, the only requirement being a sufficient number of charges in order to facilitate irreversible adsorption.[2] The frontiers in this rapidly emerging field of research embrace the in-depth analysis of the adsorption process, experimental techniques to probe the film structure, novel methods for control of structure and function, and commercial applications.

Polyoxometalates (POMs) are applied in diverse fields such as catalysis, biology, medicine, materials science,[3] and analytical chemistry because of their structural and functional versatility.[4] One of the most important properties of these structurally well-defined early transition metal oxide cluster POMs is their ability to undergo reversible multiple electron transfer reactions.[5] The reduction of the POM cluster results in an accumulation of negative charge, which increases the basicity of the POM anion. The reduction process may thus be accompanied by concomitant protonation. For these reasons, the redox properties of POMs are markedly pH sensitive. Therefore, we envisioned POMs as useful electrochemical probes to survey microenvironmental effects. Likewise, we wish to explore POM-functionalized electrodes as pH sensors. Here, we describe the pH dependence of the redox properties of the 'sandwich' type cobalt(II)-substituted POM compound $[Co^{II}_4(H_2O)_2P_4W_{30}O_{112}]^{16-}$ (Co-POM) in LbL assemblies. The Co-POM is remarkably stable in a pH window ranging from 2 to 9. The following layers are investigated: (**a**) (PSS/PAH/Co-POM/PAH)$_n$ prepared from salt-free solutions; (**b**) (PSS/PAH/Co-POM/PAH)$_n$; and (**c**) PSS/PAH(Co-POM/PAH)$_n$, where only the PAH solution contains NaCl (0.5 M).[6] As indicated by the brackets the architecture of the multilayers differs in the sequence and number of layers.[7]

Cyclic voltammograms (CVs) of an aqueous 1 mM Co-POM phosphate buffer solution (0.2 M, PBS) (pH 5.0) and an indium tin oxide (ITO) electrode show two redox couples with E(I) = -0.53 V and E(II) = -0.705 V, which correspond to $2e^-/2H^+$ redox processes. In the case of thin LbL films, such as PSS/PAH(Co-POM/PAH)$_n$ and (PSS/PAH/Co-POM/PAH)$_n$ ($n < 20$), the cathodic peak potentials shift slightly towards negative and the anodic peak potentials shift slightly towards positive potential values. In all cases, the peak current increases linearly with the number of layers, n, confirming that the assembly process is regular (not shown). The CVs are reproducible from layer to layer and also from sample to sample. Moreover, CVs of PSS/PAH(Co-POM/PAH)$_n$- and (PSS/PAH/Co-POM/PAH)$_n$-modified ITO electrodes show the characteristics of reversible surface redox electrochemistry. A plot of the cathodic (i_{pc}) and anodic (i_{pa}) peak currents as a function of scan rate, ν, is linear up to 300 mV s^{-1} with zero intercept, and the ratio $i_{pc}:i_{pa}$ is unity at all scan rates, which demonstrates that the redox processes of surface confined Co-POM anions are fast and not diffusion limited.[8] We conclude that the electrochemical property of Co-POM is fully maintained in the LbL film.

However, the details of the electrochemical response of Co-POM-containing multilayers depend on the layer architecture. The CVs of (PSS/PAH/Co-POM/PAH)$_{10}$- and PSS/PAH(Co-POM/PAH)$_{10}$-modified ITO electrodes are shown in Fig. 1 (PBS, pH 5). The (PSS/PAH/Co-POM/PAH)$_{10}$-modified ITO electrode assembled from salt-free PAH solution (solid line) shows two redox waves at E(I) = -0.545 V [E_{pc}(I) = -0.574 V, E_{pa}(I) = -0.516 V] and E(II) = -0.710 V [E_{pc}(II) = -0.73 V, E_{pa}(II) = -0.69 V], where $2E = (E_{pc} + E_{pa})$. We observe a different electrochemical response if the film is assembled with a PAH solution containing NaCl (0.5 M). During the cathodic sweep, only one reduction peak appears at a potential of -0.744 V (CIII), and during the anodic sweep two peaks appear at -0.563 (AI) and -0.687 (AII). Apparently, the two two-electron reduction steps merge into one four-electron process. Yet, a different response is observed if the layer sequence is altered. The CV of a PSS/PAH(Co-POM/PAH)$_{10}$ multilayer (Fig. 1, dotted line) assembled with PAH containing NaCl (0.5 M) exhibits two peaks at potentials of -0.643 V (CI) and -0.731 V (CII) during the cathodic, and two peaks at -0.554 V (AI) and -0.69 V (AII) during the anodic sweep. These examples demonstrate that the redox properties of the immobilized Co-POM can reveal subtle variations in film structure and composition. It is interesting to note the accumulation of electrons in the combined reduction wave (CIII) because it may give rise to novel chemical and catalytic effects of surface confined POMs. The pronounced differences of the Co-POM redox behavior are attributed to variations of the microenvironment that the clusters experience in the different multilayer architectures.[9] Similar phenomena were observed with POM anions incorporated in polymer matrices such as

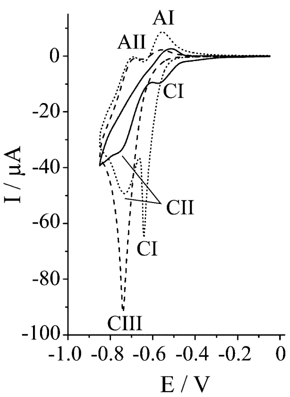

Fig. 1 Representative CVs of (PSS/PAH/Co-POM/PAH)$_{10}$ assembled with salt-free solutions (solid line), (PSS/PAH/Co-POM/PAH)$_{10}$ (dashed line) and PSS/PAH(Co-POM/PAH)$_{10}$ assembled with PAH solution containing NaCl (0.5 M) (dotted line) (scan rate 10 mV s^{-1}, potential E *vs.* Ag/AgCl)

poly(4-vinylpyridine/1,12-dibromododecane), poly(pyrrole) and poly(1-naphthol).[10]

Also, we note that the surface coverage of Co-POM clusters depends on the LbL assembly procedure. Based on the CVs, the average surface coverage of Co-POM per layer amounts to 5×10^{-11} mol cm^{-2} (**a**), 1.6×10^{-10} mol cm^{-2} (**b**), and 1.4×10^{-10} mol cm^{-2} (**c**), or 3.02 (**a**), 1.03 (**b**), and 1.18 (**c**) nm^2 Co-POM^{-1}, respectively. Assuming randomly orientated clusters, the surface area amounts to *ca.* 2 nm^2 per Co-POM.[11] These values, therefore, correspond to *ca.* one (**a**) to two (**b**/**c**) monolayers.[12] The multilayers adhere strongly to the substrate and cannot be rinsed off with aqueous solutions or organic solvents. Also, we note that extensive potential cycling has no or only little effect on the electrochemical response of the layers. After 100 potential cycles the peak current of type **a** and **c** multilayers decreases by *ca.* 10% while type **b** multilayers are hardly affected. Obviously, depositing extra polyelectrolyte layers at high ionic strength stabilizes the multilayer and prevents leakage of Co-POMs.

The electrochemical response of LbL-based Co-POM multilayers is pH dependent. With increasing pH of the solution, the potentials of the reversible redox pairs of PSS/PAH(Co-POM/PAH)$_{10}$- and (PSS/PAH/Co-POM/PAH)$_{10}$-modified ITO electrodes shift to more negative potential values. The relationship between redox potential and pH is shown in the inserts of Fig. 2. The slope of the graph of potential *E vs.* pH, d[*E*]/d[pH], depends on the number of protons and electrons exchanged in the redox process according to

$$d[E]/d[\mathrm{pH}] = -59.1m/n \quad \mathrm{mV\ pH^{-1}\ (at\ 25\ ^\circ C)} \qquad (1)$$

where *m* is the number of protons and *n* the number of electrons consumed in the redox process:

$$\text{Co-POM} + m\mathrm{H}^+ + ne \rightleftharpoons [\mathrm{H}_m\text{Co-POM}]^{-(n-m)} \qquad (2)$$

The number of electrons, *n*, is determined independently from the area of the CV because only electrons contribute to the current. With decreasing pH, the redox potentials of (PSS/PAH/Co-POM/PAH)$_{10}$ assembled form pure PAH solution shift to positive potentials with slopes of 85 (I) and 50 (II) mV pH^{-1}, as shown in Fig. 2A, indicating that *ca.* 3 and 2 protons participate in the first and second reduction processes, respectively. The corresponding slopes assigned for PSS/PAH(Co-POM/PAH)$_{10}$ and (PSS/PAH/Co-POM/PAH)$_{10}$ multilayers assembled with salt-containing PAH solution amount to 74 (I), 54 (II) (inset Fig. 2B) and to 75 (III) mV pH^{-1} (inset Fig. 2C), respectively. In this case, *ca.* 2.5 and 2 protons participate in the cathodic process of PSS/PAH(Co-POM/PAH)$_{10}$ and *ca.* 5 protons in the cathodic process of (PSS/PAH/Co-POM/PAH)$_{10}$, respectively. Apparently, the polyelectrolyte matrix changes equilibrium (2) either by affecting the concentration of protons or the pK_a of Co-POM in the layer. Currently, we cannot unambiguously determine the significance of each contribution. However, these results clearly demonstrate the high pH sensitivity of Co-POM multilayers, whereas the sensitivity d[*E*]/d[pH] is a function of the layer architecture.

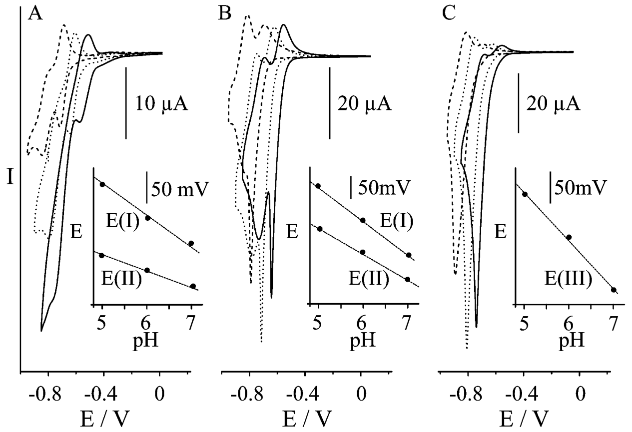

Fig. 2 Representative CVs of (PSS/PAH/Co-POM/PAH)$_{10}$ assembled with salt-free solutions (A), PSS/PAH(Co-POM/PAH)$_{10}$ (B) and (PSS/PAH/Co-POM/PAH)$_{10}$ assembled with PAH solution containing NaCl (0.5 M) (C). Solid line, pH 5.0; dotted line, pH 6.0; dashed line, pH 7.0. The inserts show the dependence of redox potentials on pH (scan rate 10 mV s^{-1}, potential *E vs.* Ag/AgCl)

Here, we demonstrate two new important features of POM clusters incorporated in LbL films. First, Co-POM can be employed to probe microenvironmental effects in LbL multilayers. Second, the electrochemistry of Co-POM-functionalized LbL multilayers is remarkably pH dependent. The origin of the pH dependence may be multifold including ion-pair formation, the distribution of ions and charge (Donnan potential), permselectivity, as well as the polarity within the LbL layer. This feature makes LbL-based Co-POM multilayers potential candidates for pH microsensors, *e.g.* in physiological media. Our approach has several advantages over other pH sensors:[13] it is simple and inexpensive to fabricate, operates reversibly, possesses long-term stability and, in addition, the electrochemical response characteristics can be adjusted by the structure and composition of the sensing layer.

Helmuth Möhwald is acknowledged for valuable discussions. S. L. thanks the Alexander von Humboldt Foundation for a fellowship. D. G. K. and D. V. thank the BMBF for a research grant (NMT No. 03N8618).

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