

## Ultrathin Composite Films Incorporating the Nanoporous Isopolyoxomolybdate “Keplerate”

$(\text{NH}_4)_{42}[\text{Mo}_{132}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}]$

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Polyoxometalates (POMs) are attractive building blocks for functional supramolecular materials with potential applications in electrocatalytic, molecular electronic, or electrooptical devices.<sup>1</sup> With the recent discovery of giant, nanoporous POMs (giant wheels<sup>2</sup> and Keplerates<sup>3</sup>), molecularly defined components are now available that bear the potential to construct selective coatings based on their molecular size-exclusion properties. To procure such POM-based devices, it will be necessary to improve existing and to develop new methods to integrate POMs into thin films and coatings.

Thin films of POMs can be made by electrodeposition, but the structure, quality, and purity of the resulting films are often ill-defined.<sup>4</sup> Another possibility is to take advantage of the characteristic feature of certain POMs to form monolayers on precious metal surfaces.<sup>5</sup> A new and more general method to fabricate highly ordered thin films of POM components utilizes surfactant-encapsulated clusters (SECs).<sup>6,7</sup> SECs are hydrophobic, structurally well-defined core-shell particles in which a discrete anionic POM cluster is encapsulated within a shell of cationic surfactants. SECs are attractive functional components because they form extended two-dimensional cluster arrays by simple evaporation techniques and three-dimensional superlattices by the Langmuir-Blodgett deposition technique.<sup>8</sup>

An alternative approach to thin film fabrication described here is the layer-by-layer (LbL) self-assembly method. This technique is based on the sequential adsorption of oppositely charged species from dilute solutions and has been commonly applied to multilayer assemblies of organic polymers.<sup>9,10</sup> It is particularly advantageous for creating coatings on arbitrary substrates with structural control at the nanometer level and for co-assembling different components, while the deposition process is easily adapted for automated processing. In a first study, we recently showed that the LbL method is also applicable for generating composite multilayer films of anionic POMs and a polycationic organic resin.<sup>11</sup>

The recently described nanoporous isopolyoxomolybdate  $(\text{NH}_4)_{42}[(\text{H}_2\text{O})_n \subset \text{Mo}_{132}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}]$ ,  $\{\text{Mo}_{132}\}$  (“Keplerate”),<sup>3</sup> provided further impetus to investigate the immobilization of a function-bearing POM component in a supporting organic matrix. The nearly spherical Keplerate cluster shows promising perspectives in host-guest chemistry and size-selective catalysis because it possesses an open Mo-O framework architecture that encloses a central cavity with an approximate inner diameter of 1.7 nm. The Keplerate framework spans (Mo-O) 9-ring openings with an average ring aperture of 0.43 nm.<sup>3,7</sup> The LbL method appears most promising to fabricate permeable coatings to exploit the nanoporous structure of Keplerates in catalytic and sensing devices.<sup>12</sup>

We report here on the preparation of stable ultrathin composite films of polyallylamine hydrochloride (PAH) and the nanoporous isopolyoxomolybdate  $[(\text{H}_2\text{O})_n \subset \text{Mo}_{132}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}]^{42-}$  by the LbL method. The film structure is characterized by UV-vis spectroscopy, ellipsometry, X-ray reflectance (XRR), and quartz crystal microbalance (QCM) measurements. The latter method shows a practical approach to transduce molecular recognition events, occurring in the composite films, into an electric signal.

Because of the dark-brown color of the Keplerate, UV-vis spectroscopy permits facile evaluation of the layer deposition process.<sup>13</sup> Figure 1 shows the UV-vis spectra of  $(\{\text{Mo}_{132}\}/\text{PAH})_n$  multilayers (with  $n = 1-6$ ) assembled on a precursor PEI/PAH film on quartz. The inset shows the Keplerate Mo-O framework as a polyhedral representation. The increase of absorbance in the wavelength range of 200–600 nm confirms adsorption of  $\{\text{Mo}_{132}\}$  anions onto the positively charged PAH interface. A plot of the absorbance at three characteristic wavelengths (210, 328, and 456 nm)

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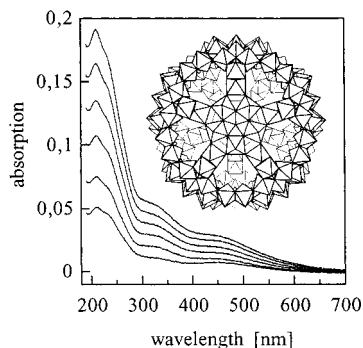
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(13) The cleaned substrates (quartz-, silicon-, or gold-coated QCMs) were immersed in a  $10^{-2}$  M poly(ethyleneimine) solution (PEI, MW 50 000) for 20 min, rinsed with water, and dried under an argon stream. Multilayers were prepared by alternating 20-min immersions in poly(allylamine hydrochloride) (PAH, MW 8 000–11 000) ( $10^{-2}$  M containing 1 M NaCl, pH ~ 5–6) and  $\{\text{Mo}_{132}\}$  ( $2 \times 10^{-4}$  M, pH ~ 3.5) solutions. Water rinsing and argon drying steps were performed after each adsorption step.



**Figure 1.** UV-vis spectra of  $\{\text{Mo}_{132}\}/\text{PAH}\}_n$  multilayer films for  $n = 1-6$  on PEI/PAH-modified quartz substrates. The bottom curve corresponds to the first  $\{\text{Mo}_{132}\}$  film ( $n = 1$ ) and the curve at the top to the last deposited  $\text{Mo}_{132}$  layer ( $n = 6$ ). The inset shows a polyhedral representation of the Mo-O framework of a  $\{\text{Mo}_{132}\}$  cluster. The outer diameter of the cluster is  $\approx 3$  nm and that of the cavity is 1.7 nm, respectively. The openings have an average diameter of 0.43 nm.

versus the number of layers,  $n$ , results in straight lines, which demonstrates that equal amounts of  $\{\text{Mo}_{132}\}$  and PAH are adsorbed in each deposition cycle (data not shown). We notice that, for the first layer, a significantly larger amount of  $\{\text{Mo}_{132}\}$  is immobilized on the PEI/PAH precursor film. This is possibly due to penetration of the Keplerate into the underlying precursor layer.

From the UV-vis spectra it is possible to calculate the surface concentration,  $\Gamma$ , of  $\{\text{Mo}_{132}\}$  anions per layer using the relation  $\Gamma = [N_A A_i / (I \epsilon_i)]$  ( $N_A$  is Avogadro's number,  $A_i$  is the absorbance,  $\epsilon_i$  is the molar extinction coefficient [ $\text{cm}^2/\text{mol}$ ] at the wavelength  $\lambda$ , and  $I$  is the total number of layers). The average surface concentration of  $\{\text{Mo}_{132}\}$  per layer is  $(4.4 \pm 0.2) \times 10^{12}$  clusters/ $\text{cm}^2$  or  $(7.3 \pm 0.3) \times 10^{-12}$  mol/ $\text{cm}^2$ .<sup>14</sup> This corresponds to an average area of  $(22.7 \pm 1.0)$  nm<sup>2</sup>/cluster. In the crystal structure of  $(\text{NH}_4)_{42} [\text{Mo}_{132}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}] \cdot \approx 300\text{H}_2\text{O} \cdot \approx 10\text{CH}_3\text{COONH}_4$  the packing density is 9.1 nm<sup>2</sup>/cluster in the [111] plane and 10.6 nm<sup>2</sup>/cluster in the [100] plane.<sup>3</sup> The  $\{\text{Mo}_{132}\}$  packing density of the LbL film is, therefore,  $\approx 50\%$  of that of the crystalline material. Most likely, the repulsive electrostatic and dipolar interactions are not compensated as efficiently in a two-dimensional film as in the solid state.

Film growth was monitored with the quartz crystal microbalance (QCM). The change of resonance frequency after rinsing and drying the film shows that the deposited quantity of Keplerate anions for a single layer amounts to  $(3300 \pm 150)$  ng/ $\text{cm}^2$ .<sup>15</sup> On the basis of the experimentally determined surface concentration  $\Gamma$ , a mass change of 158 ng/ $\text{cm}^2$  is expected for a single  $\{\text{Mo}_{132}\}$  layer.<sup>16</sup> Hence, the experimentally determined mass change corresponds to several  $\{\text{Mo}_{132}\}$  layers. If

(14) Strong absorption bands have a considerable reflectance loss, which affects the experimentally measured absorbance. We, therefore, resort to the less intense bands to determine the surface coverage from UV-vis spectra more accurately, in this case at 465 nm.

(15) QCM measurements were performed with a HP-53131 frequency counter, a HP-4194A impedance analyzer, and a custom-made resonator circuit operated by a HP-E3620A power supply. One side of the QCM was covered with a glass dome; the remaining free side was coated with the multilayer assembly. Mass changes were calculated from the Sauerbrey equation, the applicability of which was confirmed with impedance analysis of the coated QCM resonators. The gold electrode was coated with a monolayer of mercapto propionic acid as an adhesion promoter before assembly of the multilayers.

PAH is adsorbed on top of the  $\{\text{Mo}_{132}\}$  layer, the mass on the QCM crystal decreases by  $(2915 \pm 175)$  ng/ $\text{cm}^2$ . We suggest that the decrease in mass loading can be rationalized as follows: Weakly adsorbed  $\{\text{Mo}_{132}\}$  cluster anions and PAH form a soluble complex so that excess clusters are extracted from the surface. In contrast, electrostatically immobilized  $\{\text{Mo}_{132}\}$  cluster anions, directly adsorbed on the underlying PAH layer, form a surface-confined  $\{\text{Mo}_{132}\}$ -PAH complex. It is, therefore, not possible to determine the individual contribution of each component by microgravimetric measurements because adsorption of PAH on and extraction of  $\{\text{Mo}_{132}\}$  cluster anions from the interface occur simultaneously. The fact that  $\{\text{Mo}_{132}\}$  deposition is very reproducible indicates that film formation occurs under equilibrium conditions.<sup>17</sup> Using the previous results, the contribution of each component can be estimated. The final mass change for a  $\{\text{Mo}_{132}/\text{PAH}\}$  layer pair then amounts to  $(375 \pm 18)$  ng/ $\text{cm}^2$ . If a mass of 158 ng/ $\text{cm}^2$  is attributed to the  $\{\text{Mo}_{132}\}$  layer, the remaining 217 ng/ $\text{cm}^2$  would constitute the PAH layer. A PAH layer with a thickness of 1.2 nm and a density of 1.2 g/ $\text{cm}^3$  would have a mass of  $\approx 150$  ng/ $\text{cm}^2$ . The remaining mass of 67 ng/ $\text{cm}^2$  is ascribed to water, which is always present in polyelectrolyte films at ambient conditions.<sup>18</sup> Within the experimental accuracy, the mass loading for a  $\{\text{Mo}_{132}\}/\text{PAH}$  layer pair is in agreement with the previous results. Monitoring the mass change in situ shows that 90% of the finally adsorbed mass is adsorbed within  $< 5$  min and a plateau is reached within 15 min. The deposition of a single layer, therefore, occurs within a fraction of that time.

Film formation and film structure were also investigated by X-ray reflectance (Figure 2). The Kiessig fringes in the XRR spectra of  $\{\text{Mo}_{132}\}/\text{PAH}$  multilayers indicate that the resulting films are of uniform film thickness.<sup>19</sup> The increase of film thickness for consecutively deposited layers is reflected in the interference fringes becoming increasingly narrow. The average effective film thickness for a  $\{\text{Mo}_{132}\}/\text{PAH}$  layer pair is  $2.2 \pm 0.2$  nm, and a plot of the total thickness versus the layer number,  $n$ , yields a straight line for  $n > 1$ . No Bragg reflections are observed that would indicate an internal structure. The reason for this could be that due to the low  $\{\text{Mo}_{132}\}$  surface coverage the electron density contrast is (i) reduced and (ii) smeared out. The film thickness of 2.2 nm and linear film growth were independently confirmed by optical ellipsometry.<sup>20</sup> The occupied volume fraction of a single  $\{\text{Mo}_{132}\}$  layer is 30%

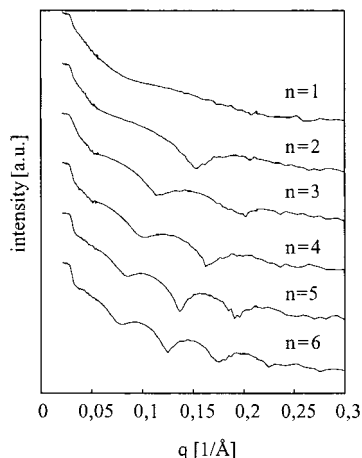
(16) Here, we assume a  $\{\text{Mo}_{132}\}$  cluster anion with the composition  $\text{Mo}_{132}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}$  and a molecular mass of 21 685 g/mol. The number of ammonium ions in the LbL film is not known. Because of the large mass of a single  $\{\text{Mo}_{132}\}$  cluster anion, their contribution to the total mass is negligible.

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(18) The water content was determined microgravimetrically to be up to 30 wt % in similar polyelectrolyte LbL multilayers (Kurth, D. G.; Sch6t6tte, M., unpublished results).

(19) XRR experiments were performed with a commercial instrument (STOE & CIE GmbH, Darmstadt, Germany) using 1.54-Å radiation. Analysis of the XRR data was performed with a box-model simulation. The experimental error in thickness and surface roughness is  $\pm 0.2$  nm. X-ray reflectivity measurements performed on multilayer films assembled on silicon wafers yielded data similar to those obtained for films on quartz substrates.

(20) Ellipsometric measurements were performed with null-ellipsometry using a Multiskop (Optrel Germany, 2-mW HeNe Laser,  $\lambda = 632.8$  nm; angle of incidence 70° for silicon substrates).



**Figure 2.** X-ray reflectance spectra of alternating ( $\{\text{Mo}_{132}\}/\text{PAH}\}_n$ ) multilayer films on a silicon substrate. The Kiessig interference fringes show that the film is of uniform film thickness on the nanometer length scale. The characteristic narrowing of the interference fringes indicates an increase of film thickness with each newly deposited layer (individual curves are set off for clarity).

because the surface coverage is only 50%.<sup>21</sup> On the basis of the cluster diameter of 3 nm, the measured film thickness of a single layer, therefore, amounts to  $\approx 1$  nm. The remaining 1.2-nm film thickness is, therefore, attributed to PAH, which is a reasonable value for a single layer.<sup>22</sup>

(21) A close-packed monolayer of spheres has an occupied volume fraction of 60%.

Ichinose et al. reported a thickness for a layer of octamolybdate  $(\text{NH}_4)_4[\text{Mo}_8\text{O}_{26}]$  ranging from 2 to 25 nm, depending on the preparation conditions.<sup>23</sup> The variable film thickness was rationalized by the loss of negative charge due to protonation and condensation of molybdate anions, resulting in excess cluster adsorption. Apparently, adsorption was carried out under kinetic control. In contrast to their observations, we found the deposition of the Keplerate  $\{\text{Mo}_{132}\}$  to be highly reproducible.

We demonstrate in this work that the Keplerate  $\{\text{Mo}_{132}\}$  can be assembled in multilayers with cationic macromolecules using the layer-by-layer deposition method. The results from UV-vis spectroscopy, QCM, ellipsometric, and X-ray reflectance measurements are consistent with monolayer surface coverage of Keplerate cluster anions. Experiments are in progress to investigate the applicability of  $\{\text{Mo}_{132}\}/\text{PAH}$  multilayers as sensitive coatings for analytical applications.

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