Ultrathin Molybdenum Polyoxometalate–Polyelectrolyte Multilayer Films

Frank Caruso,* † Dirk G. Kurth,† Dirk Volkmer,‡ Michael J. Koop,† and Achim Müller‡

Max-Planck-Institute of Colloids and Interfaces, Rudower Chaussee 5, D-12489 Berlin, Germany, and Fakultät für Chemie der Universität Bielefeld, Lehrstuhl für Anorganische Chemie I, Universitätssstrasse 25, D-33615 Bielefeld, Germany

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Ultrathin multilayer films of a novel molybdenum(VI) polyoxometalate cluster ([NH₄]₁₂[(H₂O)₁₁(M₀₅₋₁)(Mo₅₇)₉CO₃]·12H₂O) and poly(allylamine hydrochloride) (PAH) have been prepared by the consecutive stepwise adsorption of M₀₅₋₁ and PAH from dilute aqueous solution. The M₀₅₋₁/PAH multilayer films have been characterized by optical spectroscopy and small-angle X-ray reflectivity (XR) methods. UV–vis measurements reveal regular film growth with each M₀₅₋₁ adsorption. The average M₀₅₋₁ surface density was found to be (1.4 ± 0.4) × 10¹³ clusters per cm², corresponding to an average surface coverage of 56 ± 12%. XR experiments confirm uniform film growth, with the film thickness increasing with each M₀₅₋₁ adsorption step. The average thickness for the M₀₅₋₁/PAH layer pair was determined to be 0.8 ± 0.1 nm. The M₀₅₋₁ density in the film can be readily controlled by varying the polyelectrolyte interlayer separation between each M₀₅₋₁ layer, and the total film thickness can be controlled by altering the number of adsorption cycles.

Introduction

The controlled incorporation of metal nanosized particles into a well-defined solid matrix is of widespread interest in materials science. Ordered assemblies of such composite materials have potential uses as electron-transfer materials for energy storage applications, data storage systems, optical gratings, filters, and coatings and in the area of microelectronics.1–3 Several techniques have been employed to produce solid-state assemblies of metal nanoparticles. Langmuir–Blodgett deposition has been used to construct ordered nanocomposite materials.10 Ultrathin multilayer films of metal oxides have been prepared by means of a surface sol–gel process.11 More recently, the preparation of ordered layers of gold nanoparticles within porous silica matrices using a combination of colloidial adsorption and sol–gel processing techniques has been reported.12 The layer-by-layer self-assembly method originally applied to produce multilayer assemblies of polymers13–24 has also recently been used to produce various ordered metal–polymer composite films; multilayer films of colloidal gold, cadmium sulfide, lead sulfide, and titanium dioxide incorporated into polymer matrices have been fabricated.1,2,9,16,25 This technique, which involves the sequential adsorption of oppositely charged species from dilute solution, has been widely employed because of its simplicity and effectiveness in preparing multilayer films, as well as allowing the film composition and film thickness to be easily controlled.

Polyoxometalates are an attractive class of nanoparticles because of their particularly interesting nanosized structure27,28 and their potential applications in the areas of catalysis, molecular electronics, and medicine.29–31 Practical applications of polyoxometalates in these areas depend on the successful preparation of thin polyoxo-metal-containing films. Ingersoll et al. employed cyclic

Asmussen, A.; Riegler, H. 

The formation of Mo₈O₂₆ on PAH, the formation of the multilayer films Mo₈O₂₆₄ times employed, corresponding to 2 work, adsorption of the ammonium octamolybdate (NH₄)₄-

By using a quartz crystal microbalance, and film structure was studied by scanning electron microscopy. In that work, adsorption of the ammonium octamolybdate (NH₄)₂-

Multilayer films of the molybdenum oxide alternating with PAH could be formed at pH values of about 5–6 for the PAH solution, but only at lower pH values (∼3). Further, molybdenum oxide/poly(ethylene-imine) (PEI) multilayer films could not be formed due to the high solubility of the molybdenum oxide/PEI complex, nor could multilayers of [V₁₀O₃₄]³⁻/PAH.

In the present study, we report on the preparation of ultrathin multilayer polyoxometalate–polyelectrolyte films by the consecutive stepwise adsorption of a novel, well-characterized molybdenum polyoxometalate cluster [(NH₄)₂[Mo₇O₂₄(V₃(OH)₁₈(H₂O)₁₈)] (Mo₇V₃) and poly-(allylamine hydrochloride) (PAH). UV–vis spectroscopy and small-angle X-ray reflectivity (XR) are exploited for examining the growth, structure, and morphology of the composite Mo₇/PAH films. The external form of the Mo₇ cluster resembles a flattened ellipsoid with dimensions 1.6 × 2.4 nm (determined from X-ray crystallography measurements).

The electronic structure of these types of molybdenum polyoxometalate clusters has previously been investigated by MO calculations, by different spectroscopic methods, and magnetically and electronically, and their structural diversity has only recently been recognized.

The wide-spread application of polyoxometalates based on the Keggin structure type in solid-state devices, catalysis, biochemistry, and medicine provides further impetus for investigation of this new class of molybdenum polyoxometalate clusters.

Experimental Section

Materials. Poly(ethyleneimine) (PEI), MW 50 000, poly-(sodium 4-styrenesulfonate) (PSS), MW 70 000, and poly(allylamine hydrochloride) (PAH), MW 8 000–11 000, were obtained from Aldrich. PEI and PAH were used as received, whereas PSS was dialyzed against Milli-Q water (MW cut off 14 000 ) and lyophilized before use. The Mo₇ cluster was synthesized by a modified synthetic route that has been published. A mixture of (NH₄)₂-

The layer thickness depended on the adsorption time: the growth rate of the layer was 0.57 nm min⁻¹; film thicknesses were in the range 2–25 nm for the adsorption times employed, corresponding to 2–30 layers of the [Mo₈O₂₆]³⁻ unit. In addition to the unique time-dependent characteristics observed for the adsorption of (NH₄)₂-

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Results and Discussion

The formation of Mo₇/PAH multilayer films was first examined by UV–vis spectroscopy. Figure 1 displays the UV–vis absorption spectra of (Mo₇/PAH)₇ multilayers (with n = 0–6) assembled on a precursor PEI/PSS/PAH film on quartz substrates. The inset in Figure 1 shows the absorption spectrum of an aqueous Mo₇ solution, as well as a polyhedral representation of the Mo₇ cluster. The solution absorption spectrum of Mo₇ exhibits a broad band in the 500–600 nm range, with a maximum at 558 nm. The extinction coefficient at 558 nm (ε₅₅₈ = 20 000 M⁻¹ cm⁻¹) is 20 times smaller than ε₅₂₅ (~ 4 × 10⁴ M⁻¹ cm⁻¹). This explains the absence of a strong absorption band at 558 nm in the Mo₇/PAH multilayer film spectra. The absorption spectrum for the precursor multilayer film PEI/PSS/PAH (n = 0) shows a peak at 225 nm, which is due to the benzene chromophores of PSS. PAH does not absorb above 200 nm, and therefore its presence in the
A function of the number of Mo$_{57}$ layers in Figure 2. For PAH layers, since some loss of Mo$_{57}$ occurring at each step shown in Figure 1 are for multilayer films having an outer layer of PAH deposition (monitored via UV metalates species, 32 or charged organic dyes, 36 recent studies have also demonstrated a loss of polyoxometalate species on PAH, where the amount of Mo$_{57}$ is observed, compared with 0.037 at 225 nm for the three-layer film (PEI/PSS/PAH).

The surface density, $\Gamma$, of Mo$_{57}$ on the PAH surface in the (Mo$_{57}$/PAH)$_n$ films can be calculated using $\Gamma = \left( \frac{A}{2\pi r^2} \right) \times 10^{13}$, where $A_r$ is the absorbance of Mo$_{57}$ in solution $\times$ extinction coefficient of Mo$_{57}$ in solution (M$^{-1}$ cm$^{-1}$) at $\lambda$, and $N_A$ is Avogadro’s number. Using the absorbance values in the 200–300 nm range (where absorbance is largest) and the corresponding extinction coefficients calculated from the solution absorption spectrum of Mo$_{57}$, an average Mo$_{57}$ surface density of $(1.4 \pm 0.4) \times 10^{13}$ clusters per cm$^2$ is obtained for (Mo$_{57}$/PAH)$_n$ multilayer films with $n > 1$. This corresponds to an average area per Mo$_{57}$ of 7.1 $\pm$ 2.0 nm$^2$. Hence, assuming a single Mo$_{57}$ cluster occupies an area of approximately 3.2–4.8 nm$^2$, depending on its relative orientation, the average surface coverage is 56 $\pm$ 12%. The average surface density for the first layer of Mo$_{57}$ deposited onto the PEI/PSS/PAH precursor film is $(2.8 \pm 0.1) \times 10^{13}$ clusters per cm$^2$, which is twice that observed for subsequent layers of Mo$_{57}$. As discussed above, Mo$_{57}$ penetrates the precursor layers, which explains the increased coverage observed. The surface coverage values for films with $n > 1$ are approximately a factor of 2 lower than those reported by Ingersoll et al. for smaller polyoxometalate particles on native and modified conducting surfaces and more than 1 order of magnitude lower than those reported by Ichinose et al. for ammonium octamolybdate ([NH$_4$]$_4$[Mo$_{8}$O$_{26}$]) on PAH, where the amount of Mo$_{57}$ surface density of the polyoxometalate species is deposited due to condensation of the adsorbed octamolybdate species.

The effect of polyelectrolyte interlayer separation (between each Mo$_{57}$ layer) on the amount of Mo$_{57}$ deposited was also examined. Increasing the polyelectrolyte interlayer separation between Mo$_{57}$ layers from a single PAH layer to three layers (PAH/PSS/PAH) resulted in a larger amount of Mo$_{57}$ being incorporated into the film. The average absorbance at 225 nm for these films from three experiments is 0.037 $\pm$ 0.04 (two sides), demonstrating that a constant amount of Mo$_{57}$ is deposited with each step. Furthermore, the amount of Mo$_{57}$ in precursor films of increasing thickness (one to seven layers) has a linear correlation to the number of polyoxometalate layers—a

![Figure 1. UV-vis absorption spectra of (Mo$_{57}$/PAH)$_n$ multilayer films with $n = 0$–6 on PEI/PSS/PAH-modified quartz substrates. The lowest curve corresponds to the precursor film ($n = 0$). The other curves, from bottom to top, correspond to $n = 1, 2, 3, 4, 5,$ and 6, respectively. The inset shows the absorbance spectrum of an aqueous 0.033 mg mL$^{-1}$ Mo$_{57}$ solution (Mo$_{57}$ concentration is $3 \times 10^{-6} M$) and a polyhedral representation of the Mo$_{57}$ cluster.](image1)

![Figure 2. Plot of the absorbance values at 225, 275, 300, and 558 nm as a function of the number of Mo$_{57}$ layers for the (Mo$_{57}$/PAH)$_n$ multilayer films with $n = 0$–6 on PEI/PSS/PAH-modified quartz substrates. The absorbance at 558 nm has been multiplied by 5.](image2)
increasing number of Mo$_{57}$ layers, as determined from XR data. Evidence for multilayer film formation comes from the decrease in the distance between Kiessig fringes (along the $x$-axis) in the XR curves as a result of Mo$_{57}$ and PAH deposition. The thickness of the precursor film PEI/PSS/PAH on quartz (curve a) is 5.4 nm, with a surface roughness of 1.0 nm. The presence of Mo$_{57}$ on the precursor film (curve b) increases the film thickness by 1.7 nm to a value of 7.1 nm and the surface roughness to 1.3 nm. Subsequent exposure of this film to a PAH solution produces a further increase in film thickness (7.5 nm) (curve c). From this value it is clear that an increase in the total film thickness occurs, even though PAH adsorption removes some preadsorbed Mo$_{57}$ (assessed via UV–vis measurements). The surface roughness for the PEI/PSS/PAH/Mo$_{57}$/PAH film is 1.2 nm. The deposition of alternate Mo$_{57}$ and PAH layers to give a PEI/PSS/PAH/Mo$_{57}$/PAH$_n$ film results in a film thickness of 11.6 nm, and a surface roughness of 1.3 nm (curve d). Thus, the average thickness for the Mo$_{57}$/PAH layer pair (for films with $n > 1$) is 0.8 ± 0.1 nm. Estimation of the thickness of a single Mo$_{57}$ or PAH layer is complicated by the simultaneous removal of Mo$_{57}$ and PAH deposition. Furthermore, the individual layer thicknesses for Mo$_{57}$ and PAH layers cannot be reliably determined given the magnitude and error (±0.2 nm) in the experimental thicknesses. The reflectivity data, however, confirm the growth of Mo$_{57}$/PAH multilayer films. The average thickness obtained for the Mo$_{57}$/PAH layer pair is approximately 20 times smaller than that reported for the [Mo$_8$O$_{26}$]$^{4-}$ species (thickness ~20 nm) for identical adsorption times of 20 min.$^{32}$ The thickness of 20 nm for [Mo$_8$O$_{26}$]$^{4-}$ corresponds to ca. 20 layers of the molybdate unit,$^{32}$ whereas in the current work less than a monolayer of Mo$_{57}$ is deposited with each adsorption step. This also suggests that condensation of the Mo$_{57}$ can be largely ruled out over the time frame of our experiments.

Atomic force microscopy (AFM) measurements of the Mo$_{57}$/PAH$_n$ films did not produce images in which individual Mo$_{57}$ clusters could be clearly identified—largely due to the roughness of the polyelectrolyte film and the small size of the Mo$_{57}$ clusters. However, the AFM surface roughness data for the multilayer films is in excellent quantitative agreement with that obtained from X-ray reflectivity measurements. The surface roughness of the Mo$_{57}$/PAH films (ca. 1 nm) is considerably less than the roughness of ~10 nm reported for [Mo$_8$O$_{26}$]$^{4-}$/PAH multilayer films.$^{32}$

Conclusions

The present work demonstrates the successful consecutive stepwise assembly of a new class of nanosized molybdenum polyoxometalate clusters, and PAH, to produce composite multilayer films: nanocomposite supramolecular films of controlled thickness and Mo$_{57}$ density have been prepared. The control of such parameters is crucial in the development of nanostructured functional materials where molecular components are required to be integrated in an ordered macroscopic film.

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Supporting Information Available: Packing plots of $[\text{H}_3\text{Mo}_{57}\text{V}_6\text{O}_{183}\text{H}_2\text{O}_{18}]^{21-}$ clusters within the (100) and (001) crystallographic planes (3 pages). Ordering information is given on any current masthead page.


Letters

Figure 3. X-ray reflectivity curves of alternating Mo$_{57}$/PAH multilayer films on quartz substrates. The reflectivity curves have been recorded at different stages of film growth: (a) precursor film PEI/PSS/PAH; (b) PEI/PSS/PAH/Mo$_{57}$; (c) PEI/PSS/PAH/(Mo$_{57}$/PAH); (d) PEI/PSS/PAH/(Mo$_{57}$/PAH)$_6$. Individual curves are shifted in the $y$-axis direction for clarity.