

Layer-by-Layer Assembly of Intercalation Compounds and Heterostructures on Surfaces: Toward Molecular "Beaker" Epitaxy

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Chemically modified surfaces are rationally prepared in order to manifest special properties, such as vectorial electron transfer,¹ optical second harmonic generation,² selective small-molecule sensing,³ controlled wettability or tribology,⁴ and photoreactivity.⁵ The spatial orientation and separation of the molecular components of these surface films are usually critical to the realization of these supramolecular effects. While the growth of self-assembling organic monolayers on surfaces is now a well-understood process,⁶ the desired chemistry often requires construction in the *third* dimension as well, and routes to well-ordered multilayer films are less highly developed. Several different strategies for linking self-assembling monolayers into multilayers have been described, including covalent,⁷ ionic-covalent,⁸ coordinate covalent,⁹ and hydrogen bonding.¹⁰ Recently a technique based on the alternate adsorption of oppositely charged poly-

electrolytes has been explored by Decher¹¹ and others.¹² While this method is a simple and general one for preparing surface multilayer films, it suffers from the inevitability of layer interpenetration and some variability of interlayer distances. We communicate here the extension of this technique to sequential layering of structurally well-defined, two-dimensional colloidal polyanions with a variety of oligomeric and polymeric cations. This technique eliminates interlayer penetration and ensures a constant and predictable interlayer distance, while retaining the ease and generality of the polyelectrolyte adsorption process.

The acidic protons of α -Zr(HPO₄)₂ (α -ZrP) can be partially exchanged with tetra-*n*-butylammonium (TBA⁺) by reaction with TBA⁺OH⁻. Sufficient amounts of TBA⁺ can be intercalated to cause complete exfoliation, and single, separate layers can be suspended indefinitely in water. When the suspension is placed in contact with a protonated amine-modified surface, surface NH₃⁺ groups displace the TBA⁺ on one side of the inorganic layers, electrostatically anchoring them to the surface. Virtually any cation can then bind to the surface by replacing the loosely held TBA⁺ cations that remain on the other side of the α -ZrP layer. For this purpose polymeric or oligomeric cations, such as poly(allylamine) hydrochloride (PAH), Al₁₃O₄(OH)₁₂(H₂O)₂₄⁷⁺ (Al₁₃⁷⁺), and cytochrome (cyt *c*), were used. The sequence of layer deposition steps is shown schematically in Figure 1.¹³

For α -ZrP/polycation films, ellipsometric measurements following each α -ZrP adsorption step (Figure 1) show directly the linear growth of the film.¹⁴ With PAH, the layer pair thickness is 13 Å, as expected from the 7.6 Å layer spacing of α -ZrP¹⁵ plus 5 Å from a single uncoiled PAH layer.¹¹ Layer pair thicknesses of 16 and 31 Å for α -ZrP interleaved with Al₁₃⁷⁺ and cyt *c*, respectively, are nicely consistent with the crystallographic diameters of these oligocations.¹⁶ Films prepared in this way are optically transparent. The calculated thicknesses assume a film refractive index of 1.54 and a close-packed layer of anionic sheets

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(13) Polished (100) Si wafers were sonicated in CCl₄ for 15 min and then rinsed with 2-isopropanol and water. They were then sonicated in a hot solution of H₂SO₄ and H₂O₂ (2:1) for 30 min and rinsed with copious amounts of water, then methanol, and finally 1:1 methanol/toluene before the derivatization steps were begun. Au substrates were prepared as described previously.^{8f} Substrates were incubated in 5 wt % solutions of the appropriate anchoring agent (4-((dimethylmethoxy)silyl)butylamine for Si and quartz, 2-mercaptoethylamine for Au) for ca. 15 h in dry Ar over KOH, after which the surfaces became hydrophobic. Microcrystalline zirconium phosphate (α -ZrP, 0.7 mequiv/L) (Alberti, G.; Torracca, E. *J. Inorg. Nucl. Chem.* **1968**, *30*, 317) was exfoliated by titration with 0.5 M TBA⁺OH⁻ to a constant pH of 8.5. Aqueous solutions (0.01 M) of PAH (Aldrich, MW = 50 000–65 000), Al₁₃O₄(OH)₁₂(H₂O)₂₄⁷⁺ (prepared by reaction of the sulfate salt with aqueous BaCl₂), and cyt *c* were adjusted to pH 7 with TBA⁺OH⁻. Layer adsorption times were typically 15 min; substrates were washed with flowing water between adsorption steps.

(14) Ellipsometry data were acquired with a Gaetner model L2W26D ellipsometer using HeNe laser (632 nm) light. The incident angle was 70°, and the polarizer was set at 45°. Typically, thicknesses of 5–7 spots per substrate were recorded and the results were averaged. Individual measurements taken at different spots varied by ca. 5 Å.

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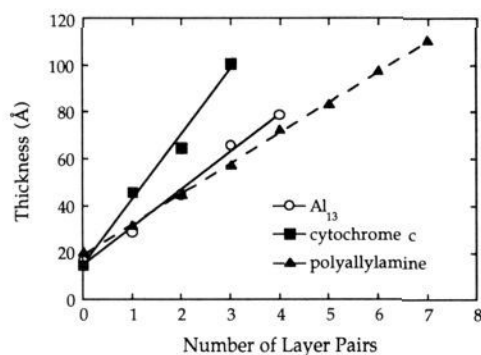
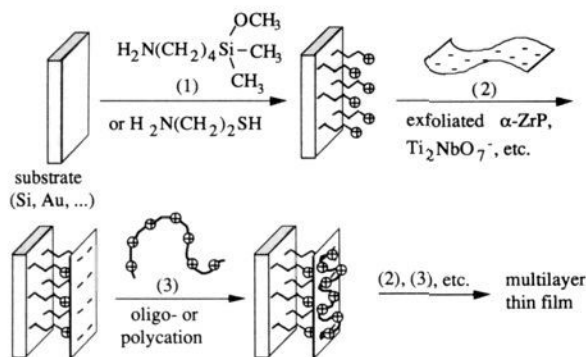


Figure 1. Top: Sequential adsorption scheme for producing multilayer films by alternate adsorption of inorganic two-dimensional anions and oligomeric or polymeric cations. Bottom: Ellipsometric data for α -ZrP/PAH, α -ZrP/cyt *c*, and α -ZrP/ Al_{13}^{7+} multilayer films on Si. Thickness was measured after the α -ZrP adsorption step. Lines represent best fits to the data and give layer pair thicknesses of 13, 31, and 16 Å, respectively. The thickness for zero layers corresponds to the amine anchoring agent and native oxide layer on the Si substrates.

making up the layer. The true refractive indices are unknown, as are the lateral packing and degree of overlap of the individual anionic sheets. We are currently exploring other techniques (X-ray reflectometry, atomic force microscopy) in order to obtain a more complete picture of film morphology.

IR reflection-absorption and UV-visible absorbance data were collected from films grown on Au and quartz, respectively. For nine α -ZrP/PAH layer pairs, the IR absorbance in the P-O stretching region at 1140 cm^{-1} was linear with layer number. The Soret band absorbance of cytochrome *c* in the visible region (410 nm) also increased linearly for α -ZrP/cyt *c* multilayers, confirming the stepwise growth of the films. SEM photographs of a single α -ZrP layer grown on Au were featureless at ca. 200 Å resolution, apart from widely separated micron-size particles on the surface, which were either dust or incompletely exfoliated α -ZrP agglomerates.

Layered metal oxide semiconductors (LMOS) such as $\text{K}_2\text{Nb}_6\text{O}_{17}$ and $\text{CsTi}_2\text{NbO}_7$ can be acid-exchanged and exfoliated with TBA^+OH^- in much the same way as α -ZrP.¹⁷ The hexaniobate is an interesting case, in that there are two distinct interstitial sites for K^+ , resulting in the alternation of two chemically different interlayer regions.¹⁸ Only one of these interlayers can be proton-exchanged under mildly acidic conditions; when exfoliated, the compound exists as two niobate sheets

(17) Exfoliation of layered perovskite-type alkali niobates to form single sheets has been reported previously: Treacy M. M. J.; Rice, S. B.; Jacobson, A. J.; Lewandowski, J. T. *Chem. Mater.* **1990**, *2*, 279.

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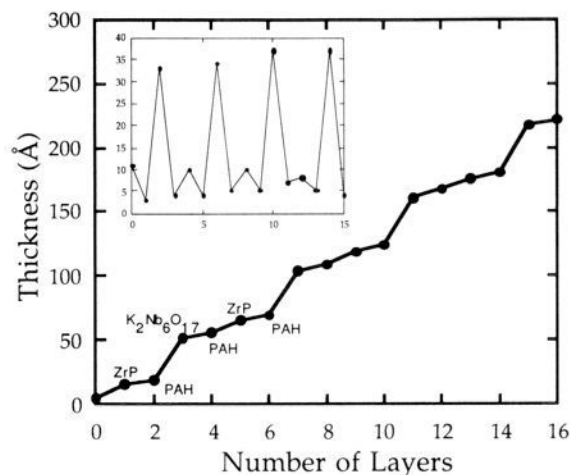


Figure 2. Ellipsometric data for the α -ZrP/PAH/ $\text{K}_2\text{Nb}_6\text{O}_{17}^{2-}$ /PAH heterostructure. Layer thicknesses were calculated using a film refractive index of 1.54. The inset shows the first derivative of the thickness for each adsorption step. Small and large peaks in the inset correspond to α -ZrP and $\text{K}_2\text{Nb}_6\text{O}_{17}^{2-}$ adsorption steps, respectively; points in between are PAH adsorption.

sandwiching a layer of K^+ . Indeed in the LMOS/PAH systems, a thickness of 26 Å is measured for $\text{K}_2\text{Nb}_6\text{O}_{17}^{2-}$, consistent with the deposition of niobate- K^+ -niobate sandwiches. A value of 16 Å (consistent with single layer deposition) is found for $\text{Ti}_2\text{NbO}_7^-$.

The reliance on purely electrostatic interaction to initiate layer-by-layer growth allows for the creation of heterostructures in which anions and cations can be deposited in any order, without manipulation of functional groups on either the polyionic species or the substrate. We have made four-layer structures with alternating anionic sheets of the form α -ZrP/PAH/ $\text{K}_2\text{Nb}_6\text{O}_{17}^{2-}$ /PAH, as well as alternating polycations, α -ZrP/ Al_{13}^{7+} / α -ZrP/PAH. The layer growth followed by ellipsometry for the former structure is shown in Figure 2. The superstructure formation (thick layer is LMOS) is clearly seen in the inset, where the derivative of the layer thickness is plotted versus the number of layers. The cation heterostructure behaved similarly.

These results confirm that electrostatic attractions can be used to construct multilayer films that can be described as surface analogs of intercalation compounds. This technique is a rapid and experimentally very simple way to produce complex layered structures with precise control of layer composition and thickness. Its potential utility comes from the fact that specific functionality of the film components is not needed; the chemical behavior/reactivity of PAH, Al_{13}^{7+} , and cyt *c* are quite varied, yet each makes well-ordered multilayer films via this method. The technique is also self-regulating. Each immersion step can only produce one layer of polyanion or -cation, because the like charges of additional adsorbing species are repelled from the surface. The deposition process allows for excellent spatial segregation of the individual components in layers, and this property should prove valuable in the preparation of multicomponent systems for energy and/or electron transfer reactions, as well as for other purposes.¹⁹

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(19) Note Added in Proof: Layering of clay platelets by essentially the same technique as that described here has recently been reported (Kleinfield, E. R.; Ferguson, G. S. *Science* **1994**, *265*, 370).