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Polymer Multilayers

Erasable Coordination Polymer Multilayers on Gold**

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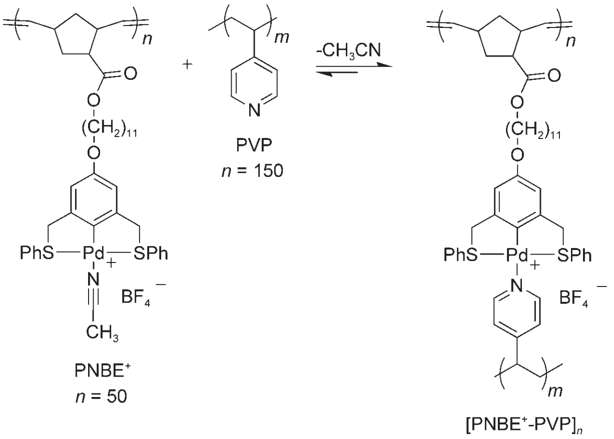
Herein we report the use of reversible coordination chemistry to assemble polymer multilayers on gold surfaces. Such multilayers have potential applications ranging from drug delivery to electro-optics. Our system 1) provides for uniform film deposition and control of multilayer thickness, 2) allows for the integration of diverse polymer components embedded in alternating polymer bilayers, 3) can potentially be employed on a wide variety of surfaces, and 4) affords stable yet responsive multilayers that can be manipulated by chemical means using coordination chemistry.

Current methods to assemble multilayers on surfaces rely predominantly on the layer-by-layer deposition of polycations and polyanions to produce polyelectrolyte multilayers (PEMs).[1–3] While PEMs have been successfully applied to a variety of applications,[4] their long-term stability as well as stability toward heat and other solution conditions, such as changes in salt concentrations or even mild changes in the pH value, is limited.[5] To overcome these shortcomings, several groups have explored the use of covalently bound multilayers[6] as a robust alternative to PEMs for use in organic light-emitting diodes (OLEDs),[7] etch-resistant materials,[8a] dielectrics,[8a] and as feature replicants.[8b] Covalently bound multilayers offer additional stability toward heat, solvent changes, pH value, and other solution conditions, but the responsiveness afforded by PEMs is largely sacrificed.

A significantly less studied area is the use of metal–ligand interactions to integrate components within polymer multilayer thin films with the goal of enhancing stability and adding functionality.[9] Metal–ligand-assisted lateral film growth has been achieved through ruthenium–pyridine complexation,[10a] while iron–bipyridine complexes have been laterally integrated between poly(styrene sulfonate) and poly(ethylene imine) multilayers.[10b] Polyelectrolyte assembly has also been assisted by intermittent integration of metal cations, namely the Cu^{2+} ion, allowing for the reductive formation of polymer–Cu nanocomposites.[11] Similarly, polyoxometalate nanoclusters have been integrated between polycations within multilayered thin films.[12] Polymer multilayers with embedded metal complexes have also been employed in biological applications.[13] Much like covalent multilayers, metal-coordination multilayers tend to increase multilayer stability while sacrificing responsiveness. A methodology that allows for the formation of metal-coordination multilayers that are stable and that can be formed fully reversibly has not been demonstrated.

Our system combines the advantages offered by covalent multilayers, traditional metal-bound multilayers, and PEMs by using strong yet reversible noncovalent[14] metal–ligand interactions to create a new class of coordination polymer multilayers (CoPMs). The method is based on the coordination of weak bases to palladium complexes to create stable yet responsive CoPMs. We utilize Pd^{II} pincer-type complexes[15] because of their association strength[16] and inertness toward a variety of functionalities,[14c] including polar, nonpolar, charged, and even acidic groups. Furthermore, Pd^{II} pincer complexes are tolerant toward many reaction conditions, including organometallic reactions,[17] yet responsive toward stronger coordinating ligands. In our study, the Pd^{II} pincer complexes are supported on poly(norbornene) derivatives, $PNBE^+$ ($M_w = 30\,000$). The acetonitrile ligand coordinated to the Pd^{II} pincer complexes along the $PNBE^+$ can be displaced quantitatively by pyridine (Scheme 1).[18] Therefore, we employed commercially available poly(vinyl pyridine) (PVP, $M_w = 20\,000$) as the complementary macroligand.

Upon exposure of a 4-mercaptopyridine-functionalized gold substrate to $PNBE^+$, the acetonitrile ligands on the Pd^{II} pincer complexes along the $PNBE^+$ backbone are quantitatively and instantaneously displaced by surface pyridine units,



Scheme 1. Pincer-type coordination of $PNBE^+$ and PVP to yield $[PNBE^+\text{-}PVP]_n$ coordination multilayers.

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thus forming a polyvalent prelayer upon which multilayers can be built. CoPM buildup then proceeds by simple alternation of PVP and PNBE$^+$ solution treatments (Scheme 2). Using this simple methodology, we can fabricate CoPMs with up to 25 bilayers in less than three hours.

Scheme 2. Representation of CoPM buildup on gold. This cycle was repeated until the desired bilayer number was reached.

Multilayer buildup was monitored by UV/Vis absorption spectroscopy. As buildup progressed, the intensity of the absorption band attributable to the π–π* transition of both PNBE$^+$ and PVP ($\lambda_{max} = 254$ nm) increased linearly with bilayer number (Figure 1 A). Grazing-angle FTIR experiments also demonstrated peak intensity increases upon bilayer buildup (see the Supporting Information). X-ray photoelectron spectroscopy (XPS) further confirmed the presence of N, S, and Pd in our CoPMs (see the Supporting Information).

Surface heights were measured using ellipsometry and AFM. Ellipsometry data indicate an average layer thickness of 28 nm and an average bilayer thickness of 58 nm. Linear trends between surface height and layer number were observed (Figure 2). Heights determined by ellipsometry for the eight- and sixteen-layer films were 200 ± 19 nm and 520 ± 50 nm, respectively. These values corresponded well with height values measured by AFM of 230 ± 24 nm and 450 ± 32 nm for the eight- and sixteen-layer films, respectively. The observed heights for the multilayers formed from 10 mM deposition solutions are thicker than expected. On the basis of molecular mechanics energy-minimized decamer models of PNBE$^+$ and PVP (see the Supporting Information), we predict multilayers[19] that are one polymer strand thick to have bilayer thicknesses of about 7 nm.

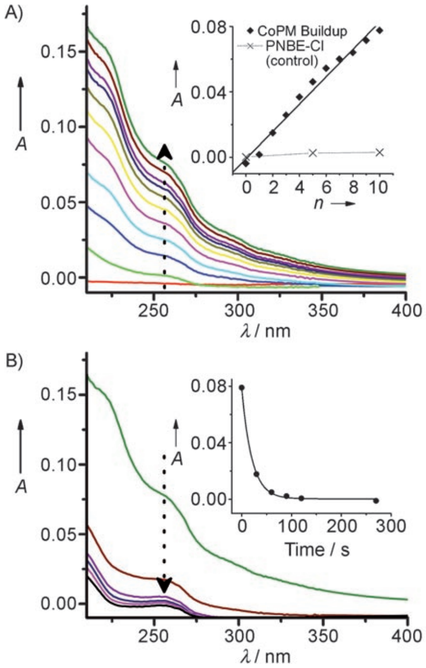

Figure 1. A) UV/Vis absorption spectra for CoPM buildup taken at every bilayer of [PNBE$^+$-PVP]$_n$ on a 20-nm Au layer deposited on quartz. The inset plot displays absorbance intensity at 254 nm vs. deposition cycle ($R^2 = 0.98$, where R is the correlation coefficient) and a corresponding control experiment to rule out nonspecific adsorption, in which unactivated PNBE-Cl was used in place of PNBE$^+$ as the deposition polymer. B) UV/Vis absorption spectra taken over time for CoPM breakdown upon exposure to PPh_3. The inset plot displays absorbance intensity at 254 nm vs. time.

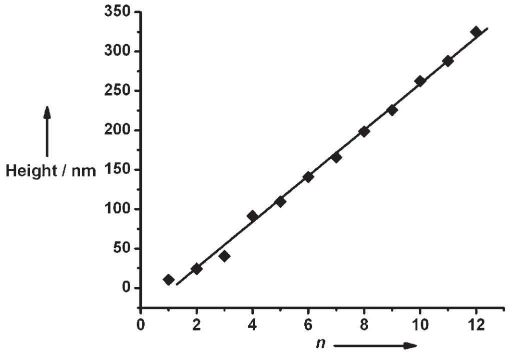

Figure 2. Surface heights determined by spectroscopic ellipsometry ($R^2 = 0.997$).

These models, however, are just rough predictions and do not take into account polymer folding and swelling. In reality, we suggest that several factors contribute to the observed thicknesses. First, PEMs are often very thin, owing to counterion expulsion upon multilayer buildup resulting in greater multilayer packing through a process known as intrinsic compensation.[20b] We would not expect the counterion of PNBE$^+$ to be expelled during the deposition process; the counterion in the multilayer can contribute to swelling through "extrinsic compensation".[20b] Second, the effects of electrostatic repulsion and charge compensation are often cited as reasons why PEMs are so thin.[20b] Since our deposition is not purely electrostatic, we would not expect our polymers to spread out as flat as PEMs. Third, we suspect that since our individual polymer recognition units have such high association strengths, entangled polymers are getting "dragged" to the surface. This should largely be an effect of the deposition concentration. To test this hypothesis, we deposited an eight-layer film at 5 mM and 1 mM concentrations, rather than 10 mM, since we reasoned that a lower concentration would reduce polymer entanglement. The height of the film deposited at 5 mM (Figure 3 C) was measured by AFM to be 130 ± 9.9 nm, a height about half that of the eight-layer film deposited at 10 mM (Figure 3 D). In contrast, the height of the film deposited at 1 mM was found to be 60 ± 7.6 nm (Figure 3 B). We observed increases in surface roughness (RMS) as the deposition concentration increases. RMS roughness measurements were found to be 7.5, 9.7, and 23.4 nm for films deposited at 1, 5, and 10 mM

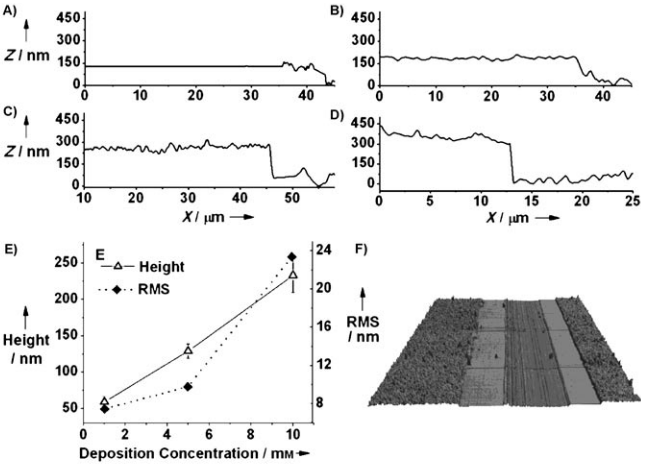

Figure 3. A)–D) Section-line height profiles of scratched CoPMs $[PNBE^+\text{-}PVP]_8$ on A) gold-plated slides for multilayers deposited at B) 1 mM, C) 5 mM, and D) 10 mM concentrations. E) Corresponding surface heights and root-mean-square (RMS) roughness measurements for the films deposited at 1 mM, 5 mM, and 10 mM. F) Example AFM image taken in air of a scratched $[PNBE^+\text{-}PVP]_8$ CoPM ($x = y = 90$ µm; $z = 4$ µm); rougher area is polymer; smooth areas are scratch edges defining center of scratch (deeper portion).

(Figure 3E), respectively. While we suspect polymer entanglement to be a source of the observed deposition concentration effect,[21] other concentration and kinetic effects might also be contributing to the observed results and cannot be excluded. Nevertheless, these results demonstrate that we are able to modulate film thicknesses in a controlled manner by merely varying the deposition concentration of the polymer solutions.

Nonspecific adsorption between the polymer and the surface was ruled out on the basis of a control experiment in which we employed unactivated PNBE instead of $PNBE^+$, in which a chlorido ligand replaced the more labile acetonitrile ligand. After fifteen deposition cycles, no absorbance was observed, thus demonstrating that little or no polymer was adsorbed to the gold surface. We also investigated the stability of the multilayers to solvent changes, temperature in solution and the solid state as well as salts. Our films were stable toward EtOH, THF, and DMF for short rinsing periods. To further test the stability of our CoPMs toward solvent etching, we placed an eight-layer CoPM in a Soxhlet extractor with DMF and monitored the etching progress over time. The CoPM was completely etched in three days. We attribute the film degradation to both solubility of the multilayers in DMF and decomposition of the metal complex at 153 °C in solution. Noteworthy, however, is that these CoPMs are far more stable than most PEMs towards polar solvents. Some of the most commonly used and stable PEMs based on poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) or poly(styrene sulfonate) (PSS) are etched almost completely after 1 hr of DMF exposure at room temperature.[21] Furthermore, no significant etching was observed after oven heating the surfaces to 140 °C for two weeks and subsequently washing with $CHCl_3$ before analysis using UV/Vis spectroscopy. The observed thermal stability is orders of magnitude greater than that of most PEMs, such as PAH-PSS or PAH-PAA, which typically either degrade or undergo crosslinking at these temperatures.[20] To test the stability of our CoPM functionalized surfaces toward salt exchange, we placed the CoPM in a $CHCl_3$ solution of AgOTf. No etching was observed by UV/Vis spectroscopy. However, if the CoPMs are exposed to excess NaCl, the metal complexation is reversed, resulting effectively in etching of the multilayers. We view this property as an advantage, since a similar responsiveness to NaCl has recently been used to spatially pattern PEMs through controlled etching in a top-down approach.[22] We intend to investigate the possibility of controlled etching of our multilayers to produce patterned surfaces using NaCl solutions.

Finally, we investigated the ability to etch our CoPMs chemoresponsively using competing ligands. Upon exposure of a multilayer to a 10 mM solution of PPh_3, a stronger base and a tighter coordinating ligand for the Pd^{II} complexes along $PNBE^+$, the absorbance intensity decreased dramatically within a few minutes (Figure 1B), thus demonstrating the removal of our multilayers and suggesting another possible trigger mechanism for top-down patterning.[22]

In summary, we have demonstrated that coordination chemistry between polymer-supported palladium complexes and polymeric bases can be used to assemble CoPMs. The CoPMs produced in this fashion rival the stability of covalent multilayers in the solid state and most organic solvents, while retaining the responsiveness of PEMs, thus adding a new surface functionalization method with unique properties to surface scientists' "toolbox". These appealing characteristics of our system make CoPMs desirable for a variety of applications, specifically, as materials in optical devices, delivery systems, catalytic systems, and templated[23] synthesis. Applying CoPMs toward these applications will be investigated.

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