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Growth, Conductivity, and Vapor Response Properties of Metal Ion-Carboxylate linked Nanoparticle Films

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PROPERTIES OF METAL-CARBOXYLATE LINKED NANOPARTICLES FILMS: GROWTH DYNAMICS, LOADING EFFECTS, AND METAL DEPENDENCE

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ABSTRACT

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INTRODUCTION

There is continuing and persistent interest in understanding the electronic, optical, chemical, and physical properties of nanoscale materials for the purposes of fundamental study and potential application in nanotechnology.[Ref] As part of this research effort, there has been substantial progress in studying the fundamental properties of metallic nanoparticles, a material that bridges the gap between bulk and molecular behavior.[Ref] Of equal interest, is the synthesis and assembly of networks of nanoparticles, as they have potential use in the sensing and nanoelectronics fields.

Due to their superior stability and ease of handling, passivated gold nanoparticles, protected by a surrounding monolayer of alkanethiolate ligands, have received much attention and have been designated monolayer protected clusters (MPCs).[Ref] MPCs are generated via a relatively simple two-phase synthesis[Ref] that yields a polydisperse product with an *average* composition, an example being the 28 kDa $Au_{140}C6_{53}$ nanoparticles (average diameter 1.6 ± 0.8 nm) used for this study. MPCs are easily "functionalized" via place-exchange reactions with free carboxylic acid-terminated alkanethiols (e.g., mercapotundecanoic acid or MUA), a process yielding nanoparticles with mixed-monolayers surrounding the gold core. The successful exchange of carboxylic acids into the peripheral skin of these MPCs has lead to the formation of networked MPC films, where neighboring MPCs are linked together via carboxylate-metal-carboxylate bridges, as previously described.[Ref]

Some of the electronic and physical properties of assembled MPC films have been examined, including evaluation of electron transfer (ET) dynamics through the film[R] and the dependence of ET on the composition mixed monolayer surrounding the nanoparticles.[R] From this work, ET through MPC films appears to occur through a self-exchange "hopping" mechanism at an extremely fast rate (i.e., XXXXXXX)[R] and is sensitive to the chainlengths of alkanethiolates comprising the surrounding monolayer, with the primary ET pathway occurring through the non-linking alkanethiolate contacts of the MPCs rather than through the lengthier carboxylic acid terminated linking ligands.[R] In a more application-based capacity, metal-carboxylate linked films of this nature have been used as a precursor to the formation of thin metal films[R] and, most recently, as promising chemiresistive sensing materials.[R,R]

This report further examines several important properties of metal-carboxylate linked nanoparticle films including (1) the structural and functional dependence of the films on the metal ion used to bridge the nanoparticles; (2) the dynamics of film growth and; (3) the role of "loading", the number of carboxylic acid functional groups on each MPC, in the physical and electronic properties of the films. We report here spectroscopic and conductive measurements that suggest a substantial linking metal dependence in the growth, structure, and behavior of networked MPC films. With the simple employment of different bridging metals, films seem to be grown either in a "collapsed" or "expanded" state suggestive that the cores may be in closer proximity with certain metal linkers. The dynamics of film growth are also investigated with different metal linkers, as is the effect of efficient mass transport – clearly beneficial toward faster and effective film formation, not surprisingly. Different loadings of carboxylic acid ligands on the MPCs have little effect on the conductivity of the MPC material, although MPCs with larger loadings form networked film faster and are the primary components of MPC films. Examining MPC film properties of this nature allows for a greater understanding of nanoparticle films for both fundamental and application based research. Other researchers have used networked films of nanoparticles for very specific and narrow studies, but few have probed the fundamental details of film growth and structure that complement such investigations.

EXPERIMENTAL SECTION

Chemicals. All chemicals were reagent grade and used as received.

Synthesis and preparation of mixed monolayer MPCs. Hexanethiolate (C6) capped monolayer-protected clusters (MPCs) wre prepared using a modified Brust reaction, as previously described.[R,R] Briefly, hexanethiol was combined in a 3:1 ratio with $AuCl_4^-$ in toluene to form a Au(I) polymer/alkanethiolate complex which was then treated with an excess of reducing agent ($NaBH_4$) for 18 hours at 0° C. The product from this reaction is was isolated via precipitation/filtration on a medium porosity glass fritted funnel where it was thoroughly washed with several hundred milliliters of acetonitrile. C6 MPC derived from this synthesis was subsequently characterized with tranmission electron microscopy and thermal gravimetric analysis to have, *on average*, a core diameter of 1.6 ± 0.8 nm and a composition of $Au_{140}(C6)_{53}$, respectively.[R,R] It should be noted that these values are *averages* due to the significant distribution of core sizes persistent in MPC samples.

"Functionalization" of MPCs with mixed monolayers of C6 and mercaptoundecanoic acid (MUA) is accomplished via place-exchange reactions where already formed C6 MPC are stirred with a selected amount of MUA for approximately 3-4 days. Adjustment of the exchange reaction stoichiometry and stir time allows for formation MPCs with an average formula of $Au_{140}(C6)_{53-n}(MUA)_n$. The actual composition of the mixed monolayer is determined by NMR of the disulfide solution liberated upon decomposition of the MPCs with iodine.[R]

MPC Film Formation and Growth. MPC films were assembled on gold, glass, and interdigitated array (IDA) electrodes by taking advantage of carboxylic acid - metal ion - carboxylic acid bridges between adjacent MPCs as previously described.[R] Procedures varied slightly depending on the substrate used and on the experiments at hand. Typical procedures for anchoring MPCs to the different substrates are described below and relevant variations to the film growth procedures are emphasized within the discussion of each set results.

Glass Substrates. MPC films were grown on glass for optical measurements. Typically, glass slides were cleaned by immersion in "piranha" solution (H_2SO_4/ 30% H_2O_2 in a 4:1 ratio) for 15 minutes. WARNING: Piranha solution reacts violently with organic compounds, use extreme caution when handling this material. Clean glass slides were than silanized in a heated propanol/H_2O solution of 3-mercaptopropyltrimethoxysilane (3-MPTMS) for 30 minutes followed by thermal curing for 30 minutes. To begin film growth, silanzed glass was placed in a 0.1-0.2 M ethanolic solution of a metal salt (e.g., $Cu(ClO_4)_2$, $AgCF_3CO_2$, $AgCF_3SO_3$, $PdCl_2$, $FeCl_2$, $Zn(NO_3)_2$) for 30 minutes, rinsed with ethanol, and immediately immersed in a ethanolic solution of C6/MUA MPC (~ 2 mgs/mL) for an additional 30 minutes. Exposure of the substrate to the metal ion solution immediately followed by immersion in the MPC solution constitutes a "dip cycle" that can be repeated successively to build-up a thick film of MPC. Films, in general, were grown until a target absorbance (Abs) of 1.0 ± 0.2 a.u. at 300 nm was achieved.

Gold. MPC films were also grown on gold quartz crystal microbalance (QCM) substrates in a similar manner. Clean gold QCM substrates (piranha cleaned) were first modified with an initial MUA self-assembled monolayer (SAM) by immersing the substrate in a 2mM MUA solution (ethanol) for 15 minutes. SAM-modified gold was than subjected to the same "dipping cycles" as described above.

IDA Electrodes. IDAs consisted of closely spaced gold fingers which act as parallel plate electrodes facing each other across a space gap. These same IDAs have been used previously[R] for conductivity measurements of assembled MPC films and their use in that capacity is continued here. Because they are comprised of both glass and gold surfaces, both of the anchoring procedures, silanization and SAM modification, repectively, were used to tether the initial layer of MPC to the IDAs. The modification procedure for IDAs has been described in detail in prior work.[R]

UV-Visible Spectroscopy. As in prior work with MPC films, spectroscopic measurements were performed on C6/MUA MPC films grown on glass using a UV-Vis spectrometer (ATI – Unicam), typically scanned from 300 to 800 nm.

Conductivity Measurements and Current-Based Vapor Response. Electronic conductivity of MPC films on IDAs were determined from the slope of current-potential responses generated by potentiostat (EG&G – PAR Model 273) controlled potential sweeps at 100 mV/sec. Current-based responses of the MPC films to ethanol and dichloromethane vapor were accomplished by testing conductivity of the MPC films (IDA) in a sealed flow cell where the partial pressure of the vapor could be controlled. The same flow cell has been employed previously.[R,R]

Quartz Crystal Microbalance Measurements. QCM techniques were used to evaluate vapor (dichloromethane, ethanol) sorption into the assembled film. QCM crystals (Maxtek, Inc., polished 5 MHz AT cut crystals, 1.13 cm^2) were mounted in the same flow system used for conductivity measurements and were alternately exposed to various partial pressures of solvent vapor and pure nitrogen. QCM frequency changes were measured using a home-built instrument and a HP 53131A Universal Counter interfaced to a PC with Labview 4.0 software. The Sauerbrey equation with integral sensitivity, C_F = 56.6 Hz cm2 μg-1, was used to relate frequency changes[R] to mass changes.

RESULTS AND DISCUSSION

Film Growth Dynamics. The growth dynamics of metal carboxylate-linked MPC films on glass were examined using UV-Vis spectroscopy. As described in the experimental section of this report, dip cycles were used to assemble multi-layer MPC films on glass slides. In similar fashion as prior reports,[R] each dip cycle increases the absorbance of the MPC film (shown graphically in Figure 1A). The effect of using a stirred MPC solution during that part of the dipping sequence was examined. Figure 1B illustrates that stirred MPC deposition solutions result in more effective film growth, especially for thicker films after initial layer of MPC have already been assembled on the surface (i.e., dipping cycles 3 and 4).

Figure 1C also shows that there is a substantial difference in growth dynamics using stirred and unstirred MPC solutions. In these results, the substrate is immersed in either a stirred (open circles) or quiet (closed circles) MPC solution during that phase of dipping and the absorbance of the film is monitored over time. Overall, the film exposed to stirred MPC solutions grow at a faster rate than those immersed in unstirred solutions. Film growth in both, however, appears to level off over time and, in some cases, displays a slight degradation of film thickness (decrease in the monitored absorbance). When growth ceased, the film was exposed to a fresh solution of Cu^{2+}, which subsequently causes a significant increase in film growth upon being placed back in the stirred MPC solutions. The same increases in film growth were not observed after films in unstirred MPC solutions were also exposed to Cu2+ solutions and returned to unstirred MPC solutions.

These results are not surprising considering the probably importance for film to have efficient mass transport of MPCs to the substrate surface. Furthermore, these results support our current understanding of the mechanism of MPC film growth – the “preconcentration of *mobile* metal ions into the film during dips into metal ion solutions followed by subsequent “leeching” of those ions to form new coordinative metal-carboxylate bridges between film bound MPCs and MPCs in the dipping solution. It follows then that hydrodynamic solutions (stirring) with efficient mass transport would be more effective for film growth. Even though film growth clearly benefits from stirring the MPC solution, films for other studies in this report were grown without stirring for consistency.

Carboxylic Acid Loading Effects. Different amounts of MUA ligands can be place-exchanged into C6 MPCs. The properties of the C6/MUA MPCs and of their films appears to be somewhat dependent on the extent of MUA that has been incorporated into their periphery. Most notably, C6/MUA solubility changes with differing number of MUA ligands. MPC films of this nature are usually grown from ethanolic solutions, but C6/MUA MPCs are relatively insoluble at low loadings of MUA (< ~14 MUA ligands) and at very high MUA loadings (> ~33 MUA ligands).[FN =]

We suspect that the polydispersity of core sizes inherent in initial MPC samples prior to place exchange, as well as the consistency of place exchange from core to core will also have an influence on the solubility of the C6/MUA MPCs, although neither phenomena has been specifically studied at this point.

Figure 2 shows the electronic conductivity (σ_{EL}) of C6/MUA *dropcast* films as a function of MUA ligands exchanged. C6/MUA MPC samples with different numbers of exchanged MUA ligands were cast as thick films onto an IDA electrode from solution and allowed to dry. Only samples that were within the range of ethanol solubility were tested so that the same C6/MUA MPCs could be used to form *assembled* films as well. For the case of the *dropcast* films (shown in Figure 2), σ_{EL} is somewhat consistent over a range of MUA loadings before an abrupt decrease at higher MUA loadings (≥ 30). The exponential-like decrease in σ_{EL} is attributed to the highly exchanged C6/MUA MPCs having a markedly lessened ability to interdigitate, a phenomenon likely to both increase core-to-core spacingand significantly extend electron tunneling distances.[R] This result illustrates that the properties of C6/MUA MPC film will likely be sensitive to the average number of MUA ligands on the MPCs.

The effect of MUA loading on film growth dynamics has also been investigated. In our initial testing, two separate films, one with low-loaded MPC ($Au_{140}C6_{49}MUA_{4}$) and the other with a higher load of MUA ligands ($Au_{140}C6_{35}MUA_{18}$) were grown using Cu^{2+} ions. As before, films were grown on glass while monitoring the changes in absorbance (ABS) over time. Figure 3 shows the results of these experiments where the higher loaded MPC yields a higher rate of growth. This observation is clearly noted when comparing the ABS after dip 6, where the lower loaded MPC film has an ABS of only 0.06 compared to an ABS of 0.27 for the higher loaded MPCs. Note the incremental growth is much more substantial with the higher loaded MPC during the first six dipping cycles.

Further evidence that higher loaded MPCs yield more efficient film growth is observed in the latter dipping cycles of Figure 3 when the MPC solutions used for growing each of the films are switched. The film initially grown with lower loaded MPCs, Figure 3a, experiences an increase in growth after exposure to the $Au_{140}C6_{35}MUA_{18}$ solution (note the sharper slope of the data starting from dip 10). Likewise, the film first grown with higher loaded MPCs, Figure 3b, experiences an attenuation of growth when exposed to only the low loaded MPC dipping solutions (after dip 6). These results strongly suggest that higher loaded MUA MPCs are more favorable for film growth.

Loading effects on film growth and the σ_{EL} of assembled films was examined further with a series of experiments where MPC films of different MUA loadings were grown on both glass slides and IDA electrodes. Again, as illustrated in Figure 4, more effective growth was found to occur with MPCs having a higher fraction of MUA ligands. Surprisingly, however, the σ_{EL} of the films with different MUA loadings varied only slightly (average $\sigma_{EL} = 2.6\ (\pm 0.1_5) \times 10^{-6}$ $\Omega^{-1}cm^{-1}$) with no obvious trend.

Each film made from a specifically loaded MPC solution was disassembled using acetic acid/ethanol solutions and subsequently decomposed with iodine for NMR analysis. From the NMR of the liberated disulfides, it appears that all the MPC films are comprised of higher loadings of MUA, regardless of the loading present in the MPC dipping solutions. The revelation that higher loaded MPCs, at the limit of ethanol solubility, are somehow *selected* for film growth is significant…………

[SECTION WILL HAVE TO BE REVISED PENDING THE RESULTS OF FURTHER EXPERIMENTS – ROBERT DONKERS]

Metal Dependence of MPC Films. It is desirable to identify the range of metal ions capable of coordinating MPCs and the role those metals play in determining the film's structure, growth dynamics, and electron transfer (ET) properties. Films are most commonly grown with both Cu^{2+} and Zn^{2+} ions, but several other ions have been evaluated in terms of forming MPC film as well. The following experiments clearly show that the metal ion used in these films has a substantial impact on the film's growth dynamics and structure.

Figure 5 monitors the growth via absorbance measurements of glass anchored MPC films where linking metal ion has been varied. C6/MUA MPCs used have an average composition of 20-25 MUA ligands. Notice that film growth varies distinctly with the metal ion used. Ag and Cu ions are relatively more effective at coordinating film growth compared to Pd, Fe, and Zn. It should be noted that the addition of KOH to deprotonate surface bound acids sites on the substrate and on the C6/MUA MPCs make Zn ions very potent at forming assembled films.FN = Films grown with Zn yield an absorbance of > 1.0 after only a few 30 minute dip cycles. As seen in Figure 5, however, without KOH film growth with Zn ions is virtually nonexistent.

A substantial difference also exists in the UV-visible spectra of MPC film assembled with different metal ions. Depending on the metal ion used to link the MPCs within the film, a surface plasmon band (SPB) is observed. As shown in Figure 6, films assembled with metal ions of Ag or Fe salts display a SPB at ~ 520 nm whereas films of Cu, Zn, and Pd salts show no SPB. These different spectra seem to indicate that core-to-core spacing within these films may be metal dependent.

Additional metal dependence research continued with a focus on those metal ions that are more effective at film growth (i.e., Zn, Cu, Ag) and exhibit fewer complications.FN=Many metal ions previously used for carboxylate coordination,R including Mg2+, Pb2+, and Hg2+, were tested but suffered from solubility complications that rendered film growth unfeasibly slow. Additionally, film grown with Fe ions were susceptible to auto-oxidation (results not shown), causing Fe(II) oxidation to Fe(III) – the effect of this redox degradation on the film properties is unknown. Film growth and film σ_{EL} was monitored over dipping cycles for film linked with Cu and Ag ions. Even after only the first few dipping cycles, there is a readily observable difference in the two UV-vis spectra for the films (Figure 7a,b). Films coordinated with Ag ions clearly show an obvious and intense SPB that is not evident in the spectra of Cu-linked films. This trend persists throughout the growth of the film to a greater thickness (Figure 7c). These optical measurements again suggest that there are significant differences in the structure (i.e., core-to-core spacing) of the two films depending on the metal ion being used.

Measuring the σ_{EL} of these different films is helpful in addressing the structural hypothesis established in the previous section. The current-voltage curves, shown in Figure 7d, from which σ_{EL} values are derived, clearly show that films made with Ag ions are almost an order of magnitude more conductive than their Zn and Cu counterparts. If core-to-core spacing of MPCs with the film was sufficiently lowered using Ag ions, one would expect films to be more conductive.

An interesting diagnostic that has been used to evaluate the structure of assembled MPC films is to study their response toward exposure to organic vapors.[R] Films assembled with different metal ions (Cu, Ag, Zn) on IDA electrodes, as well as, QCM crystals were placed in a sealed flow cell system where they could be exposed to different partial pressures of organic solvent vapor. Prior work has shown that MPC films of this nature "swell" in the presence of certain vapors, causing a decrease in the film's σ_{EL}, an attenuation of SPB intensity, and an increase in quartz crystal microbalance (QCM) measured mass changes. If indeed the films grown with Ag ions are more compact than those grown with Cu ions, it should be reflected in the extent that each film can swell and partition vapor. Table 1 lists the vapor responses, in terms of percent change in current, of three MPC films grown with Cu, Ag, and Zn ions, respectively. The current change through Ag-linked films, which exhibit an comparatively intense SPB, is markedly less than that for Cu and Zn based MPC films, implying that Ag films swell to a lesser degree than the others.

QCM experiments with the same three films indicate...

[DIMITRA]

Immersion of these films on glass into pure solvents...

CONCLUSIONS

Properties of metal-carboxylate linked MPC films have been investigated including the film's growth dynamics, loading effects, and metal ion dependence. Experimental results reveal that both the number of carboxylate-terminated ligands and the metal linking ion significantly influence the growth of the film. Inferred from these results is the importance of mobile metal cations within the film's network of MPCs for effective film growth. The mobility of the metal ion is affected by several factors identified in this report including, 1) the ion's ability to coordinate with carboxylate groups; 2) its solubility in the ethanolic dipping solution; and 3) the metal's anion component. All of these factors are identified as contributions to metal ion mobility. Likewise, efficient mass transport of MPCs to the substrate is clearly beneficial to growth dynamics.

The metal ion incorporated in the film also seems to impact the overall structure of the assembled film. The results presented indicate that the film's structure can be more "expanded" or "collapsed" depending on whether Cu/Zn or Ag ions are used, respectively. The reasons for the metal ion's dramatic impact on film structure are not presently understood as is the metal ion's specific role in electron transfer (ET) through the MPC films. Advanced studies on this latter topic are currently underway using specifically designed MPCs that direct ET directly through the carboxylate-metal-carboxylate bridges.

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CAPTIONS

Figure 1. (a) UV-Visible spectra of a MPC film ($Au_{140}C6_xMUA_{53-x}$) assembled on glass with carboxylate-metal ion-carboxylate bridges; (b) absorbance monitored over several dip cycles comparing film growth when using stirred and unstirred MPC solutions; (c) comparison of film growth via absorbance over exposure time of the films to both stirred and unstirred MPC dipping solution. Note the absorbance is monitored after new exposure to Cu^{2+} ions as well.

Figure 2. Electronic conductivity (σ_{EL}) as a function of the number of MUA ligands exchanged into the C6 MPCs. Shaded areas of the plot represent loadings of MUA ligands that render the C6/MUA MPCs insoluble in ethanol, the solvent used for dipping solutions. Data for unexchanged C6 MPC (△) is included for comparison. The trend is most likely due to exchange-induced differences in the C6/MUA MPC's ability to interdigitate (see scheme below figure).

Figure 3. Absorbance of assembled MPC film on glass where a film (a) is initially grown in a low-loaded MPC dipping solution ($Au_{140}(C6)_{49}(MUA)_4$) and later switched (*) to a higher loaded MPC dipping solution ($Au_{140}(C6)_{35}(MUA)_{18}$); (b) film initially grown with $Au_{140}(C6)_{35}(MUA)_{18}$ and switched (*) to $Au_{140}(C6)_{49}(MUA)_4$.

Figure 4. Absorbance of C6/MUA MPC assembled films with different number of carboxylic acid terminated ligand loadings.

Figure 5. Growth monitored as a function of absorbance of C6/MUA MPC films (average number of MUA ligands ~ 20-25) grown with a range of different metal ions. Note that 18 hour dipping cycles were used for growing these films.

Figure 6. UV-Visible absorbance spectra for C6/MUA MPC films (average number of MUA ligands ~20-25) grown with different metal ion linkers on glass substrates. Spectra are offset for viewing (absorbance at 300 nm for all films is ~ 1.0).

Figure 7. Absorbance of (a) Cu^{2+} and (b) Ag^{+} linked MPC films during initial stages of film growth (average MUA loading of MPC is 20-25); (c) UV-vis spectra of fully grown MPC films made with Zn^{2+}, Ag^{+}, and Cu^{2+} ions; (d) current-voltage curves for fully grown MPC films linked with Zn^{2+}, Ag^{+}, and Cu^{2+} ions.