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Dan Sheibley

Renee Szymanik

Michael C. Leopold

University of Richmond, mleopold@richmond.edu

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Ultra-fast formation of stable nanoparticle film assemblies

Dan Sheibley, Renee Szymanik, and Michael C. Leopold*

*Department of Chemistry, Gottwald Science Center, University of Richmond**Richmond, VA 23173, USA. Email: mleopold@richmond.edu***Abstract**

Novel assembled films of monolayer-protected clusters (MPCs) can be grown on gold and glass substrates with a 20-fold higher efficiency than established procedures. Thick MPC films grown using this innovative method, which can easily be scaled up or automated, are extremely stable and have properties identical to traditionally formed nanoparticle films.

Keywords: metallic nanoparticle, monolayer-protected cluster (MPC), assembled films, nanotechnology, organized molecular architectures, nanomaterials, vapor sensors

Of all the interesting materials emerging from the field of nanotechnology, metallic nanoparticles continue to attract immense research attention.¹ Nanoparticles, congregates of metal atoms possessing intriguing size-dependent properties, are unique in that they have both bulk and molecular metal characteristics.¹ Nanoparticle research continues to focus on the nanoparticles themselves but has also recently expanded to exploring organized assemblies of nanoparticles on surfaces.²⁻³ Highly ordered, nanoparticle architectures of this nature have important implications as

innovative sensory materials and for fundamental electron transfer (ET) study relevant to nanoelectronics.²⁻³

Colloidal gold nanoparticles passivated with a layer of alkanethiolate ligands, known as monolayer-protected clusters (MPCs),⁴ are particularly stable, easy to handle, and can be readily isolated or redissolved in solution without aggregation. MPCs can be characterized by several analytical methods, including spectroscopy, electrochemistry, and microscopy.^{4,5} Several reports have examined the properties and behaviors of thin films of MPC cast from a solution onto a substrate, known as “drop cast” films.⁶ MPCs can also be functionalized via simple place-exchange reactions⁷ which introduce ligands with terminal functional groups extending out from the peripheral alkane layer surrounding the gold core. The “functionalization” of MPCs has prompted the exploration of assembled films of MPCs.⁶ Murray and coworkers have been very successful in creating networked films where carboxylic acid-modified MPCs are linked to each other and tethered to a substrate via carboxylic acid-metal ion (M^{n+})-carboxylic acid electrostatic bridges.⁸⁻¹⁰ These novel multilayer films have shown excellent promise for electron transfer (ET) studies¹⁰ and chemical sensing applications¹¹⁻¹² and are the subject of this report.

In spite of the excellent preliminary work investigating thin films of MPCs,⁸⁻¹³ problems with the assembly process itself have hampered progress. The aforementioned dropcast films usually lack defined structure and suffer from poor adhesion to a substrate.⁶ Both of these properties limit the usefulness of drop cast

MPC films, especially as chemical sensors in certain environments (i.e., liquids).⁶ Likewise, assembled MPC films, while much more stable, are very tedious and time consuming to construct.⁸⁻¹³ For certain applications requiring thicker films on substrates, including ET studies,¹⁰ conductivity measurements,¹¹ chemical vapor sensors,¹¹⁻¹² or use as a precursor to thin gold films,¹³ several days of preparation are required.

Established procedures⁸⁻¹³ for assembling MPC films revolve around the repeated and prolonged exposure of a modified substrate (e.g., silanized glass or ω -substituted alkanethiol-modified gold) to alternating solutions of the metal ion and carboxylic acid-functionalized MPC solutions, successively for 45 minutes to 1 hour each time.⁸⁻¹³ Carboxylic acid exchanged MPCs are anchored to modified substrates and networked into multilayer films through carboxylic acid – metal ion – carboxylic acid linkages (see Fig. abstract). Each time the substrate is successively exposed to these two solutions, known as a “dipping” cycle, multi-layers of MPC are subsequently assembled on the surface over the course of approximately two hours. Formation of multiple monolayers of MPC during a single dip cycle has been explained through a mechanism where, after metal exposure, films retain a reservoir of weakly coordinated, non-bridging metal ions that can migrate to the surface of the film to participate in the linking of new MPCs. This mechanism is proposed to be very slow, thus requiring the extended exposure times to allow for metal ion

migration into and out of the existing film structure as well as the mass transport of the relatively large nanoparticles to the surface.^{8,12,13}

For certain applications where MPC films are required to be extremely thick traditional procedures of assembly (described above) can require approximately ten dipping cycles in excess of 20 hours of growth.¹⁰⁻¹³ Factoring in time for analytical monitoring of the film formation and growth, the procedures can take several days, a substantial barrier to research progress.

We have modified established protocols by Murray et al.⁸⁻¹³ to substantially increase the efficiency of growing thick MPC assembled films. In a typical procedure, we synthesize highly monodisperse MPCs with a hexanethiolate (C6) periphery and *average* composition of $\text{Au}_{140}(\text{C6})_{53}$ through a modified Brust reaction¹⁴ and subsequent annealing procedures with hexanethiolate as reported by Hicks et al..¹⁵ The monodisperse MPC (core diameter ~ 1.6 nm)¹¹ is then place exchanged with 11-mercaptoundecanoic acid (MUA) to form MPC with an *average* composition of $\text{Au}_{140}(\text{C6})_{28-33}(\text{MUA})_{20-25}$ as verified by NMR of iodine-treated samples of the nanoparticles.¹⁶ MUA-modified MPCs are then used to form the assembled films.

Following modification with 3-mercaptopropyltrimethoxysilane¹⁷ or a self-assembled monolayer of MUA, the substrates were placed in 1 mM KOH ethanol solution (EtOH) for 20 minutes to ensure deprotonization of most exposed carboxylic acid groups. Deprotonated slides were soaked in a 0.2 M metal ion/EtOH solution for

only one minute before being rinsed with EtOH and immersed in a 2.4 mg/mL EtOH solution of Au₁₄₀(C6)₂₈₋₃₃(MUA)₂₀₋₂₅ for an additional minute.¹⁸ During the one minute dips in MPC, the solution surrounding the slides was constantly agitated. After each dip cycle the slide was thoroughly rinsed in EtOH and dried under argon. Dipping cycles were repeated until deposition of a desired film thickness was achieved and films were electrochemically and spectrophotometrically characterized as described below.

Fig. 1 shows UV-Vis spectra of a MPC assembled film grown using our alternative procedure where the dipping cycles are shortened to only one minute in each solution. One minute exposures are repeated rapidly and successfully form a very thick film in a brief time (< 1 hour total). The spectra, each one taken immediately after a dipping cycle, indicate that the film growth is both consistent and comparable to films assembled using longer dipping cycles. Compared to traditional methods of assembling MPC films, this “ultra-fast” procedure shows a 95% decrease, on average, in the time required to form films of the same thickness. Fig. 2 compares the growth efficiency between the two methods and highlights the versatility of the new procedure. As shown, ultra-fast films could be successfully grown with a variety of metal ion linkers, including Cu²⁺, Zn²⁺, and Ag⁺, on both gold and glass, with equal success.

In addition to being more efficient, the ultra-fast films appear to have the same structure and properties as traditionally grown films. In comparison, the size and

shape of the surface plasmon band (Fig. 1, at 520 nm) in the film spectra is very similar to that of traditional films, indicative of very similar core-to-core spacing.¹¹⁻¹² Likewise, the electronic properties of the films were found to be comparable. Due to the tiny capacitances inherent to the MPCs, differential pulse voltammetry (DPV) of MPC assembled films usually displays quantized double layer (QDL) charging effects in the form of single electron transfers.^{8,10} Fig. 3 shows these signals, notably very similar, from assembled films created using the two methods. Moreover, the electronic conductivity of the ultra-fast film was comparable to that of traditionally formed films. Despite vast differences in the time of formation, the results collectively suggest that the film assemblies have the same composition in terms of nanoparticle core size, MUA loading, and connectivity.

Mechanical stability is an important issue for certain applications of assembled MPC films, including use as a vapor sensor¹¹⁻¹² or as a precursory material to thin gold films.¹³ Tape tests²⁰ confirm the stability of our ultra-fast grown films with the adhesive unable to remove material from the film. Our films were also grown very thick and thermolyzed into thin gold films that were also extremely stable toward the tape test. Fig. 4 displays these two forms of the assembled MPC films.

We have shown an innovative and versatile new method of growing assembled films that significantly improves upon existing techniques in creating very thick, highly stable, organized films of MPC. Whereas the effectiveness of agitation to promote efficient film growth is not surprising,¹² the success of using extremely

short dip cycles was unexpected. Our results suggest that the ability of assembled MPC films to swell in the presence of solvent and mobilize uncoordinated metal ion linkers within the film to participate in linking additional MPCs from solution may have been previously underestimated.⁸⁻¹³ The exact details of this mechanism are still under investigation, as are further innovations regarding the assembly of MPC films, including growth under potential control.²¹ It is our hope that the ease, simplicity, and effectiveness of the method introduced here will encourage more widespread research on assembled MPC films and their applications.

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Notes and references

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18. Films assembled using Zn^{2+} as the linking ions required the addition of base to promote film growth, as has previously been reported.^{8,9,12}
19. The x-axis, time, refers to actual contact time in both the MPC solution and metal ion solution (dip cycle). It does not account for analysis time (UV-Vis).
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Figure captions

Abstract (≤ 20 words) Networked films of metallic nanoparticles, novel materials for sensing applications, can be formed with 20-fold higher efficiency than existing methods.

Fig. 1 UV-Vis spectra, taken after each dipping cycle, tracking ultra-fast growth of a C6/MUA MPC assembled film on a glass substrate using Zn^{2+} as a metal ion linker.

Inset: Film thickness monitored with each dipping cycle over time.¹⁹

Fig. 2 Comparison of traditional (open symbols) and ultra-fast (closed symbols) of assembled C6/MUA MPC films on glass substrates using various metal ion linkers.

Inset: Expansion of ultra-fast growth before one hour.¹⁹

Fig. 3 DPV showing cathodic QDL charging peaks of (a) C6 MPC in solution and assembled C6/MUA MPC films on gold from (b) traditional and (c) ultra-fast growth methods [Au working / Pt counter electrodes in 0.1 M Bu_4NClO_4/CH_2Cl_2 at 50 mV/sec].

Fig. 4 Digital photograph illustrating stable C6/MUA MPC films grown ultra-fast on glass slides (2.5 cm x 1.0 cm) before (left) and after (right) thermal treatment to create a thin gold film.

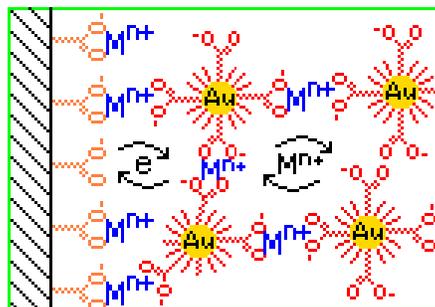
Abstract Figure

Figure 1.

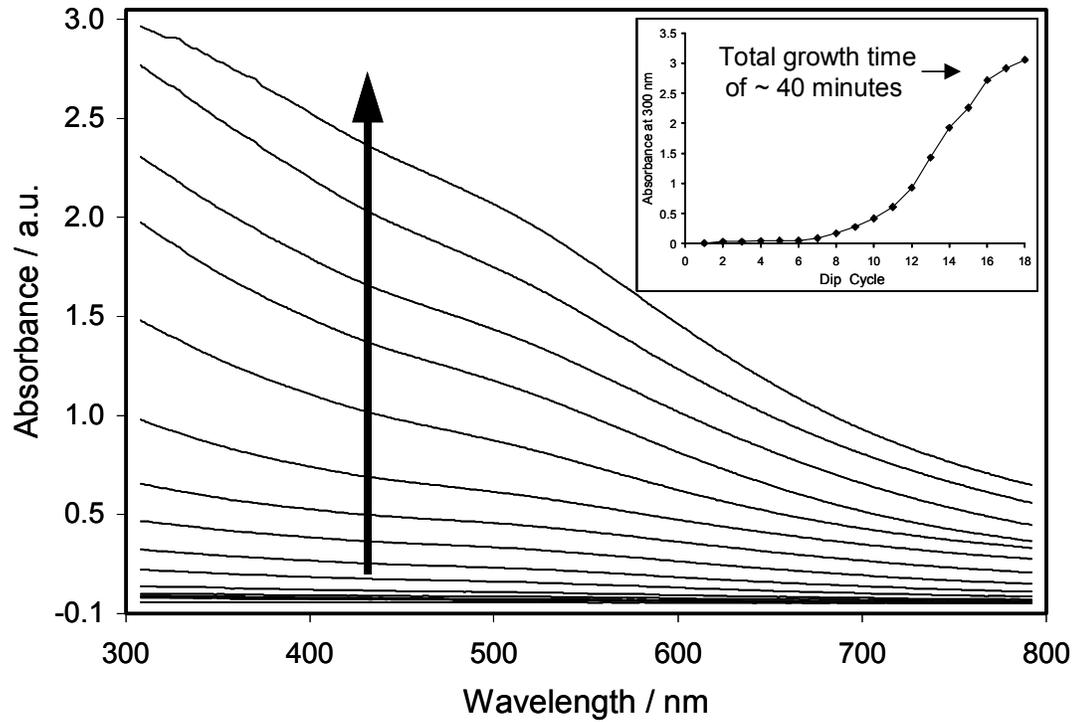


Figure 2.

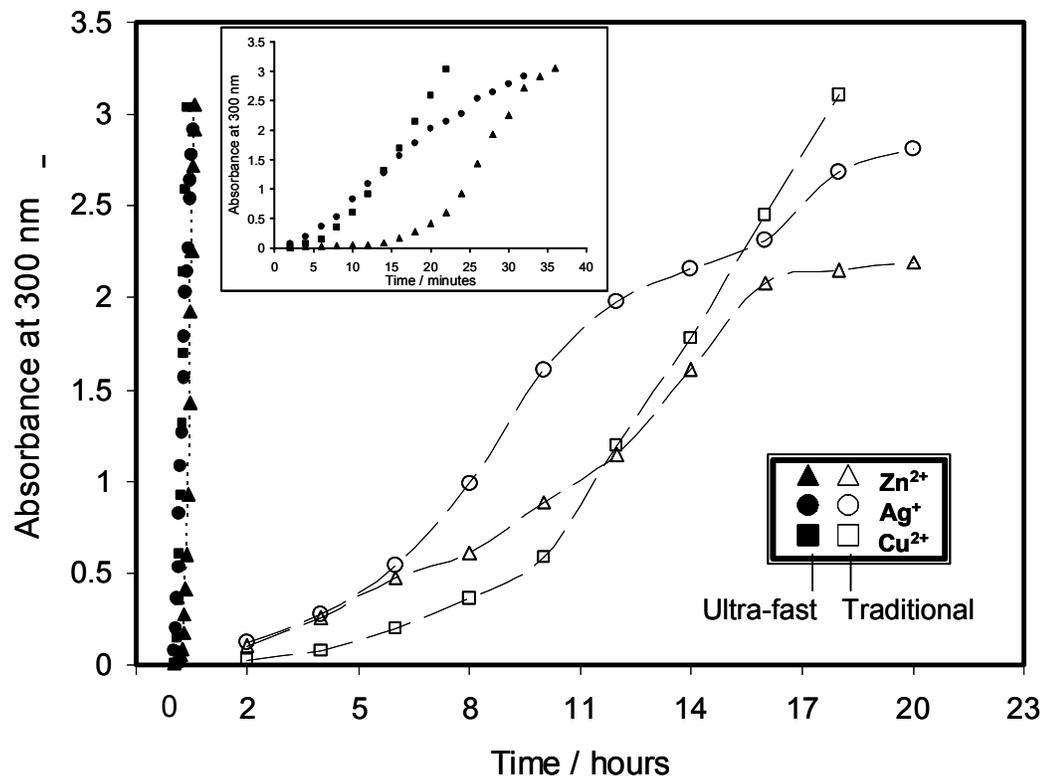


Figure 3.

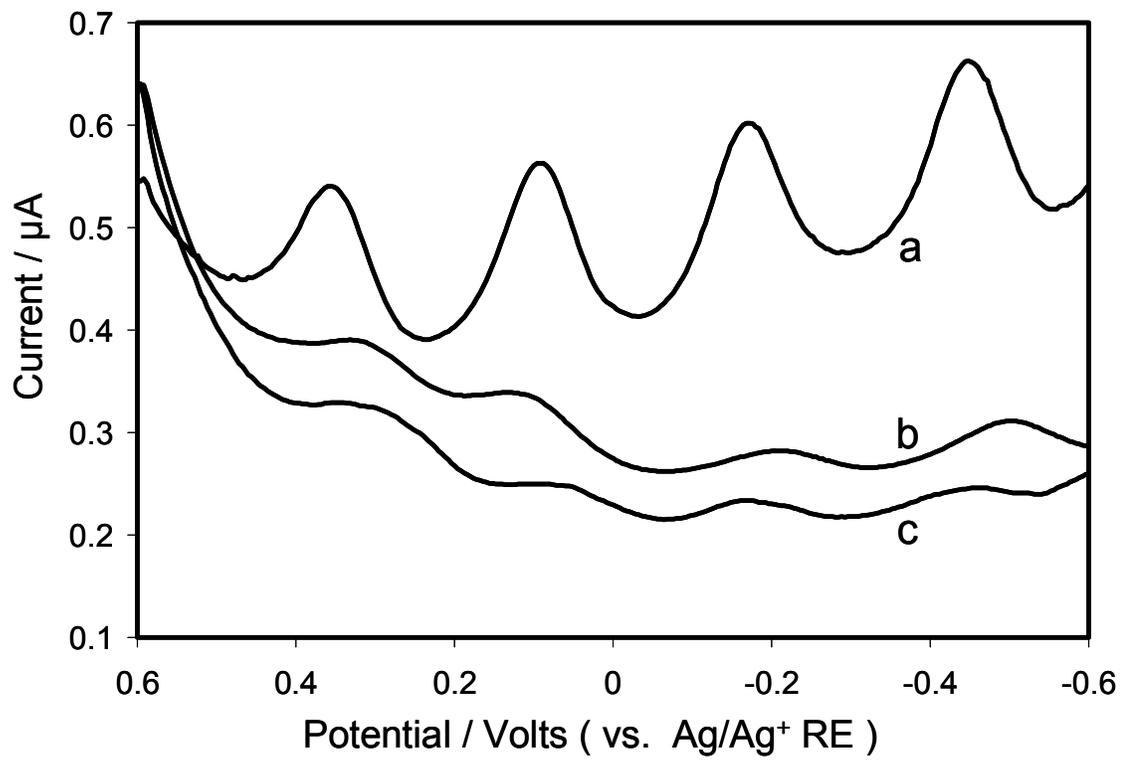


Figure 4.

