Construction of Coordination Multilayers Using Accelerated Self-Assembly Procedure (ASAP)

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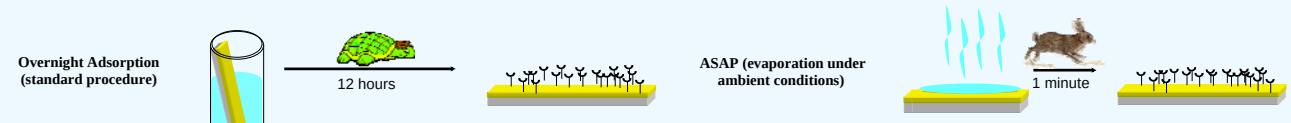
Layer-by-layer (LBL) self-assembly is a popular method for obtaining molecular-scale structures on surfaces. Our group has pursued this approach using metal-organic coordination as the basic motif for constructing multilayer structures comprising various bi- and multi-dendate organic ligands and nanoparticles.[1-4] An inherent drawback in the construction of multilayer materials based on metal-organic coordination is the slow (many hours) binding of the organic ligands.[3] The latter introduces a major difficulty in the study and possible applications of such systems.

Here we describe a novel method for the synthesis of self-assembled coordination multilayers based on a new Accelerated Self-Assembly Procedure (ASAP), where binding of a full organic ligand layer occurs on the time scale of minutes. In this protocol a small volume (ca. 3 µl/cm^2) of ligand-containing solution (possibly highly diluted) is spread on the substrate surface and evaporated under natural convection conditions. In the case of ethanol as the solvent, complete evaporation occurs within approx. 1 minute, leaving the surface covered with excess ligand. Extensive rinsing in pure solvent results in complete removal of the physisorbed molecules from the surface, leaving only the new coordinated layer. The latter was confirmed by comparing ellipsometric, contact-angle and FTIR data for samples prepared by the standard (overnight adsorption) procedure and the ASAP scheme.

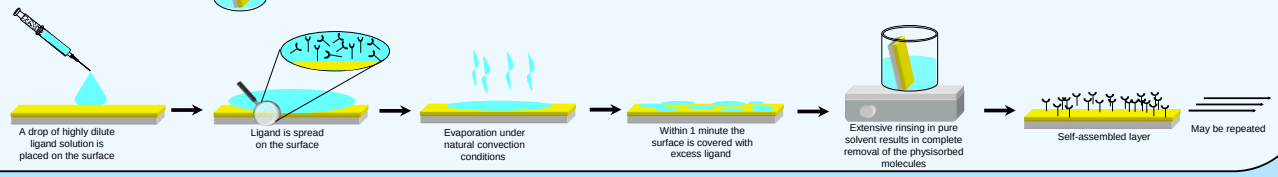
Although a detailed structural analysis has yet to be performed, ASAP presents a viable approach to rapid preparative LbL assembly of coordinated nanostructures.

The aim: Reduce substantially the adsorption time and the ligand concentration needed in the synthesis of self-assembled coordination multilayers.

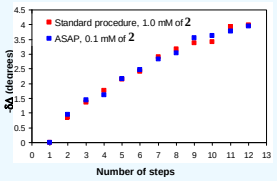
The concept:

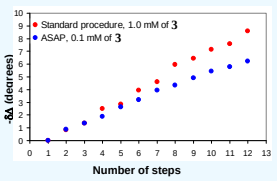


ASAP details:

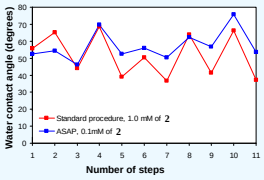


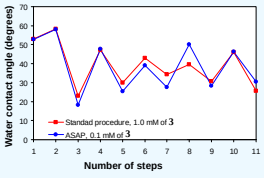
Changes of the ellipsometric parameter Δ with the number of steps in the construction of multilayers of **1**/(Zr^{4+}/**2**)$_n$ (top) and **1**/(Zr^{4+}/**3**)$_n$ (bottom) on gold. Odd step numbers: organic ligand, even step numbers: Zr^{4+} ion.



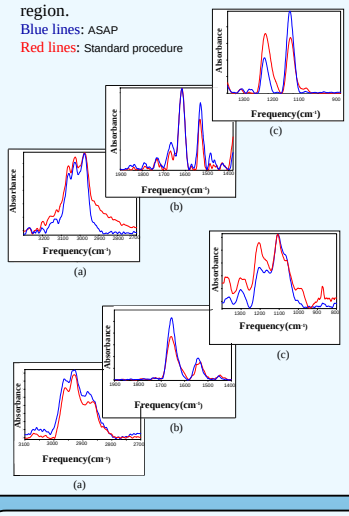


Variations of water contact angles during construction of multilayers of **1**/(Zr^{4+}/**2**)$_n$ (top) and **1**/(Zr^{4+}/**3**)$_n$ (bottom) on gold.

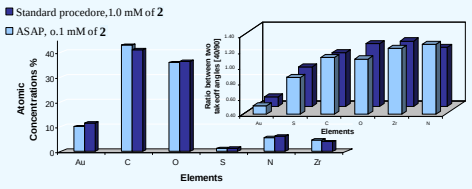




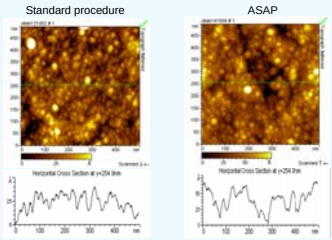
FTIR spectra obtained during construction of multilayers of **1**/(Zr^{4+}/**2**)$_n$ and **1**/(Zr^{4+}/**3**)$_n$ on gold: (a) methylene region; (b) carbonyl region; (c) ether region.
Blue lines: ASAP
Red lines: Standard procedure



XPS results for the construction of **1**/(Zr^{4+}/**2**)$_n$ multilayers on gold.

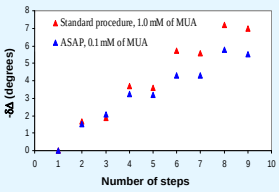


AFM results for the construction of **1**/(Zr^{4+}/**2**)$_n$ multilayers on gold.



Changes of the ellipsometric parameter Δ with the number of steps in the construction of MUA/(Cu^{+2}/MUA)$_n$ multilayers on gold. Odd step numbers: MUA, even step numbers: Cu^{2+} ion.

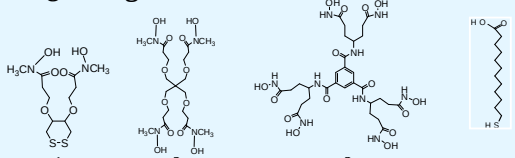
(After: Freeman et al., *Thin Solid Films* **1994**, *244*, 784.)



Conclusions

A new procedure for LbL construction of coordination multilayers was presented, based on Accelerated Self-Assembly Procedure (ASAP). The ASAP shows a regular growth mode, which may be different from that of multilayers grown by the common prolonged self-assembly. The new scheme provides considerably faster assembly and enables the use of much more dilute organic ligand solutions. These properties make ASAP a promising option for self-assembly in research and applications.

Organic ligands



References

[1] A. Hatzor, T. Moav, H. Cohen, S. Matlis, J. Libman, A. Vaskevich, A. Shanzer, I. Rubinstein, *J. Am. Chem. Soc.* **1998**, *120*, 13469.
[2] M. Wanunu, R. Popovitz-Biro, H. Cohen, A. Vaskevich, I. Rubinstein, *J. Am. Chem. Soc.* **2005**, *127*, 9207-9215.
[3] M. Wanunu, A. Vaskevich, S. R. Cohen, H. Cohen, R. Arad-Yellin, A. Shanzer, I. Rubinstein, *J. Am. Chem. Soc.* **2005**, *127*, 17877.
[4] M. Wanunu, A. Vaskevich, A. Shanzer, I. Rubinstein, *J. Am. Chem. Soc.* **2006**, *128*, 8341.