

A VERSATILE SCHEME FOR LAYER-BY-LAYER ASSEMBLY OF GOLD NANOPARTICLE MULTILAYERS

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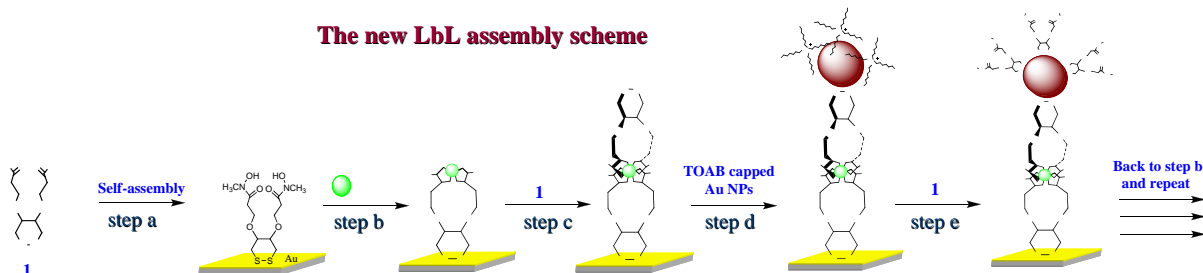
Abstract. Metal nanoparticles (NPs), in particular gold, are among the most widely-used building blocks in nano-scale applications, owing to their unique optical and electronic properties. These properties are related to the structural characteristics of the individual NPs, as well as to their environment and spatial distribution. Hence, various methods for obtaining Au NP assemblies have been reported, resulting in a myriad of structural, optical and electronic characteristics. Yet, a convenient scheme for constructing Au NP multilayers with variable 3D spacing and distribution of the NPs is highly desirable.

Layer-by-layer (LbL) assembly has been a popular method for constructing multilayered structures on surfaces. Our group has studied extensively the use of metal-organic coordination as the binding motif in LbL assembly schemes. Alternate binding of organic ligands and metal ions resulted in regular growth of coordination-based multilayers on Au or oxide (e.g., glass, silicon oxide) substrates [1, 2]. The same procedure was used to construct Au NP monolayers and multilayers with controlled spacing [3]. The latter required special modification of NP building blocks by partially substituting the capping layer with ligand molecules. Although proven successful, the preparation of ligand-derivatized Au NPs is complicated and time-consuming, thus hindering the use of coordination LbL assembly for obtaining NP multilayers.

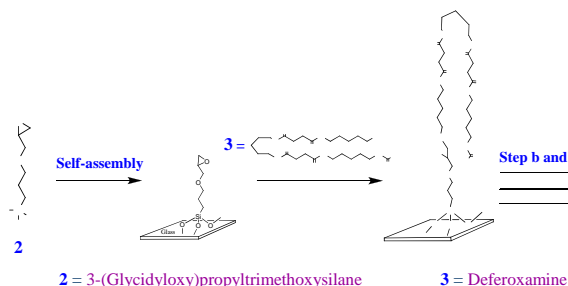
In the present work a new coordination-based LbL assembly scheme is presented, enabling versatile construction of NP multilayers using ordinary, easily synthesized Au NPs. The method allows LbL construction of NP multilayers with controlled layer spacing on Au or oxide surfaces, using tetraoctylammonium bromide (TOAB) stabilized Au NPs as the basic building blocks. Binding between the NP layers is achieved using Zr(IV)-coordinated bishydroxamate disulfide ligands.

The new LbL assembly scheme

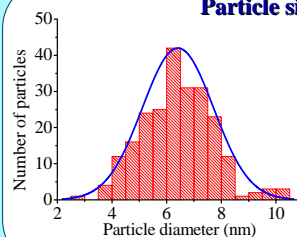
LbL assembly on Au surface



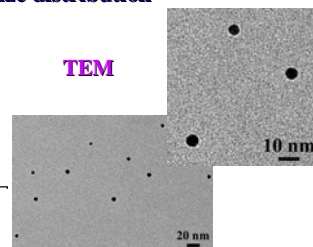
LbL assembly on oxide surface



Particle size distribution

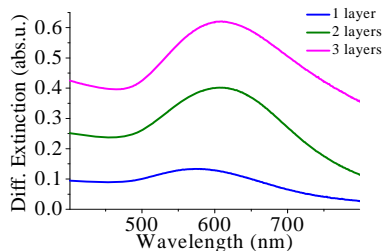


TEM



Au NP layers on glass

Transmission UV-vis spectra



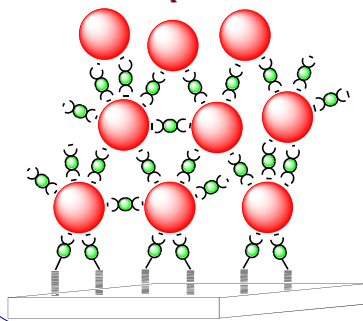
Bare glass

1 layer of NPs

2 layers of NPs

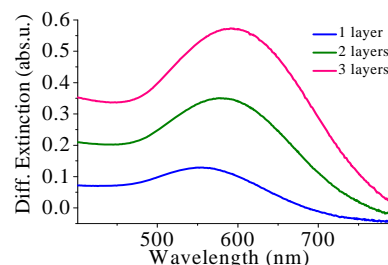
3 layers of NPs

Schematic presentation



Au NP layers on a gold film (20 nm, on glass)

Transmission UV-vis spectra



Bare gold

1 layer of NPs

2 layers of NPs

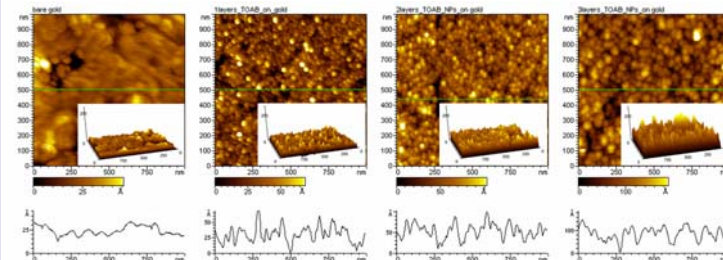
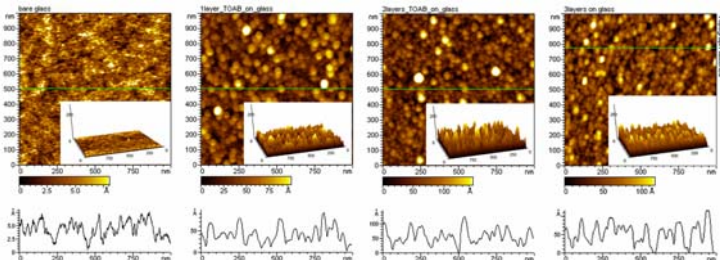
3 layers of NPs

HRSEM* →

HRSEM →

AFM ↓

AFM ↓



* For HRSEM imaging, the slides were coated with 3 nm Chromium.

References

- [1] M. Wanunu, A. Vaskevich, S. R. Cohen, H. Cohen, R. Arad-Yellin, A. Shanzer, I. Rubinstein, *J. Am. Chem. Soc.* 2005, 127, 17877-17887.
- [2] M. Wanunu, S. Livne, A. Vaskevich, I. Rubinstein, *Langmuir* 2006, 22, 2130-2135.
- [3] M. Wanunu, R. Popovitz-Biro, H. Cohen, A. Vaskevich, I. Rubinstein, *J. Am. Chem. Soc.* 2005, 127, 9207-9211.

