

Toward Electrochemically-Triggered Assembly of Metal Nanoparticles

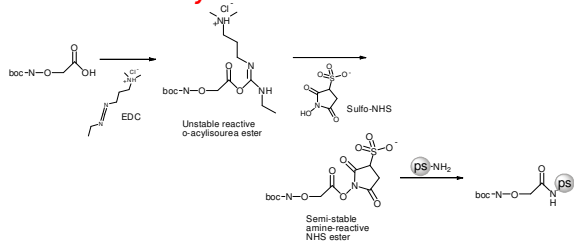
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Creation of Aminoxy-Terminated Surfaces

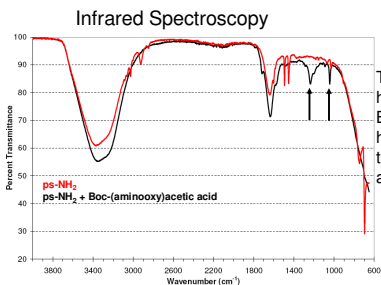
Goal: Test the introduction of aminoxy groups to amine-functionalized, nanometer-sized particles. The procedure includes:

- EDC/sulfo-NHS coupling to form an amide bond between the carboxylic acid group of Boc-(aminoxy)acetic acid and the primary amine group of the 0.33 μm aminated-polystyrene spheres;
- purifying product using 0.233 μm cellulose acetate syringe filter;
- concentrating product using centrifugation.

Synthetic Scheme



Characterization



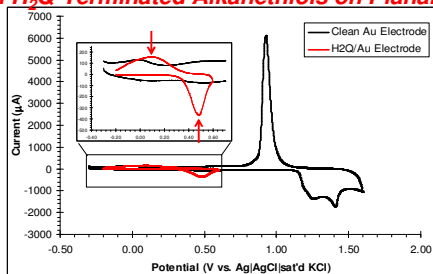
The product from the reaction has peaks characteristic of Boc-(aminoxy)acetic acid, highlighted by the arrows in the figure to the left, in addition to the ps-NH₂ peaks.

Toward Electroactive AuNPs

Goal: Create electrochemically active AuNPs that display hydroquinone (H₂Q) moieties. Steps toward achieving this goal include:

- using cyclic voltammetry (CV) to test the electrochemical activity of H₂Q-based films on planar gold substrates;
- developing protocols for creating H₂Q-modified AuNPs;
- using CV to test the electrochemical activity of H₂Q-terminated alkanethiols on AuNPs.

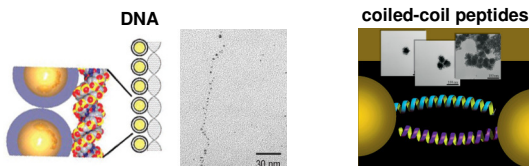
CV of H₂Q-Terminated Alkanethiols on Planar Gold



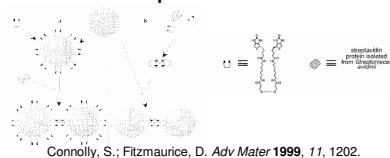
Formation of self-assembled monolayer of H₂Q-terminated alkanethiol leads to redox active layer on gold electrode as indicated by arrows

Introduction

The directed assembly of nanostructures is of widespread interest. Organization of nanostructures into two- and three-dimensional arrangements holds promise with potential applications in areas such as biosensing and optoelectronics. Although some methods have been developed to assemble metallic nanoparticles, one important class of nanostructures, most of these techniques rely on a single triggering method—biomolecular recognition. Assembly processes are driven by interactions of biomolecules such as:



streptavidin-biotin

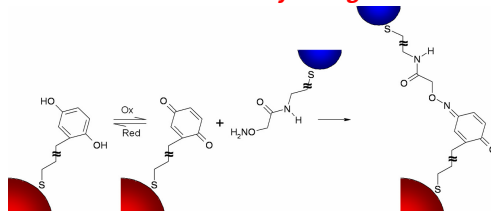


that are conjugated to the surface of the nanoparticles. The use of biomolecules for assembly places limits on the reaction conditions, including temperature, solvent, pH, and ionic strength.

Here, we aim to develop a new, potentially more universal triggering method—namely, electrochemistry—to drive nanoparticle assembly. Our objectives are to:

- synthesize the molecules necessary for electrochemical actuation;
- develop protocols to surface functionalize the AuNPs;
- use cyclic voltammetry to trigger redox of these active AuNPs.

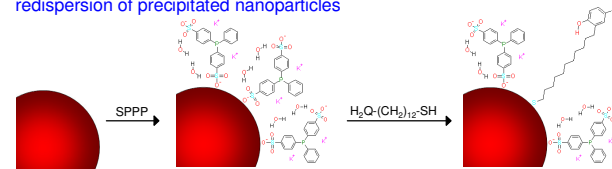
Illustration of AuNP Assembly Using Electrochemistry



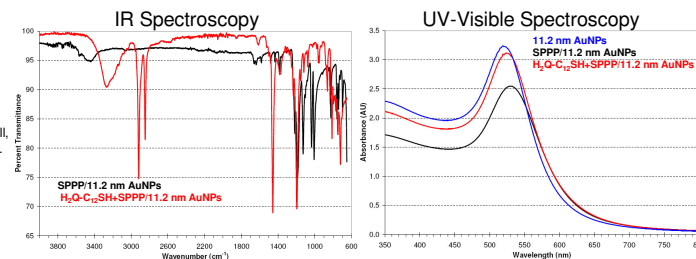
As shown above, two nanoparticle populations will be created—the first possessing a terminal hydroquinone group and the second a terminal aminoxy group. To date we have focused on preparing and testing the hydroquinone-functionalized nanoparticles and on developing model reactions to create the aminoxy functionality on AuNPs.

Procedure for Functionalizing AuNPs

- functionalized 11.2 nm AuNPs with bis(p-sulfonatophenyl)-phenylphosphine dihydrate dipotassium (SPPP)
- used place exchange to add hydroquinone-terminated alkanethiol (H₂Q-C₁₂SH) to SPPP/11.2 nm AuNPs
- purified H₂Q-C₁₂SH+SPPP/11.2 nm AuNPs using centrifugation and redispersion of precipitated nanoparticles

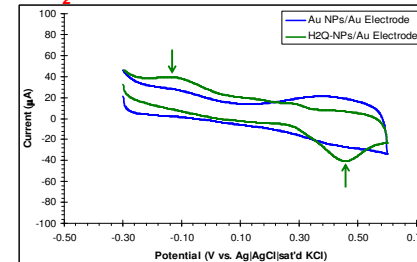


Characterization



The spectral changes upon addition of H₂Q-C₁₂SH to the SPPP/11.2 nm AuNPs confirm the presence of both molecules on the surface of the nanoparticles.

CV of H₂Q-terminated Alkanethiols on AuNPs



H₂Q-C₁₂SH+SPPP/11.2 nm AuNPs show redox activity absent in SPPP/AuNPs and characteristic of the H₂Q group.

Conclusion

- Created aminoxy-terminated layers on PS spheres.
- Introduced molecules containing electroactive H₂Q terminal groups onto 11.2 nm AuNPs.
- Future directions include:
 - deprotecting PS-Boc(aminoxy)acetic acid;
 - coupling H₂Q-C₁₂SH+SPPP/11.2 nm AuNPs to aminoxy-terminated PS;
 - creating AuNPs with terminal aminoxy groups.

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