Synthesis of Self-Assembling Silver Nanoparticles for Surface Enhanced Raman Spectroscopy

Jennifer Gilbertson
Chemistry, Beloit College

NNIN REU Site: Center for Nanotechnology, University of Washington, Seattle, WA
NNIN REU Principal Investigator: Danilo C. Pozzo, Chemical Engineering, University of Washington
NNIN REU Mentor: Kjersta Larson-Smith, Chemical Engineering, University of Washington, Seattle WA
Contact: gilbertj@beloit.edu, dpozzo@u.washington.edu, kjersta.larson@gmail.com

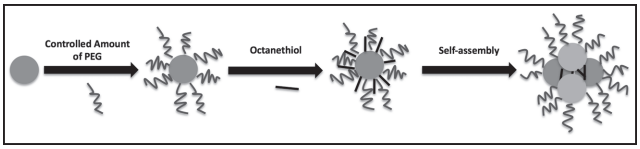

Figure 1: Schematic representation of silver nanoparticle clustering.

Introduction:

Research in metallic nanoparticles has become a topic of great interest due to potential applications across a diverse range of fields including photonics, nano-electronics and catalysis. Silver nanoparticles in particular have a special interest due to their unique optical properties. There were several possible methods to synthesize silver nanoparticles. However, silver nanoparticles have a tendency to aggregate and to oxidize. Moreover, synthesis routes are difficult to control due to their strong dependence on reaction parameters. On the other hand, these particles show stronger plasmonic effects when compared to other metallic nanoparticles due to increased absorption and light scattering. The focus of this project was to create a standardized and reproducible synthesis route for monodisperse amphiphilic silver nanoparticles that would self-assemble into stable clusters with controllable geometry. Previous research done by Larson-Smith and Pozzo [1] demonstrated the clustering of gold nanoparticles with controlled geometries using specific dose concentrations of 10 kilodaltons (kDa) thiolated polyethylene glycol chains (PEG). The steric interactions of the nanoparticles were controlled by different concentrations of polyethylene glycol chains. These silver nanoparticle clusters will be used in surface enhanced Raman spectroscopy (SERS) to enhance Raman scattering of specific analytes.

Methods:

Monodisperse 20 nm silver nanoparticles were synthesized with sodium citrate as a stabilizing agent and sodium borohydride as a reducing agent in a protocol based off of the Turkevich and Lok methods [2, 3]. Silver nanoparticles were then sterically stabilized by functionalizing with varying amount of 10 kDa thiolated PEG ranging in dose concentration from 0.01 to 20 PEG/nm^2 Ag. The silver nanoparticles were then treated with octane-thiol, rendering them amphiphilic. This initiated particle self-assembly due to hydrophobic attraction. The initial PEG concentration controlled the cluster size and geometry. Ultraviolet-visible spectroscopy was performed using a Thermo Scientific Evolution 300 systemin the range of 200-800 nm. Dynamic light scattering (DLS) was carried out using a Malvern Zetasizer Nano ZS with a 633 nm wavelength. Clustered silver nanoparticles were coated on a copper transmission electron microscope (TEM) grid and looked at under a FEI Technai G2 F20 TEM. An Anton Paar SAX Sess small angle x-ray scattering (SAXS) instrument with a wavelength of 1.54Å was used to examine the structures of the silver clusters in water.

Results:

Bare 20 nm silver nanoparticles had an absorption peak at 396 nm due to the surface plasmon resonance. The peak was shifted for different sized particles and clustered particles. The width and location of the absorption peak increased once the silver nanoparticles were treated with

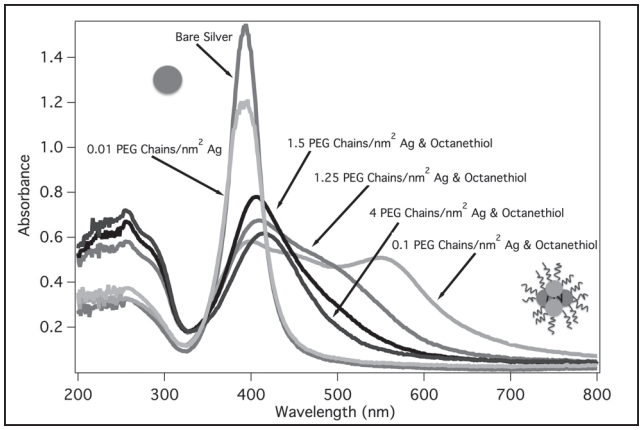

Figure 2: UV-Vis absorption spectra of bare, unclustered, and octane-thiol clustered silvernanoparticles in water.

• chemistry • chemistry • chemistry • chemistry • chemistry • chemistry •

PEG and then again, once they were clustered. Samples with a higher concentration of PEG chains/nm^2 Ag turned from yellow to red. Once the particles were clustered, the lower concentrations of PEG-treated samples aggregated into larger clusters. Figure 2 demonstrates that the larger the size of the clusters, the wider the absorbance peak reading on the UV-Vis. As the concentration of PEG chains/nm^2 Ag reached saturation, the silver nanoparticles remained as singlets.

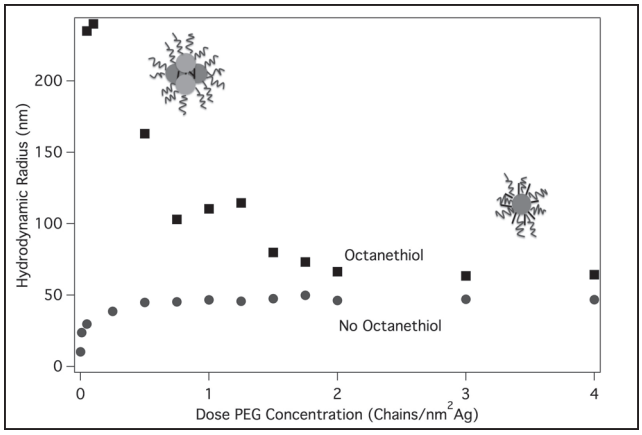

Figure 3: Hydrodynamic radii for octane-thiol clustered and unclustered silver nanoparticles inwater.

DLS was used to determine the hydrodynamic radius (R_H) of the entire silver-PEG complex. The hydrodynamic size increased with PEG concentration as the chains were more tightly packed. Figure 3 shows that the hydrodynamic size of octane-thiol functionalized clusters increased at low PEG concentration because more particles were in each cluster.

TEM was used to confirm the radii and size distribution of the bare silver particles and to examine the clustering of the PEG and octane-thiol treated samples. Figure 4 a-c shows examples of the nanoparticles clustering. The TEM images demonstrate that although we had achieved control over cluster geometry, there was still some polydispersity.

SAXS was used to analyze the radius and size distribution of the bare silver nanoparticles. It was also used to analyze the clustering of the PEG and octane-thiol treated silver nanoparticles. PEG has a low scattering length density compared to silver, therefore the scattering curve was primarily from the silver nanoparticles. Thus, samples that did not cluster scatter similar to bare silver particles.

The scattering plots demonstrated that the scattering was changing as a function of PEG concentration. The size of the silver nanoparticle clusters decreased as the concentration of PEG chains/nm^2 Ag increased and approaches bare silver. This data illustrated that we can control the steric interactions of the silver nanoparticles on the nanoscale.

Conclusions:

Our synthesis route reproducibly produced amphiphilic 20 nm spherical silver nanoparticles. While some polydispersity exists, the silver nanoparticles were still able to cluster. While we recognize that the trend of cluster size to PEG concentration was not perfect with the silver nanoparticles, our research with silver nanoparticles has demonstrated the application of this controlled assembly onto other metallic nanoparticles.

The controllable geometry of these nanoparticle clusters has important future applications for selective SERS detection based on steric effects or hydrophobicity. The center of the silver clusters will be able to selectively separate analytes based on size and chemical functionality.

Acknowledgements:

I would like to thank Dr. Danilo Pozzo and Kjersta Larson-Smith for their guidance and patience. I would like to acknowledge the National Science Foundation and the NNIN Research Experience for Undergraduates Program for funding this research. I would also like to thank the NanoTech User Facility at the University of Washington for the use of their equipment.

References:

[1] Larson-Smith, K. and Pozzo, D.C. Soft Matter. 7, 5339 (2011).

[2] Turkevich, J. et al. Discuss. Faraday Soc. 11, 55. (1951).

[3] Lok, C. et al. J Biol Inorg Chem. 12, 527. (2007).

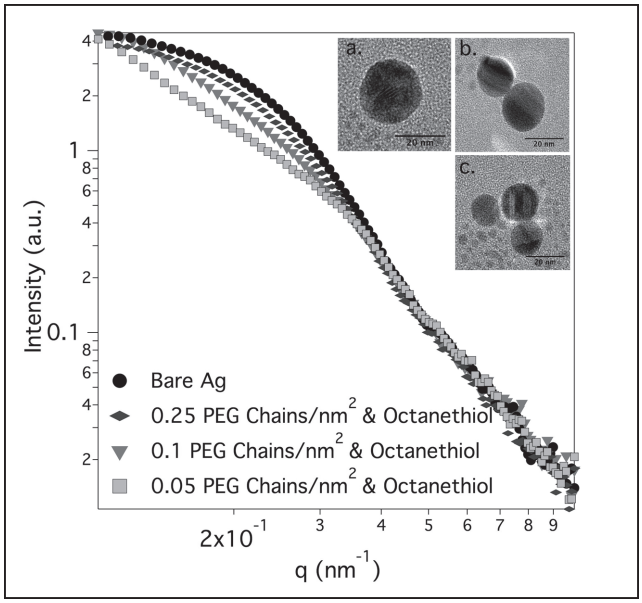

Figure 4: Slit-smeared SAXS scattering data of clustered silver at varying PEG concentrations.The TEM images (a-c) show several of the clustering geometries.