Microwave-Assisted Synthesis of Triangular Silver Nanoplates: Influence of Seed Clusters

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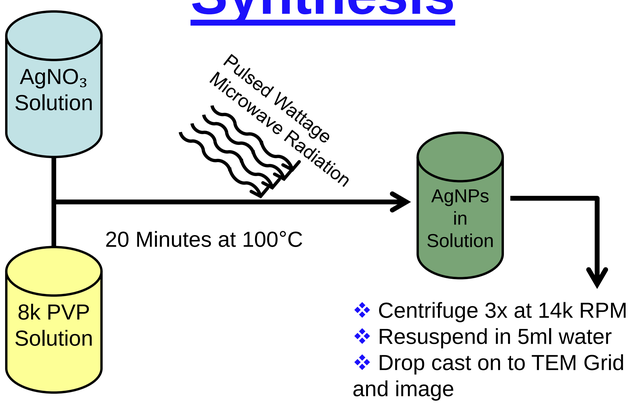
Abstract

Silver nanoparticles were produced by an aqueous synthesis using a variable frequency microwave reactor system, where silver nitrate is reduced by polyvinylpyrrolidone, with no other reagent present. Here, microwave-assisted synthesis reduces reaction time significantly (from days to minutes) compared to conventional heating methods, even if the nominal reaction temperature is identical. Thermodynamic nanocrystal growth mechanisms predict that the only shape present after microwave synthesis should be spheres due to the ultrafast evolution of particles, but a bimodal population of triangular nanoplates and spheroidal particles was obtained under microwave conditions. The development of triangular nanoplates provides further evidence that, in the absence of other shape directing agents, nanocrystal shape is largely dictated by the configuration of the initial seed clusters.

Accelerated Microwave Synthesis

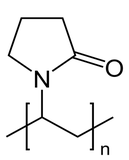


- ❖ Centrifuge 3x at 14k RPM
- ❖ Resuspend in 5ml water
- ❖ Drop cast on to TEM Grid and image

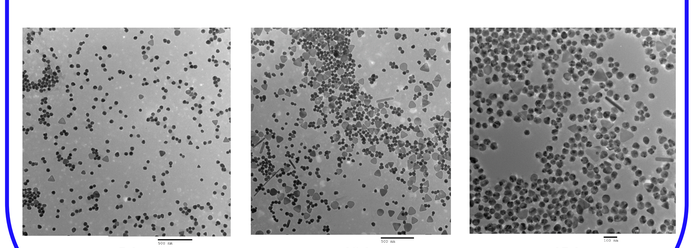
Optimization of Reaction Conditions

$PVP:AgNO_3$

- Investigation of 30, 15, 10 and 5:1 ratios and impact on the final products
- Ratio calculated from PVP repeat unit



Ratio $PVP:AgNO_3$	Average Sphere Diameter (nm)	Average Triangle Edge Length (nm)	Ratio Spheres: Triangles
30:1	54.0	100.8	13:1
15:1	53.4	89.5	13:1
10:1	52.7	96.1	22:1
5:1	50.1	77.6	13:1

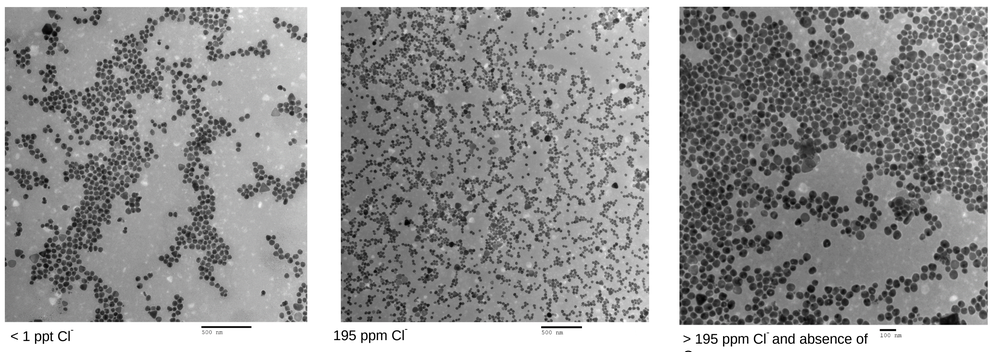


5:1 10:1 15:1

Quality Control & Role of Chloride

- $PVP:AgNO_3$ ratio is 10:1
- Data supports an accelerated oxidative etching mechanism and a chloride sculpting mechanism.
- Investigation into quality of reagents and solvents is recommended.

Chloride Concentration	Average Sphere Diameter (nm)	Average Triangle Edge Length (nm)	Ratio Spheres:Triangles
< 1 ppt	49.9	71.7	46:1
24 ppm	51.0	96.1	22:1
195 ppm	38.7	59.6	26:1
195 ppm and absence of O_2	40.1	52.3	72:1



< 1 ppt Cl^- 195 ppm Cl^- > 195 ppm Cl^- and absence of O_2

Aged $AgNO_3$ Solution

- Trimeric clusters are a proposed site for triangle formation in kinetically controlled thermal chemical reduction synthesis.
- Concentration of seed clusters decreases over time.
- Number of triangles decreases over time supporting the claim that trimeric clusters provide a site for triangular nanoplate formation, even under rapid reduction conditions.

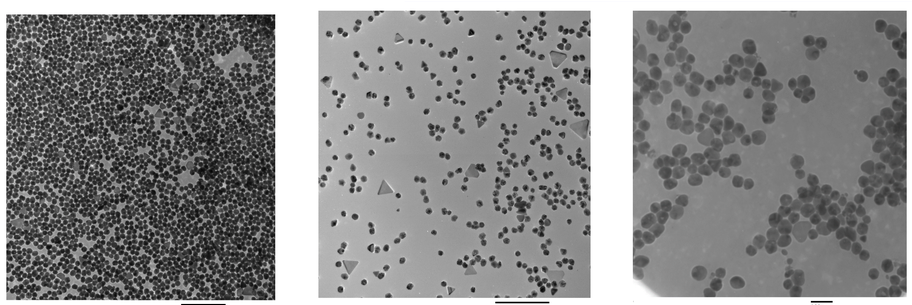
Xiong, Y.; Washio, I.; Chen, J.; Sadilek, M.; Xia, Y., Trimeric Clusters of Silver in Aqueous AgNO3 Solutions and Their Role as Nuclei in Forming Triangular Nanoplates of Silver. *Angewandte Chemie International Edition* **2007,** *46* (26), 4917-4921.

Age of $AgNO_3$ Solution	Ratio $PVP:AgNO_3$	Average Sphere Diameter (nm)	Average Triangle Edge Length (nm)	Ratio Spheres:Triangles
< 1 hour	30:1	54.0	100.8	13:1
	10:1	52.0	96.1	22:1
> 12 hours	30:1	49.6	95.5	24:1
	10:1	51.0	80.9	40:1

Particle Stability

- $PVP:AgNO_3$ ratio is 30:1
- The time period of a week was decided based on most general education labs only meeting once a week.

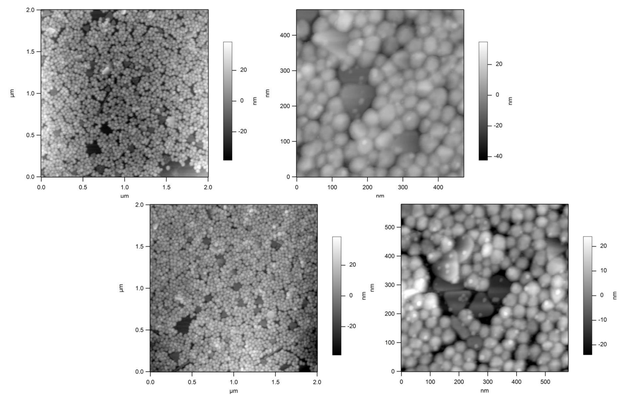
Pathway to Imaging	Average Sphere Diameter (nm)	Average Triangle Edge Length (nm)
Synthesize Centrifuge Prep Same Day	54.0	100.8
Synthesize, Centrifuge, 1 Week, Prep	57.1	95.0
Synthesize, 1 Week, Centrifuge, Prep	53.3	66.1



- Synthesize, Centrifuge, and Prep (all same day)
- Synthesize, Centrifuge, age one week then Prep
- Synthesize, age one week, Centrifuge then prep

Atomic Force Microscopy

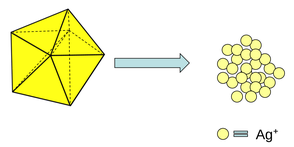
- Synthesis originally developed as part of curriculum development.
- Triangular plates offer excellent contrast with the spherical particles.
- AFM was used to confirm that triangles were nanoplates.
- Complete synthesis and imaging via bench-top AFM in an introductory Materials Science course has been successful.



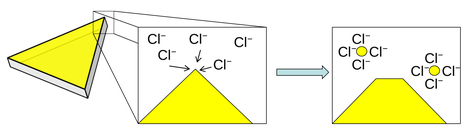
Directed Crystal Growth Theories

❖ **Face-Blocking**
- Polymeric or surfactant molecule preferentially binds to a specific crystal face inhibiting crystal growth

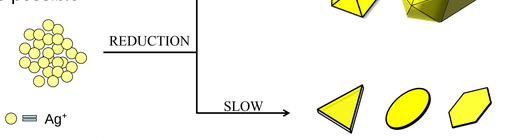
❖ **Oxidative Etching**
- Cl^- or Br^- and O_2 combination oxidize metal atoms from highly energetic sites



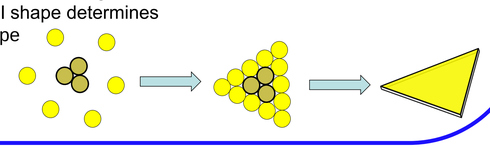
❖ **Sculpting**
- Group 17 Ligands (Cl^-, Br^-) selectively remove low coordinated metal



❖ **Kinetics**
- By controlling the rate at which the metal is reduced energetically less favorable shapes are possible



❖ **Seed-Mediated Growth**
- A seed provides a site for growth and it's initial shape determines the final shape



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