Rapid Microwave-Assisted Shape Controlled Synthesis of Silver Nanoparticles

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Abstract

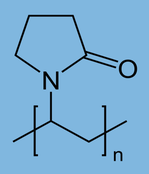
The majority of procedures for shape-controlled silver nanoparticle synthesis report the use of a common set of reagents: a source of silver ions, a reducing agent, a shape directing agent, and a capping/protective agent. Associated reaction times are long, typically ranging from 24-72 hours. We have developed a rapid microwave-assisted synthesis that includes only water, silver ions, and polyvinylpyrrolidone (PVP), producing predictable sizes and shapes of silver nanoparticles in 20 minutes. This result is notable on two fronts: the large reduction in reaction time and the elimination of purported shape-directing agents, marking a clear departure from commonly accepted theories of shape-controlled nanosynthesis. Additionally, we are first group to characterize silver nanoparticles with both transmission electron microscopy (TEM) and atomic force microscopy (AFM), offering clear evidence for the existence of flat triangular nanoplates. The synthesis has great potential to be adapted for undergraduate Materials Science coursework due to its simplicity, rapid product formation, and facile characterization by AFM. We anticipate that further investigation into this synthesis will reveal the true role that PVP plays in the formation of silver nanoparticles and will lead to better control of size, shape, and dispersity.

Synthesis Objectives

- Reduce reaction time scale from days to minutes
- Generate nanostructures with distinct shapes than can be easily imaged using benchtop AFM.
- Adapt procedure that can be implemented in undergraduate Materials Science courses.
- Understand the mechanism of silver nanocrystal growth.
- Determine the stability of the AgNPs in solution and in the solid state.

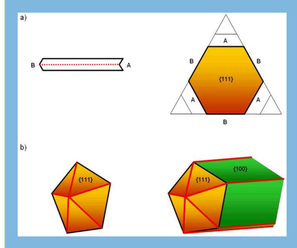
Directed Crystal Growth Theories

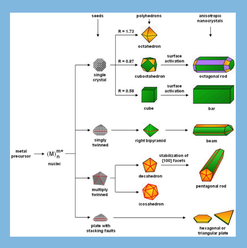
- Polymeric Reagents
  - Capping/protective agent
  - Shape directing due to its affinity to bind to the (100) facet of silver
  - Reducing agent
  - Kinetic controlling agent, PVP is a weak reducing agent it controls the amount of Ag^0 produced
- Group 17 Ligands (Cl^-, Br^-)
  - Preferentially bind to (100) face of silver, leading to passivated growth
  - Selectively etch low-coordination surface atoms



Particle Shapes

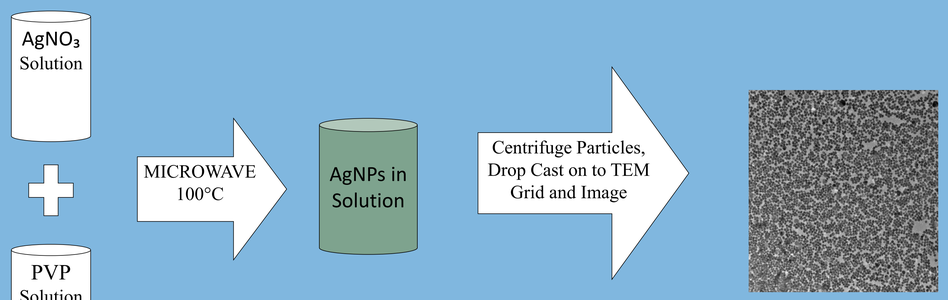
- Multiply Twinned Particles
- Triangular Nanoplates





The figures above taken from Xia, Y., Xiong, Y., Lim, B. and Skrabalak, S. (2009), Shape-Controlled Synthesis of Metal Nanocrystals: Simple Chemistry Meets Complex Physics? Angew. Chem. Int. Ed., 48: 60–103.

Accelerated Microwave Synthesis

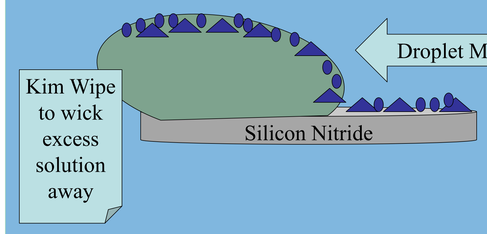


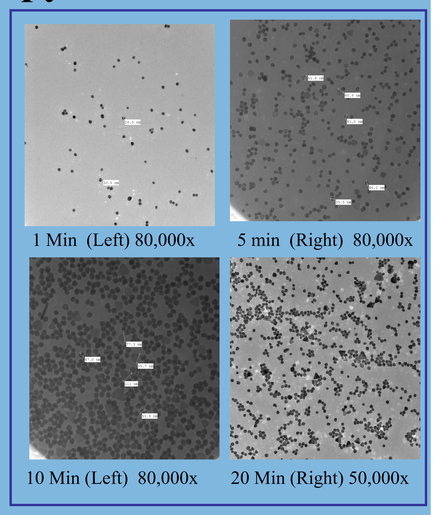
- Reaction time in microwave varied
- All results reported are from a 30:1 mole ratio PVP: $AgNO_3$
- Centrifugation to remove excess PVP

Transmission Electron Microscopy

- Used to image and characterize particle size and shape

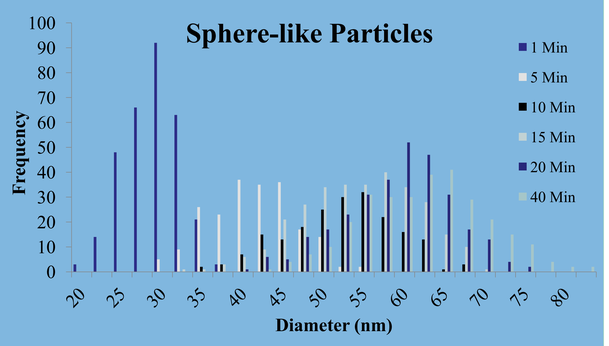
TEM Sample Prep

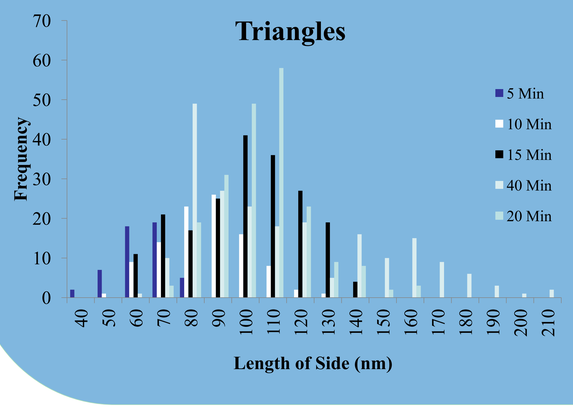




Size and Shape Evolution

- Time reacted affects size, shape, and polydispersity of the products
- What shapes and sizes can we expect at different times?
- How long can the particles sit in solution and still maintain their integrity?





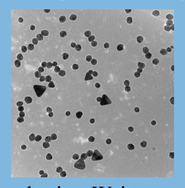
	Sphere-like Particle Diameter Data		Triangle Side Length Data	
Time (min)	Mean (nm)	STD DEV (nm)	Mean (nm)	STD DEV (nm)
1	27.90	3.44	n/a	n/a
5	40.25	5.23	58.86	8.93
10	50.88	6.64	81.55	15.90
15	53.08	7.11	95.22	20.45
20	57.64	6.77	100.84	16.83
40	60.77	7.65	108.94	34.79

Stability of Particles

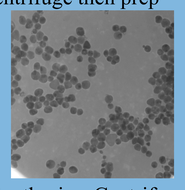
To evaluate the stability of particles in solution, we compared three different paths the AgNPs could take before being placed on a grid of characterization. The time period of a week was decided based on most general education labs only meeting once a week.

	Triangles		Sphere-like particles	
	Mean (nm)	STD DEV (nm)	Mean (nm)	STD DEV (nm)
Synth Centrifuge Prep Same Day	100.84	16.83	57.64	6.77
Synth, Centrifuge, 1 week, Prep	95.01	33.27	57.09	7.59
Synth, 1 Week, Centrifuge, Prep	66.11	11.95	53.29	8.34

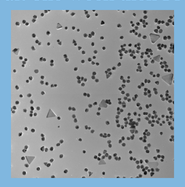
- Synthesize, Centrifuge, and Prep (all same day)



- Synthesize, Wait one week, Centrifuge then prep

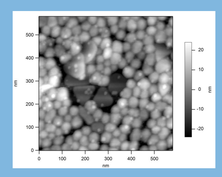


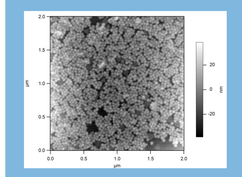
Synthesize, Centrifuge, wait one week then Prep

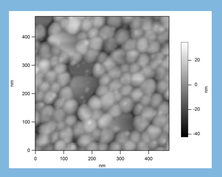


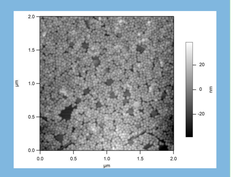
Atomic Force Microscopy

- The use of AFM was used to confirm that triangles were nanoplates.









Future Studies

- XPS- Confirm the absence of halogens, which may impact shape.
- Bench Top AFM- simulate integration into an undergraduate materials science lab experiment.
- Higher Temperature synthesis- Can the reaction produce the same or better results at higher temperatures?
- Mole ratio of PVP:$AgNO_3$ investigation
- Additional Reagents- Can more control over the size and dispersity be gained by adding ONE additional reagent?
- Address the special role of microwave radiation- how does this modify the role of reagents?

Acknowledgments

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