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In Situ Characterization of Silver Nanoparticle Synthesis in Maltodextrin Supramolecular Structures

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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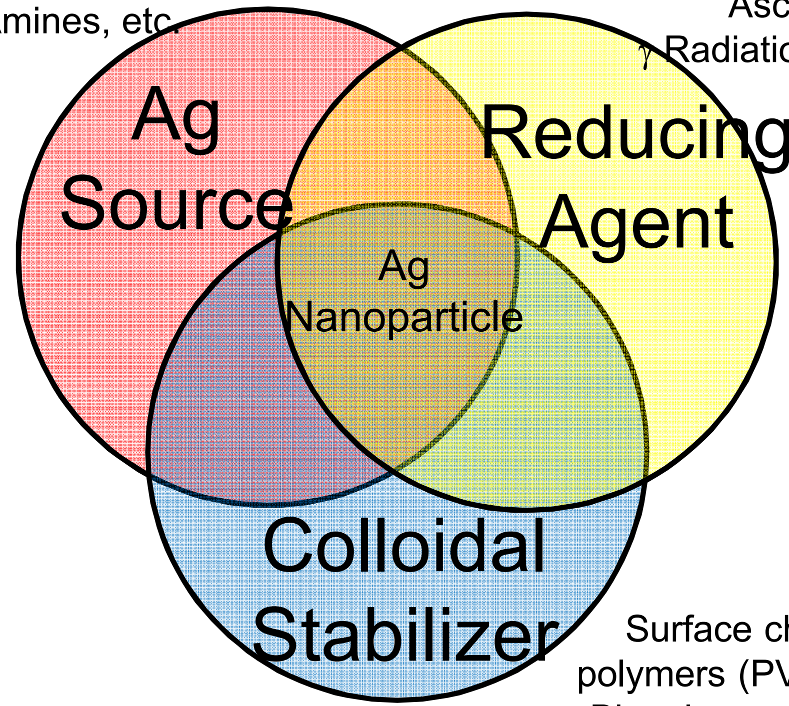
Interest in Silver Nanoparticles Span multiple decades of research

Ag Nitrate, Acetates, Amines, etc.

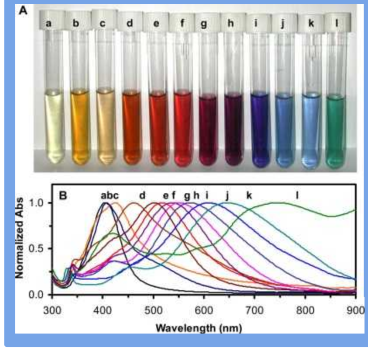
H_2, $NaBH_4$, Citrate, Sugars, Ascorbic acid, γ Radiation, Polyols



Surface charge, polymers (PVP, PAA), Biopolymers (Arabic gum, Starch, Chitosan), Citrate ions, etc.

Sondi, I. et al. *J. Coll. Interf. Sci.* **2003,** *260* (1), 75.
Goia, D. V. et al. *New J. Chem.* **1998,** *22* (11), 1203.
Krutyakov, Y. A. et al. *Russ. Chem. Rev.* **2008,** *77* (3), 233.
Sun, Y., *Chem. Soc. Rev.* **2013,** *42* (7), 2497.
Moulton, M. C. et al. *Nanoscale* **2010,** *2* (5), 763.

Optical Properties



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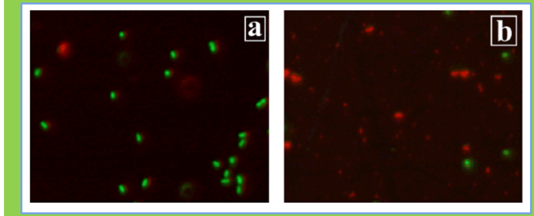
Anti-bacterial Application



Chamakura, K. et al. *Colloids Surf. B Biointerfaces* **2011,** *84* (1), 88-96.
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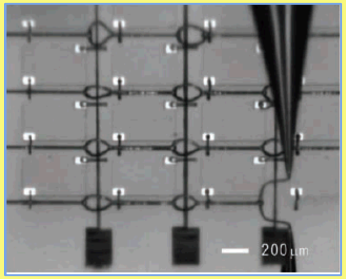
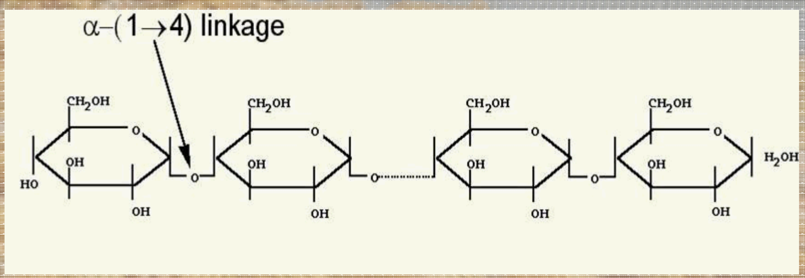
Direct Write Printing



Ahn, J. H. et al. *Science 323* **2009,** 1590.
Balantrapu, K. et al. *J. Mat. Res.* **2011,** *24* 2828.
Perelaer, J. et al. *Adv. Mat.* *18*,**2006,** 2101.

Maltodextrin is a polysaccharide suitable for synthesizing and dispersing silver nanomaterials

- **Maltodextrin is composed of α-D-glucose sugars with glycosidic linkages along the 1-4 bonds.**
- **Maltodextrin is produced from starch products, derived by enzymatic or acidic degradation.**
- **It exhibits cold water solubility unlike starch**
- **Maltodextrin is terminated with a sugar molecule, and has the potential to act as a reducing agent, behaving similarly to glucose, fructose, dextrose or other sugars in silver nanoparticle synthesis.**
- **Maltrin MO40 produced from corn has a dextrose equivalent value DE = 5, thus contains 5% equivalent glucose. The degree of polymerization is approximately 20.**



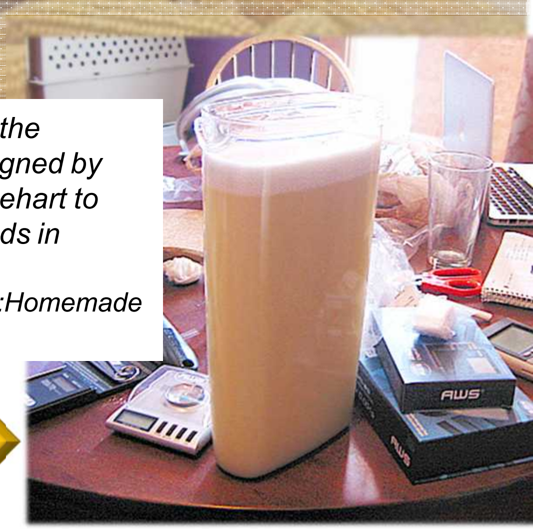
$H(C_6H_{10}O_5)_nOH$,
where n is between 2 and 20.

Maltrin® MO40 Uses:

- Powdered carbohydrate
- Fat or oil replacer in food formulations
- Spray drying aid due to low hygroscopic behavior
- Film forming aid in personal care products
- Pharmceutical binder and ceramic processing aid

Grain Processing Corporation

Maltodextrin is contained in the Soylent product recipe, designed by software engineer Rob Rhinehart to meet all human nutrient needs in minimal preparation time.
http://en.wikipedia.org/wiki/File:Homemade-Soylent.jpg



Maltodextrin Solutions Associate into Structures and Crystallites

- SAXS and Light scattering studies of maltodextrin solutions establish the self assembly of oligomers into larger structures. Oblate spheroids of about 280 nm diameter and thickness of 28-36 nm.
- Crystallite regions of 17 nm were also modeled in maltodextrin gels.
- Many investigations explore the interaction of silver nanosynthesis within biopolymer structures, like Starch.
- This study investigated how oligomeric derivatives of starch (i.e. Maltodextrin) acts as a reactive medium.

Raveendran, P. et al. , *J. Am. Chem. Soc.* **2003,** *125* (46), 13940-1.
Vigneshwaran, N. et al. *Carbohydr. Res.* **2006,** *341* (12), 2012-8.
Andreescu, D. et al. *J. Mat. Res.* **2007,** *22* (9), 2488-2496.
Huang, L. et al. *J. Nanopart. Res.* **2008,** *10* (7), 1193-1202.
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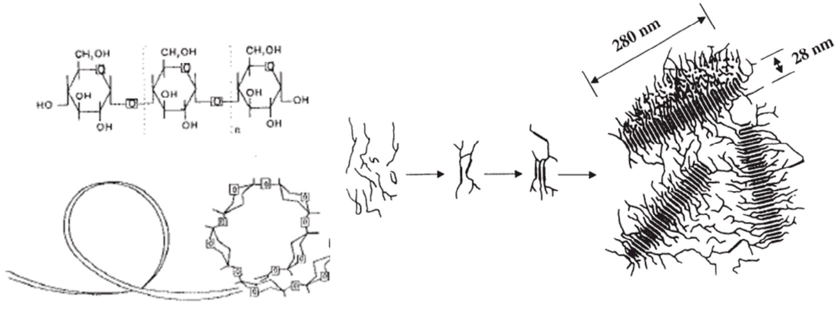
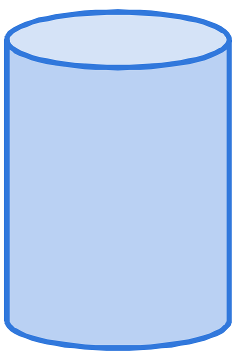


Amylose

F. Reuther, P. Plietz, G. Damaschun, H.-V. Piirschel, R. Kr6ber, and F. Schierbaum, *Colloid and Polymer Science* **261** (1983) 271 -276.
Ch. Gernat, . et al. *Acta Polymerica* 38 (1987) 603-607.
I. S. Chronakis *Critical Reviews in Food Science and Nutrition*, 38:7 (1998) 599-637.



Silver reactions with maltodextrin were performed using $AgNO_3$, dissolved Maltrin MO40, and KOH in deionized water using benchtop chemical techniques.

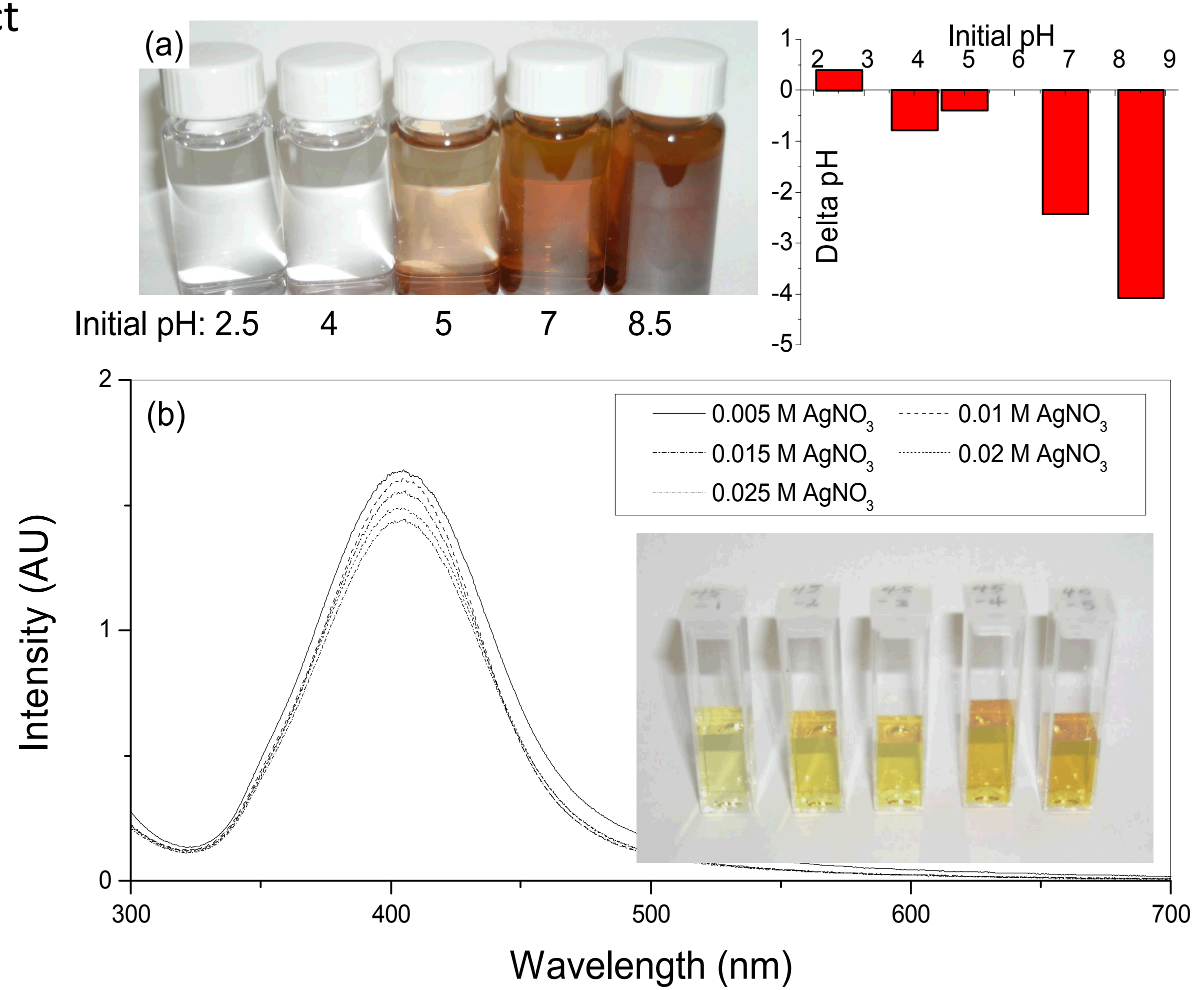
- Low shear rate, no micro-reactor design.

Maltodextrin becomes a reducing sugar as pH is increased

- $AgNO_3$ solutions weakly react as pH ranges from acidic to mildly alkaline conditions.
- Large drops in pH are noted as the starting pH value becomes alkaline.
- Sugar reducing power is known to increase under alkaline conditions.

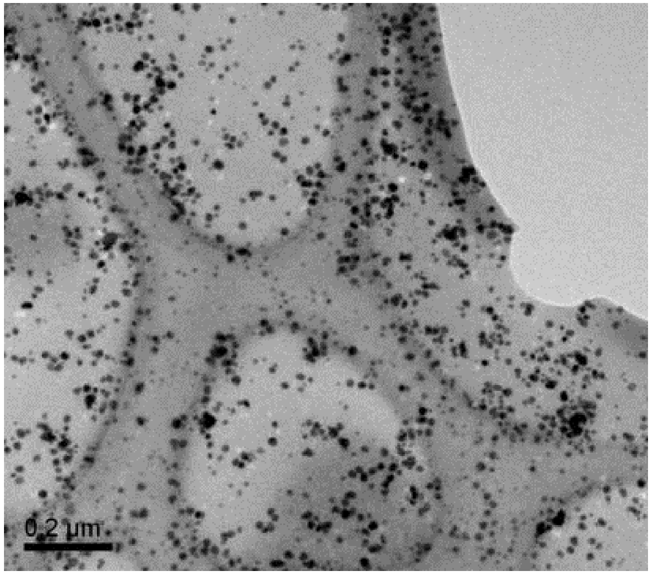
$$R\text{-}CHO + OH^- \rightarrow R\text{-}COO^- + 2H^+ + 2e^-$$

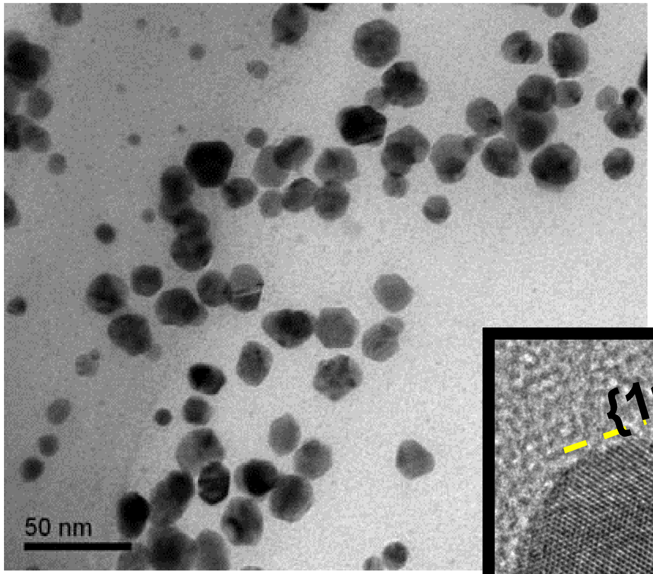
- Reactions at pH > 12 lead to nanoparticle solutions, indicating dispersed nanoparticle production.

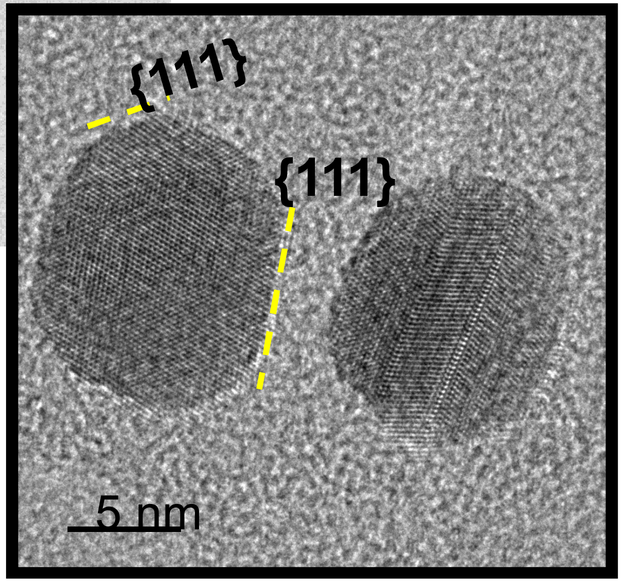


TEM Analysis shows Single Crystal and Twinned particles, with {111} termination

- After 24 hours of reaction, a dispersion of silver nanoparticles is found ranging from 5 -50 nm in diameter, with no agglomeration.







The shape and structure of the particles is common to starch protected Ag-np, both from solution and from micro-reactor synthesis.

P. Raveendran, Jie Fu, and Scott L. Wallen, *J. Am. Chem. Soc.* **2003**, 125, 13940..
N. Vigneshwaran, et al., *Carbohydrate Research* **341** (2006) 2012.
C. Y. Tai, Yao-Hsuan Wang, and Hwai-Shen Liu, *AIChE Journal*, **54** (2008) 445.
K. Balantrapu and D. V. Goia, *J. Mater. Res.* **24** (2009) 2828.

Alkaline reaction of $AgNO_3$ with Reducing Sugars are expected to undergo *two* precipitations

1. Initially, Ag^+ react to form Ag_2O precipitates.

   $$2\ Ag^+ + OH^- \rightarrow Ag_2O\ (s) + H^+$$

2. Silver np are formed by dissolution-precipitation or direct conversion.

   $$R\text{-}CH{=}O + 2[Ag^+OH^-] \rightarrow R\text{-}C(OH){=}O + 2Ag + H_2O$$

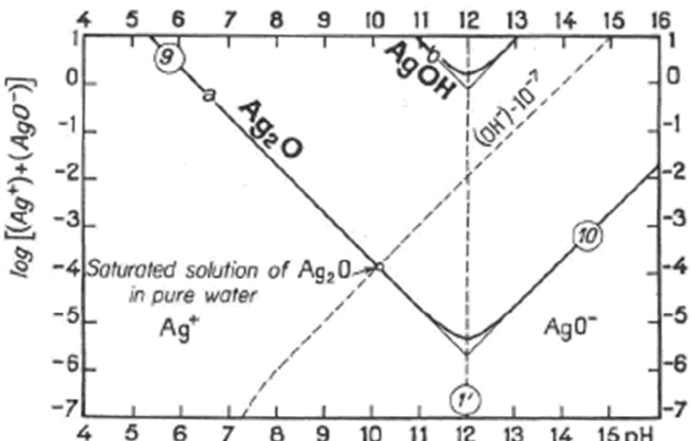


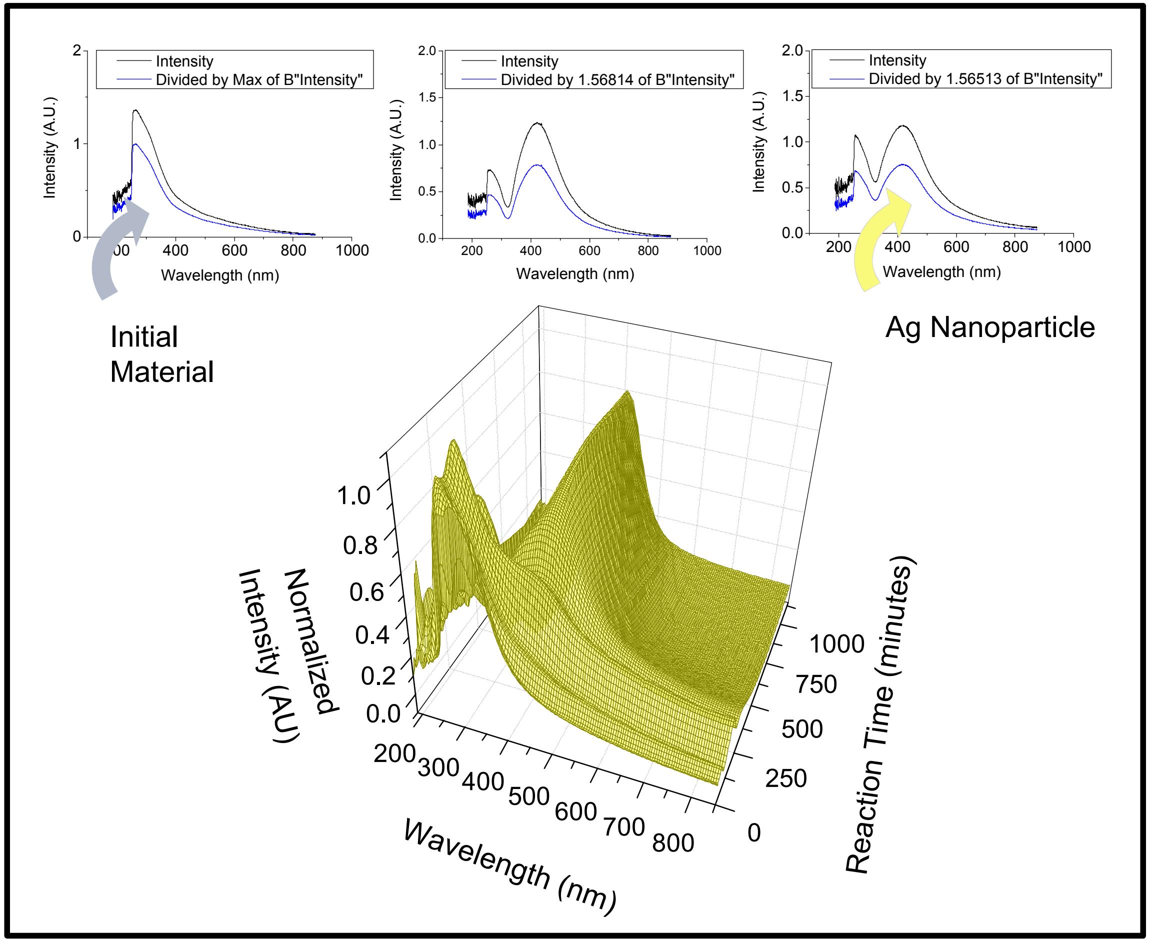
FIG. 3. Influence of pH on the solubility of Ag_2O and AgOH, at 25°C.

M. Pourbaix, Atlas of Electrochemical Equilibria, Section 14.2 Silver, Pergamon Press, Oxford 1966.

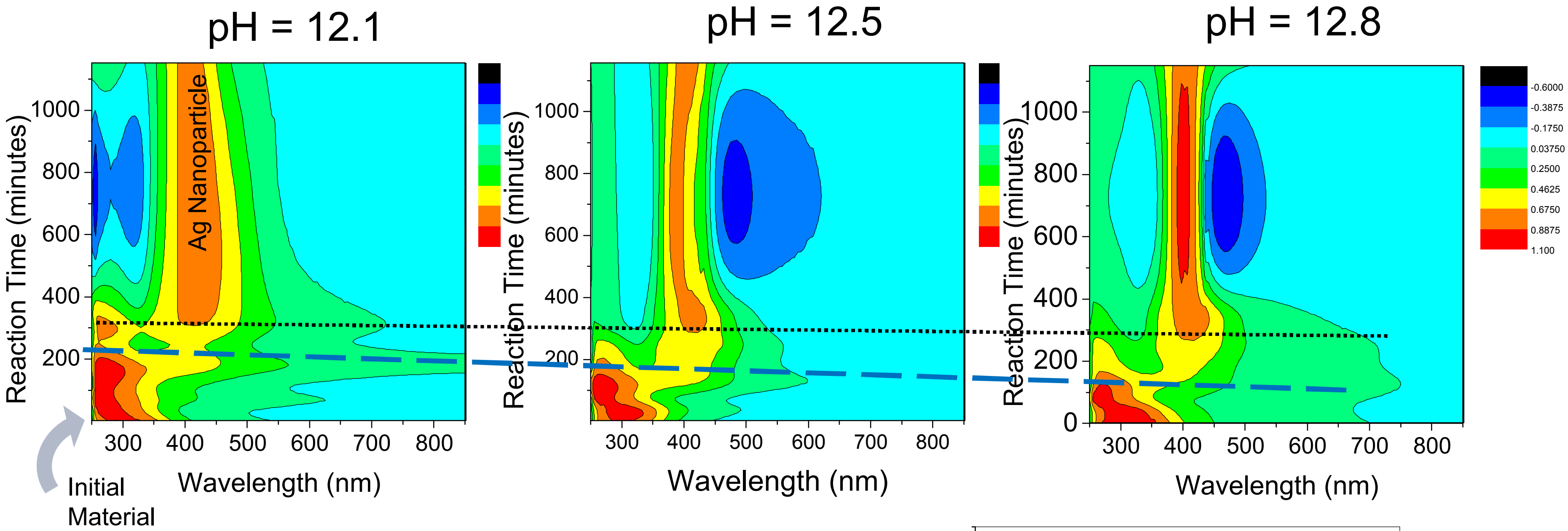
- The Pourbaix diagram shows the solution species will vary based on pH, and the solubility minimum is pH = 12 for both the oxide and hydroxide.
- The reaction kinetics of the precipitations were conducted using UV-vis, Raman, and SAXS measurements.

Reaction Kinetics were followed using UV-Vis Spectrometry

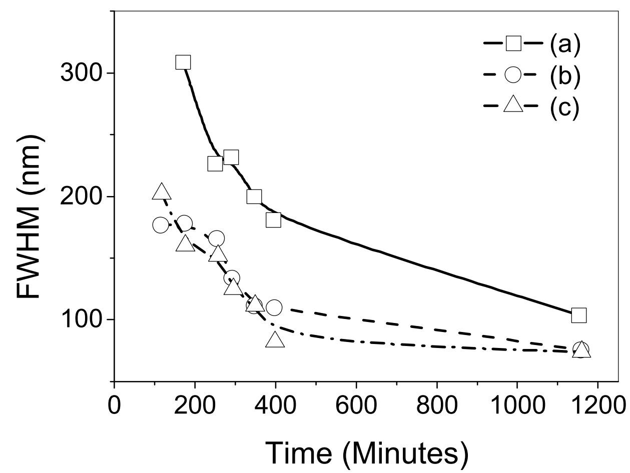
- The Initial Material is absorbing near 300 nm with a broad peak.
- UV-Vis spectra show a transition between two peaks with the reaction time.
- For kinetic comparison, peak intensities were normalized to a total value of 1, based on both materials.
- Normalized data were converted into surface plots for comparison of the reaction process.



A pH of 12.5 Gives Uniform Nanoparticles in Six Hours



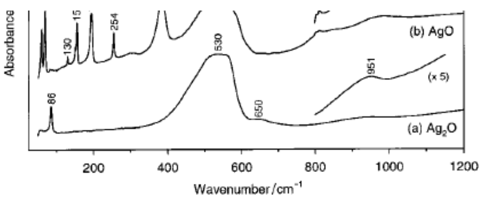
- All materials show initial precipitate at ~300 nm, decreasing to 50% intensity in 200 minutes. Higher pH gave more rapid fading of intensity.
- The plasmon resonance peak of Ag np at 400-420 nm becomes dominant at 300 minutes for all pH.
- The width of the Ag np peak is decreased as pH is increased, indicative of more uniform particle size.



Raman Spectroscopy of Reacting Materials Does Not Show Ag_2O

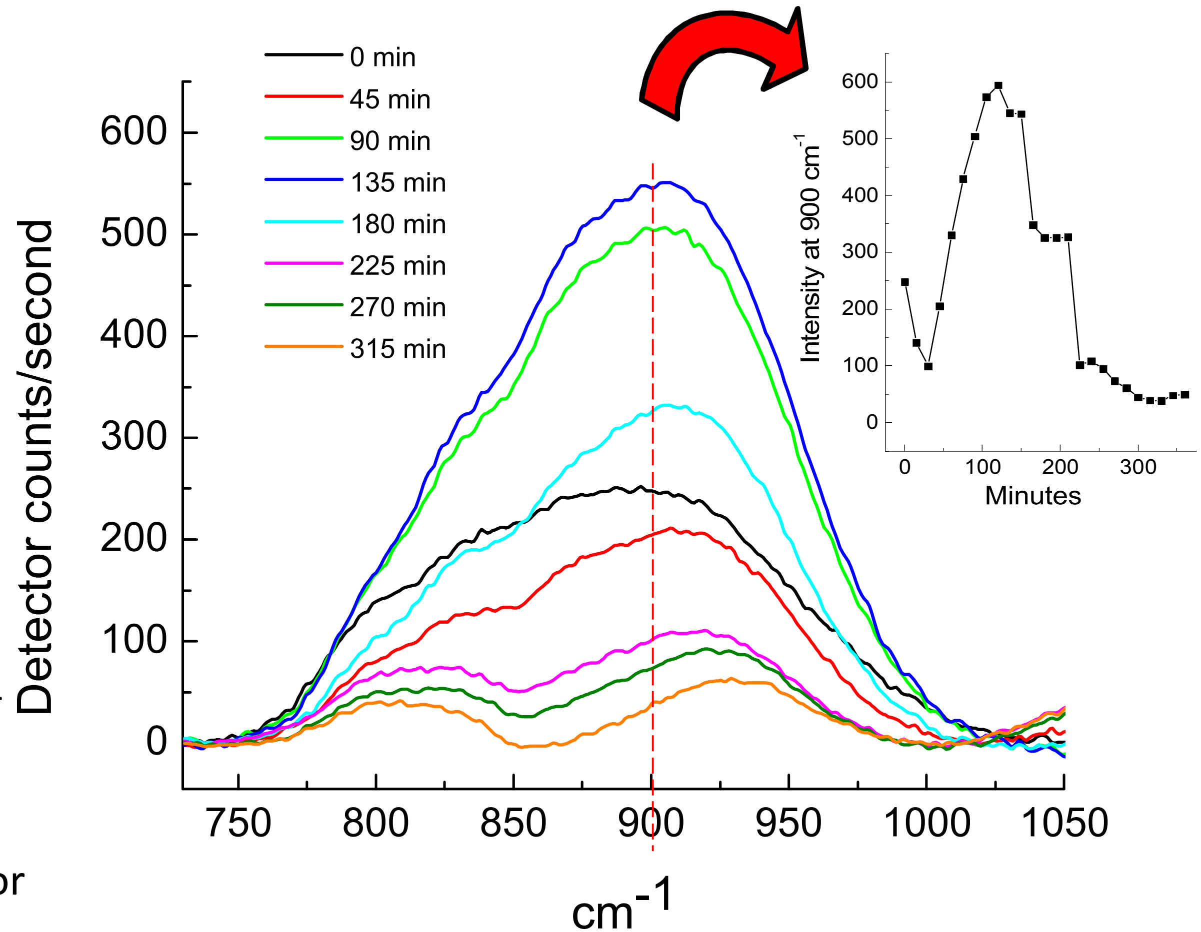
- Raman spectra do *not* match Ag_2O expectations.

There are bands at 85, 460(sh), 530, 565(sh), 650 and 951 cm^{-1}.



G.I.N. Waterhouse *et al. PCCP* **3** (2001) 3838-3845.

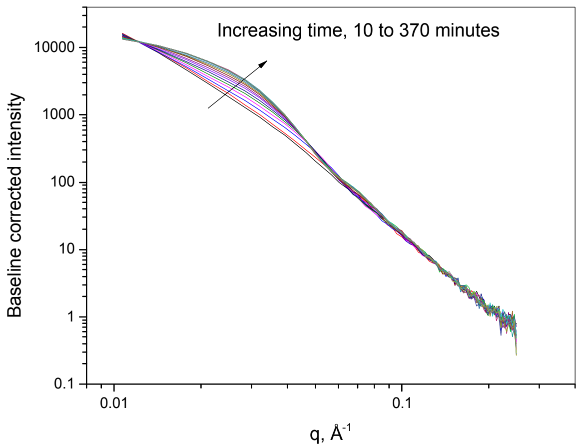
- The transition follows the growth and decline of a new species at ~900 cm^{-1}, perhaps the AgO$^-$ species.
- The kinetics align with the UV-vis results.
- Maltodextrin is believed to be incorporated into the initial material as a nanostructured or defective silver (hydr)oxide.

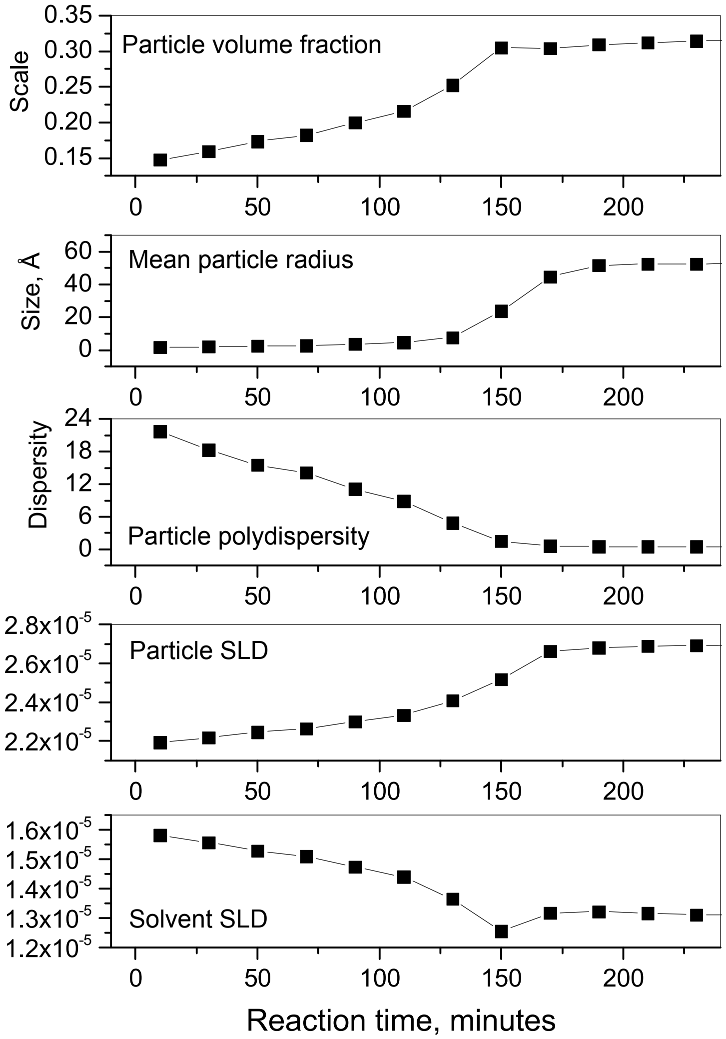


SAXS Measurement Found Size Focusing Growth of Uniform 5 nm Ag Nanoparticles

The formation of Ag np between 150 and 200 minutes is in good agreement with the formation of the UV-vis peak at 400 nm.

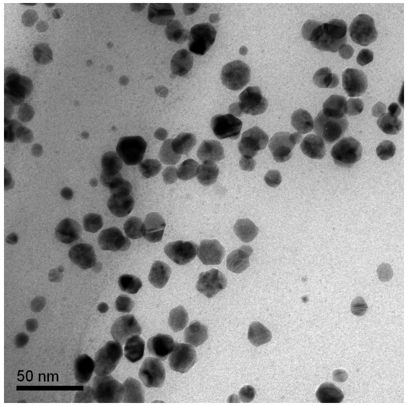
The particle uniformity becomes very good in this timeframe as well, even in this stirred reactor system.

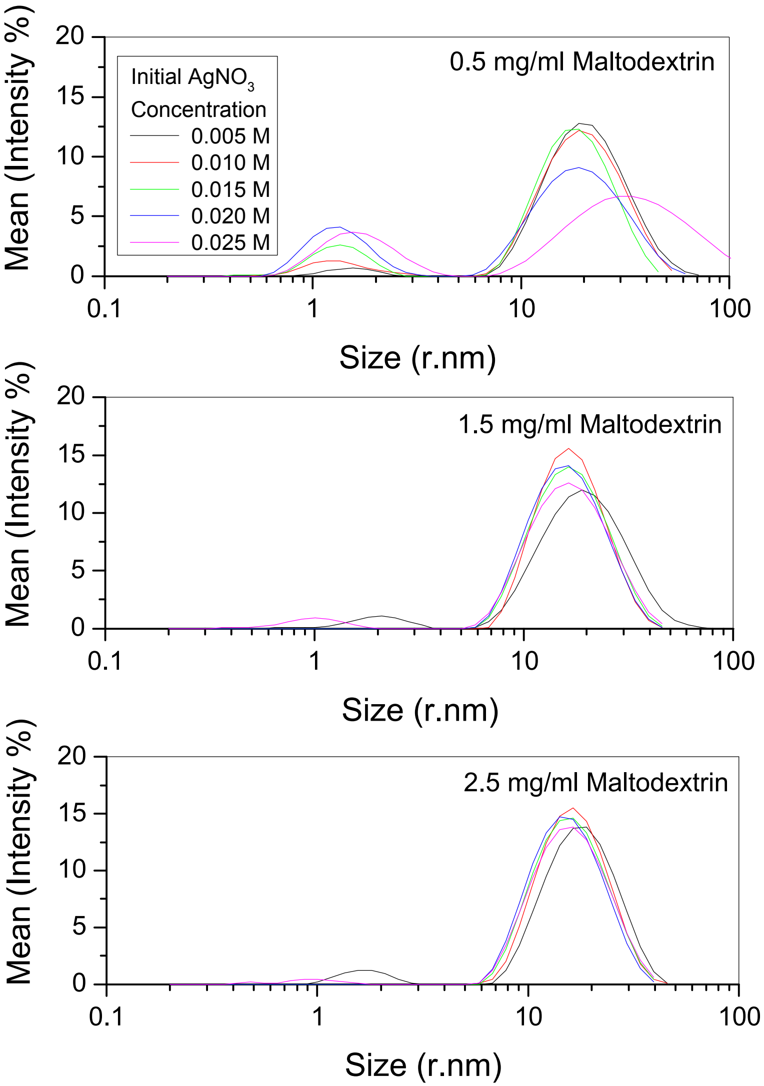




Additional Aggregation with Reaction Time Shows Colloidal Instability

24 hours later, Particle Size Increases to ~30-35 nm, with a distribution agreeing with the TEM images.

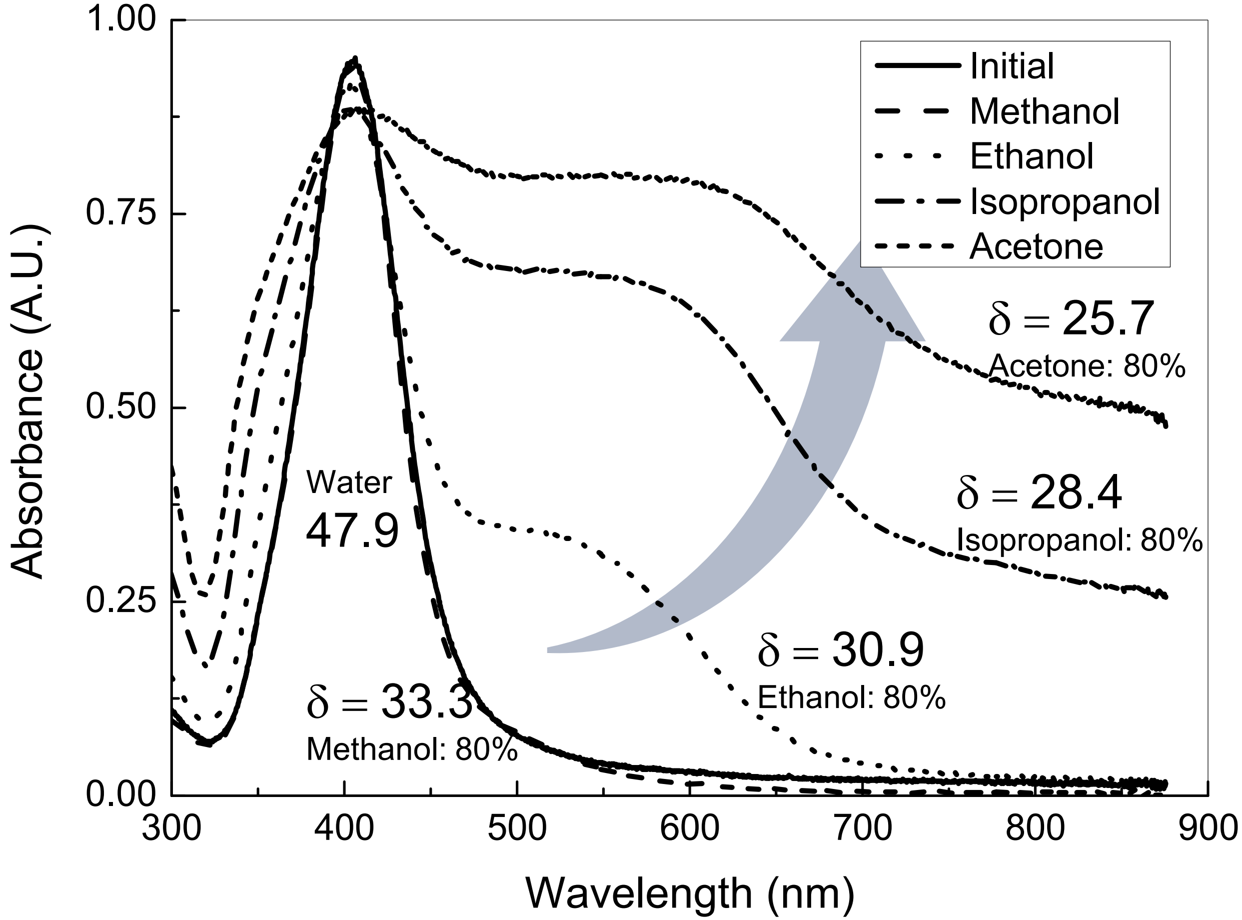




Increasing Maltodextrin content forms more uniform nanoparticles at 30 nm. Low $AgNO_3$ content leaves some "primary" nanoparticles.

Aggregation of the initially formed 5 nm Ag nanoparticles within maltodextrin aggregates could lead to bimodal distributions based on fusion.

The H-bonding Character of the Solvent Controls Colloidal Stability of the Nanoparticles



Ag np destabilized by addition of 80% non-solvent

Hildebrand parameter For each solvent δ ($MPa^{1/2}$)	
Water	47.9
Methanol	29.6
Ethanol	26.0
Isopropanol	23.5
Acetone	20.2

Aggregation is induced by non-H-bonding solvent character, establishing the surface adsorption of maltodextrin to Ag np via hydroxyl groups.

Methanol washes can be used to obtain cleaned suspensions without aggregation.

Summary and Conclusions

- A simple benchtop reaction shows that Maltodextrin behaves as a sugar reducing agent, and a colloidal stabilizer.
- The initial precipitate differs from the expected Ag_2O, and an unknown species characterizes the initial stages of the reducing reaction.
- Very uniform ~5 nm diameter nanoparticles are formed in the first 6 hours, as is characteristic of the size focusing regime for high soluble species growth.
- Further aging leads to 30-35 nm particles that are very similar to starch synthesis examples.
- Increasing maltodextrin concentrations lead to larger supermolecular structures, but the particle size stabilizes at 30-35 nm.
- In this second stage, association and fusion are proposed to lead to the larger particle size.
- The association forces between the silver nanoparticles and the maltodextrin are related to the hydrogen bonding character of the solvent, suggesting weak surface bonding.