In Situ Characterization of Silver Nanoparticle Synthesis in Maltodextrin Supramolecular Structures

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1 Table, 6 Figures

Abstract

The use of maltodextrin supramolecular structures (MD SMS) as a reducing agent and colloidal stabilizing agent for the synthesis of Ag nanoparticles (Ag NPs) identified three key points. First, the maltodextrin (MD) solutions are effective in the formation of well dispersed Ag NPs utilizing alkaline solution conditions, with the resulting Ag NPs ranging in size from 5-50 nm diameter. Second, *in situ* characterization by Raman spectroscopy and small angle X-ray scattering (SAXS) are consistent with initial nucleation of Ag NPs within the MD SMS up to a critical size of ca. 1 nm, followed by a transition to more rapid growth by aggregation and fusion between MD SMS, similar to micelle aggregation reactions. Third, the stabilization of larger Ag NPs by adsorbed MD SMS is similar to hemi-micelle stabilization, and monomodal size distributions are proposed to relate to integer surface coverage of the Ag NPs. Conditions were identified for preparing AgNPs with monomodal distributions centered at 30-35 nm Ag NPs.

Keywords: silver, nanoparticles, maltodextrin, synthesis, *in situ*

Introduction

Metal nanoparticles have been synthesized using a variety of biopolymers where the biopolymer often acts as the colloidal stabilizing agent.[1-7] However, the addition of a reducing agent such as ascorbic acid [3] or sugar [4, 8-10] can be necessary to control the properties of the nanoparticle, such as its size. Due to our interest in exploiting a biopolymer synthetic approach for the production of silver nanoparticles (Ag NPs) for direct write printing,[5, 11] control over the size, shape and aggregation of the Ag NPs was desired. To garner this control, it is necessary to understand the reaction and processing conditions (temperature, pH), the activity of the reducing agent with the silver precursor, and the colloidal stability of the resulting Ag NPs.[12-17] Polysaccharide biopolymers including starch are used in the synthesis of Ag NPs, and the Ag NPs nucleation is believed to occur within the hydrophobic regions of the swollen polymers.[18-25] For example, Ag^+ are reported to associate within the amylose backbone of starch,[26] allowing the starch to contain the Ag NPs during nucleation and growth.[1, 18] The properties of the starch biopolymer directly impact the final Ag NPs properties, including size,[9, 25, 27] morphology,[21, 24] colloidal stability,[10, 18, 23, 28] and chemical sensing capabilities.[29, 30]. Maltodextrin (MD) as a derivative of starch has demonstrated high solids loadings when used with ceramic powders as a plasticizing agent,[31] and hence MD stabilized Ag NPs could be useful in direct write printing.

MD is derived from starch by enzymatic based partial hydrolysis of the amylose polymer, resulting in largely linear oligomers (2-20 repeat units) of D-glucose molecules linked by α -1,4 bonds.[32, 33] These sugars are known to be moderate reducing agents due to their terminal aldehyde functionality, their reducing activity is promoted under alkaline conditions. [4, 10, 34] In contrast to higher molecular weight starch, maltodextrin forms supramolecular structures in

aqueous solutions due to the alignment of the amylose [i.e. oligo(D-glucose)] chains.[32] Thus, it was reasoned that maltodextrin supramolecular structures (MD SMS) could act as both the chemical reducing agent and as the colloidal stabilizing agent, greatly simplifying the formation of tailored Ag NPs. However, in contrast to many higher molecular weight ($> 10^5$) biopolymers, [4, 5, 35-37] MD has been surprisingly under explored for production of Ag NPs. The effects of the structural differences between MD and starch upon the development of Ag NPs were unclear and required further investigation.

In this work, the synthesis of Ag NPs using MD SMS under alkaline conditions was performed and characterized by UV-VIS and transmission emission spectroscopy (TEM). Detailed analysis of the Ag NPs nucleation process was conducted using *in situ* small angle X-ray scattering (SAXS) and Raman spectroscopy [1, 6, 38] Finally, dynamic light scattering (DLS) was used to characterize the size distributions and relate them to reactant concentrations to evaluate the scale-up potential of the process. The function of MD SMS as (1) the reducing agent and how the MD affects Ag NPs (2) nucleation and (3) particle size development as the colloidal stabilizing agent in the production of Ag NPs is elucidated.

Materials and Methods

The following chemicals were used as received: silver nitrate [$\text{Ag}(\text{NO}_3)$] and potassium hydroxide (KOH) (from Aldrich); maltodextrin (MD) (Maltrin MO40 from Grain Processing Corporation (Muscatine, IA)). Deionized water was purified using a Millipore Synergy 185 system to 18.2 M Ω resistance. Aqueous stock solutions of 0.1 mol L⁻¹ $\text{Ag}(\text{NO}_3)$, 0.1 mol L⁻¹ KOH, and 5.0 mg mL⁻¹ MD solutions and higher concentrations (1.0 mol L⁻¹ or 80 mg mL⁻¹) were freshly prepared as needed.

The representative synthesis was prepared by rapid addition of an aliquot of AgNO_3 stock solution to a solution of deionized water, KOH(aq) and MD to obtain final concentrations of 2.5 mg mL^{-1} MD, 0.05 mol L^{-1} KOH , and 0.015 mol L^{-1} AgNO_3 . The initial mixture of H_2O , MD, and KOH(aq) had a $\text{pH} = 12.5$. To this stirring clear solution, the 0.1 mol L^{-1} $\text{Ag(NO}_3\text{)}$ stock solution was added, and a dark brown color immediately formed, coupled with a decrease of 0.2 pH units. After 24 h of reaction time, the solution had darkened to black, with a yellow colored meniscus. Further detail is given in the Supplemental Information as “Synthesis Study”.

Transmission electron microscopy (TEM). Images were taken using a Philips CM 30 TEM operating at 300 kV, which is equipped with a Thermo Noran Six Energy Dispersive X-ray Spectroscopy (EDS) system for compositional analysis. Samples were prepared by diluting reaction suspensions in deionized water or by dispersing solids in water, and then allowing a droplet placed onto a carbon TEM grid to evaporate.

Raman Spectroscopy. Raman measurements were obtained using a Thermo Scientific DXR instrument at a wavelength of 785 nm and beam power of 25 mW. *In situ* Raman data was collected by focusing the instrumental optics through the bottom of a glass vial containing the reaction. Control experiments for Raman were run to confirm that the time dependence of the Raman spectra was not a result of sample illumination (indirect heating, or photoreduction of Ag^+ compounds).

Small-angle X-ray scattering Spectroscopy. (SAXS) SAXS was performed on a Bruker NANOSTAR instrument equipped with a microfocus Cu source and a $400 \text{ }\mu\text{m}$ beam definition pinhole. Identical concentrations as for Raman were used for SAXS analysis, making their characterization results a direct comparison. The solution was loaded into a 1 mm borosilicate capillary and sealed with wax. Evolution of the SAXS curve shape was obtained by taking

spectra every 20 min, with the initial point taken at 10 min after solution mixing allowing for sample loading and beam alignment. A background sample containing identical concentrations of MD and KOH(aq) but no AgNO₃ was collected under identical conditions for subtraction of this signal from the *in situ* data. Data fits were performed using NIST Center for Neutron Research SANS package for Igor Pro, using appropriate scattering length densities (SLDs) for X-rays rather than neutrons.[39]

Dynamic light scattering (DLS). DLS measurements of particle size distribution (PSD) were conducted using a Zetasizer NS from Malvern Instruments. MD solutions were prepared in deionized water adjusted to pH 12.2 using NaOH (1 mol L⁻¹), and measured for particle size using the protein model parameters. Ag NPs samples were prepared by diluting 100 µL of the reactant suspension with 1.5 mL of deionized water, producing a visibly transparent suspension. Five measurements of 10 iterations (50 total) were performed on each sample, leading to an average for the peak position and standard deviation for both MD SMS and Ag NPs samples.

Viscosity: Shear rate sweeps of MD solutions at pH 12.2 were measured using a ramp from 1 to 1000 s⁻¹ over 120 sec, a dwell at 1000 s⁻¹ for 60 sec, and a ramp from 1000 to 1 s⁻¹ over 120 sec. The viscometer is a ThermoFisher MARS II, using a C60 1° cone and plate measuring configuration. The temperature was set at 25 °C using a Phoenix water bath system.

Results and Discussion

1. The Reducing Action of Maltodextrin for Silver Nanoparticles

Literature studies of alkaline solutions of Ag⁺(aq) in the presence of OH⁻ ions reportedly yield an unreduced silver precipitate,[9, 10] that should be the thermodynamically stable Ag₂O.[40] Therefore, the initial addition of reactants was expected to precipitate Ag₂O (Eq 1).

The solubility minimum for Ag₂O is pH 12, with solubility levels increasing both at lower pH (via Ag⁺ ions) and at higher pH (as the [Ag(OH)₂][−] ion).[40] Increasing alkalinity above pH 12 favors the solubility of the [Ag(OH)₂][−] species, leading to the more rapid dissolution kinetics as the Ag reduction reaction progresses. The formation of Ag NPs in the MD SMS was expected to follow a dissolution-crystallization process between the initially precipitated Ag₂O phase and the final Ag NPs material. Within the MD SMS, the [Ag(OH)₂][−] would be reduced as the MD was oxidized due to the conversion of a terminal aldehyde to a carboxylic acid (Eq. 2), [41] resulting in the formation of the desired Ag NPs.

As soluble Ag species are reduced according to Eq. 2, solubilization of Ag₂O precipitates in alkaline conditions within the MD SMS would supply new [Ag(OH)₂][−] until the reaction to form Ag NPs is completed. The Ag NPs should form slowly under near constant growth conditions, allowing for *in situ* observation of the nucleation and growth.

Synthesis. From a series of scoping experiments, the production of Ag NPs in a MD alkaline solution (or MD SMS) was verified and optimized. Additional information regarding these studies can be found in the supporting information (see S.I. Fig. S1 – S5 for PXRD, TEM, and UV-VIS, respectively). For the representative synthesis, the addition of Ag(NO₃) to a stirring MD solution at room temperature rapidly formed a dark brown solution, which over 24 h, yielded a black solution as described in the Materials and Methods section. The sample was destabilized with excess acetone and centrifuged to yield a black powder for characterization.

Ex-Situ Characterization. The dried sample after acetone precipitation was analyzed by XRD and found to be consistent with the formation of Ag⁰ [PXRD pattern (JCPDS 04-0783 as shown in SI Fig. S1 and S2). Selected area diffraction TEM analyses also revealed Ag NPs had formed as shown in Fig. 1. The Ag NPs have faceted interfaces and range in size from ~5 to 50 nm in diameter at 24h. A high-resolution TEM image of smaller Ag NPs (Figure 1b) indicated that the Ag NPs were found to be terminated with {111} habit planes and that twinning occurs within the nanoparticles. This is consistent with the literature reports where FCC metals are typically bounded by habit planes of {100}, {100}, or {111} facets [42] and exhibit structures with multiple twinning.[43] The reaction at room temperature was found to have a timescale on the order of hours (see S.I. Fig. S4 and S5). This data demonstrated that the alkaline MD SMS system was a viable method for the production of Ag NPs. Furthermore, the slow timescale of the rate of reaction indicated that the nucleation and growth of the Ag NPs in this system could be readily followed using *in situ* techniques.

2. *In Situ* Characterization of Silver Nanoparticles Nucleation in MD SMS

A pH value of 12.5 was chosen for both characterization methods based on the initial scoping studies from UV-VIS (see S.I. Fig. S4 and S5). Samples were directly analyzed from the representative synthesis to observe the transition between the precursor and Ag NP precipitates. The use of complimentary *in situ* techniques was chosen to follow (a) the precipitation of the silver oxide precursor by Raman spectroscopy and (b) the subsequent nucleation and growth into Ag NPs by SAXS.

a. *Raman Spectroscopy.* The only Raman spectral region where significant changes were observed was between ca. 750 and 1000 cm⁻¹ (Figure 2). Initial peaks are present as three overlapping bands at ca. 800, 850, and 890 cm⁻¹. The location of these peaks shifts to 795, 835

and 900 cm^{-1} , and grows in intensity to a maximum value at 135 min. Then, the measured peaks decrease into two weaker bands appearing at 805 cm^{-1} and 930 cm^{-1} upon the completion of the reaction.

The observed 900 cm^{-1} band is not reported to relate to either Ag_2O or MD.[44, 45] Based on Ostwald's rule of stages, a metastable phase can be formed in place of the thermodynamically stable Ag_2O under rapid precipitation conditions. It is surmised that the initial material formed upon mixing of $\text{Ag}(\text{NO}_3)$ with alkaline solution is a poorly crystallized $\text{AgO}(\text{OH})$ material and not the previously reported thermodynamically stable Ag_2O phase.[40] The origin of these Raman peaks was tested using two non-reducing systems as controls (See S.I. Fig. S6) as: (a) a substitution of starch for MD SMS and (b) the reaction without any polysaccharide (MD SMS or starch). In both cases, the development of a broad strong peak at 900 cm^{-1} was observed, with the rate of formation varying depending on the exact conditions. In both controls, the strong 900 cm^{-1} peak does not decrease in intensity over time. Thus, it is reasoned that the formation of the initial precipitate accounts for the growth of the 900 cm^{-1} peak. The rate of $\text{AgO}(\text{OH})$ formation (as inferred from the Raman 900 cm^{-1} peak) was: no polysaccharide control (10 min) > starch control (60 min) > Ag MSDS reaction (135 min). The slower rate of reaction for starch or maltodextrin as compared to no polysaccharide can be attributed to the fact that polysaccharides are surface active in the $\text{AgO}(\text{OH})$ crystallization, and complexation of Ag^+ ions within or on the surface by hydroxyl groups will slow reaction kinetics.

Small-angle X-ray scattering. The nucleation and growth of the Ag NPs in real time was monitored using SAXS using identical solution composition as examined by Raman spectroscopy in Figure 3 (background corrected data is given in S.I., Fig S7). Analysis of SAXS

data was done by fitting to a ‘scattering polydisperse spheres’ model. (S.I. Fig. S8). Inspection of the SAXS data for the Ag MD SMS reaction shown in Fig. 3 revealed a particle growth mechanism consistent with an initial nucleation step, and slow growth of the initial nuclei from 0.35 to 0.9 nm diameter at 135 min. After 135 min, rapid growth ensues resulting in a monodisperse size of ca. 10 nm (i.e. after 200 min). The Ag NPs volume fraction is found to grow steadily to a maximum at 150 min, and the poly(dispersity) of the particles consistently decreases during the nucleation and growth process. Narrowing of the particle poly(dispersity) with time is typical of a size focusing growth process, typically occurring in the presence of a high concentration of solution species.[46] In our case, the initially precipitated AgO(OH) material acts as a source of Ag ions via dissolution, until all the AgO(OH) is consumed. The reduction of Ag⁺ by MD aldehyde moieties forms the initial nuclei within the MD SMS, and the subsequent linear growth rate indicates that chemical reduction is the rate limiting step in Ag NPs formation, i.e. that dissolution of AgO(OH) and/or ion transport to the MD SMS is not the rate limiting factor.

3. Colloidal Stabilization in Ag NPs Growth

Scheme 1 shows a generalization of the overall reaction as determined from the data. As stated previously, the initial AgO(OH) precipitate is proposed to be in equilibrium with the [Ag(OH)₂]⁻ (Scheme 1 – Stage 1). The Ag⁺ incorporate into the MD SMS structures, where reduction occurs to form the initial Ag NPs nuclei. This is analogous to starch stabilized Ag NPs reported in the literature.[26] The following data verifies this reaction mechanism.

It is known that the MD SMS are stable, micelle-like associated polymers based on helix alignment of glucose oligomers.[32] The average size of MD SMS were measured by DLS using a protein model (see Table 1). A bimodal size distribution of the MD SMS was found with peak

sizes that are concentration dependent on the MD. Larger sizes of MD SMS become more prevalent as the MD concentration was raised, as is commonly noted in turbidity studies.[32] Nevertheless, the 15-25 nm MD SMS are an appreciable fraction of the *in situ* arrangements formed. In dilute conditions, over 80% of the MD SMS associates into structures of 15-25 nm diameter. It is of note that these *in situ* MD SMS assemblies exist in solution and cannot be isolated. For convenience of discussion, a term for these smaller structures as “primary” MD SMS will be used.

These “primary” MD SMS would be large enough to incorporate the initial <1 nm Ag nuclei (Scheme 1 – Stage 2). Continued particle growth in the “primary” MD SMS results in the disruption of the packing structure of the amylose chains. The Ag NPs nuclei are proposed have a critical size for inclusion or expulsion from the MD SMS, related to the MD SMS self-assembly energy. This variation in behavior between starch and MD SMS for Ag NP nuclei is the significant feature of these MD SMS.[1] Starch biopolymers form helical coils in solution,[32] creating stronger supramolecular associations.[1] In contrast, MD solutions exhibit Newtonian viscosity behavior with concentration due to weak H-bonding forces between the chains.[33] Thus, MS SMS are easily sheared and reformed in solution. This would favor transport of a critical Ag NP nuclei to the surface region of the MD SMS where MD alignment is less disrupted. The expelled Ag NPs nuclei would be poorly protected from aggregation and fusion between multiple MD SMS during Brownian motion induced contacts, similar to surfactant micelle interactions. Shear-induced or micelle exchange reactions of the growing Ag NPs would further broaden the particle size distribution, causing processing conditions to influence the development of a ripened particle size distribution (PSD). Although classic

Ostwald ripening mechanisms affect PSD, increasingly aggregation mechanisms for crystal growth are found to control nanoparticle size development. [47-49]

High molecular weight starches produce a stable colloidal dispersion for adsorbed polymer layers that completely cover the nanoparticle. [1, 18, 38] MD SMS are proposed to adsorb to Ag NPs with little variation from their supramolecular structural state (Stage 3 of Scheme 1). As the extent of surface coverage of the MD SMS on Ag NPs will strongly affect an aggregative mechanism of particle growth, the PSD development of the Ag NPs for varying MD SMS contents was studied. DLS measurements were undertaken to determine how ratios of solution components produced the Ag NPs from a 24 h growth process (Ag-24h) as related to the final particle size and distribution. The AgNO_3 source concentration was varied from 5 to 25 mmol L^{-1} in two concentrations of MD solution (0.5 and 2.5 mg mL^{-1}) under a common KOH(aq) level of 0.05 mol L^{-1} , giving a pH of 12.5. Ag NPs samples were directly diluted into deionized water from the stirred reaction vessel, without a washing step or non-solvent addition in order to characterize the native state of aggregation. Figure 4 shows the PSD for each sample after 24 h of reaction, and Table 1 compares characterization results for pure MD solutions and Ag NPs synthesis reactions in alkaline solution.

Origin of Particle Distribution. In broad terms from Figure 4a, the lowest MD concentration (0.5 mg/mL) resulted in a bimodal size distribution with peaks located at 5 and 35 nm as a function of AgNO_3/MD ratio. The 5 nm peak agrees with the SAXS measurements of the initial Ag NPs but the larger particle size for Ag NPs-24h confirms further aggregation. At the highest ratio of silver reactant to the solution (25 mmol L^{-1} Ag/0.5 mg mL^{-1} MD), the dominant peak center increased to ~70 nm, showing that further silver reactant in solution leads to greater particle size. Insufficient protection by primary MD SMS at a high silver concentration

predictably results in greater particle size and a broader distribution. It is clear in Figure 4b that an increase in the solution MD concentration to 2.5 mg mL⁻¹ results in a monomodal particle size distribution of the Ag NPs (mean size of 30-35 nm), for all silver reactant concentrations. These particles are significantly larger than the “primary” MD SMS and would require multiple MD SMS to adsorb over the nanoparticle surface for colloidal stability.

Suitable conditions for uniform particle formation were found for MD concentrations of 2.5 mg mL⁻¹ and Ag(NO₃) at 15 mmol L⁻¹, at pH 12.5. This ratio was used for increasing the concentration in Ag NPs synthesis, and PSD results are given in Table 1. Up to 0.12 mol L⁻¹ AgNO₃ and 20 mg mL⁻¹ MD, the formation of stable 30-35 nm diameter Ag NPs was maintained. At 40 mg mL⁻¹ and higher concentrations of MD, the silver particle size increased. Additionally, pure MD solutions begin to exhibit larger viscosity values in Table 1, indicating greater interaction between MD SMS.

The aggregative growth of Ag NPs between MD SMS after the nuclei are expelled explains the development of the PSD under the various conditions tested here. Because the MD SMS are self-assembled structures, they do not behave as typical molecular or polymeric stabilizers. Assuming MD SMS retain their self-assembled structure during adsorption, the MD SMS would pack as integer units over the Ag NPs surface, similar to the hemi-micelle stabilization of colloids.[50] As Scheme 1 Stage 3 illustrates, the coverage of the Ag NPs surface is accomplished by stacking equal units (circles) of MD. Geometric coverage can create optimal or “perfect” sizes based on the sizes of the sphere and the covering circles. [51-53] Tarnai and Gaspar detail the best covering and density of coverage for equal circles over a sphere, and as integer circles are added (in this case, growth of the Ag NPs under constant MD SMS surface adsorbates), the density of surface coverage is not a smooth function. There are

integer values with locally greater coverage, such as 6, 12, or 22 circles.[53] This suggests, as a crude approximation, that there is a ratio of particle size to MD SMS size that will develop well-protected Ag NPs. If so, such a stable size should be maintained as solution components are concentrated. This is proposed as the mechanism for stabilizing the mean peak of the Ag NPs at a value of 30-35 nm.

As an approximation, this model would explain the variation of the factors controlling the particle distribution. For example, low MD concentration allowed for the 5 nm Ag NPs to be present over many AgNO₃ concentrations. A low concentration of MD SMS will result in a greater separation distance between MD SMS, and therefore less aggregation events. The 5 nm size Ag NPs are present due to a low frequency of interaction, rather than from efficient stabilization. The intermediate concentrations of MD (2.5 – 20 mg mL⁻¹) are populated with the “primary” MD SMS, and the packing theory for circles on spheres is applied to their stability. At 40 mg mL⁻¹ and higher, increased viscosity of the solution indicates closer proximity of the MD SMS and greater interaction during shear. Agglomeration of the initial nanoparticles within or between aggregates is likely a particle concentration and proximity effect. Due to the variation in shear and closer separation distance, it is believed that these particles can easily diffuse together and fuse into larger sizes, as observed.

Conclusions

The use of MD as a single reagent for reduction and stabilization of Ag NPs has been evaluated. MD forms supramolecular structures in alkaline solution having a “primary” size of 15-25 nm. AgNO₃ reacts in alkaline solutions with the rapid formation of a dark brown solution, reasoned to be a nanosized Ag(O(OH)). Reduction of silver species occurs by dissolution-precipitation within MD SMS structures. *In situ* characterization (Raman and SAXS) found the MD SMS act as protectants for < 1 nm Ag NPs nuclei, but due to their lower molecular weight, expel the ~1 nm diameter Ag NPs with a rapid increase in growth rate at 135 min. These single digit nanoparticles further associate and ripen into 30-35 nm diameter faceted nanoparticles after 24 h. A stable particle size centered at 30-35 nm diameter Ag NPs was observed for Ag(NO₃) solution concentrations as high as 0.12 mol L⁻¹. The integer coverage of Ag NPs similar to hemi-micelles on surfaces is proposed as the stabilization mechanism for this observed size. MD SMS restructuring based on shear forces and closer proximity at higher reactant concentrations is proposed to lead to larger particle size. The variation in stabilization behavior between MD SMS and starch is proposed to result from the molecular weight based associative property differences between the two biopolymers.

Supporting Information Available: A description of the reaction procedure and images of the products from the typical reaction are provided as supplementary information. Figures showing the Raman spectra for the reaction tested without MD and in the presence of starch in place of MD show the development of the initial precipitate. Data fits for the SAXS data using polydisperse sphere and core-shell models are given as a residuals graph. The material is available free of charge via the Internet at <http://www.sciencedirect.com>.

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Figure 1. (a) TEM and (b) HRTEM of synthesized Ag NPs. Inset is the diffraction spot pattern from Ag NPs, indexed for FCC silver metal.

Figure 2. Raman data showing changes in Ag chemical speciation over time during the synthesis of Ag NPs.

Figure 3. SAXS fit values, obtained using a model for polydisperse spheres.

Figure 4. Particle size distribution (intensity based) for 0.05 M KOH concentration, with rising Ag(NO₃) content. (a) 0.5 mg mL⁻¹ MD; (b) 2.5 mg mL⁻¹ MD.

List of Schemes

Scheme 1. Proposed reaction processes in formation of silver nanoparticles in maltodextrin supramolecular structures.

List of Tables

Table 1. Concentration effects on MD solution properties and results of optimal Ag NPs synthesis.

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Table 1. Concentration effects on MD solution properties and results of optimal Ag NPs synthesis.

Maltrin MO40 (mg/mL)	Maltrin MO40 - PSD Diameter & Std Dev (nm); [Intensity %]		Viscosity at 500 s ⁻¹	Ag(NO ₃) (mol L ⁻¹)	KOH (mol L ⁻¹)	Ag NPs Diameter & Std Dev (nm)
0.5	25.7 ± 17.8 [93%]	3454 ±1304 [4.8%]	1.067			
1.5	25.6 ± 18.7 [95%]	2512 ±954 [2.3%]	1.076			
2.5	17.4 ± 9.8 [85%]	633 ±560 [12%]	1.088	0.015	0.05	35.0 ±16.0
5	17.0 ± 9.5 [80%]	331 ± 234 [17.4%]	1.102	0.03	0.10	39.8 ±15.3
10	16.8 ± 10.1 [68%]	367 ±254 [29.4%]	1.141	0.06	0.20	30.4 ±10.1
20	17.9± 13.2 [88%]	302 ±220 [8.2%]	1.233	0.12	0.40	32.0 ±12.8
40	16.9± 13.0 [68%]	250 ± 167 [28%]	1.425	0.24	0.80	65.5 ± 31.6
80	17.7 ±14.2 [59%]	1107 ±597 [33%]	1.925	0.48	1.6	86.7 ±51.8

Figure(s)

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Scheme 1.