



In situ characterization of silver nanoparticle synthesis in maltodextrin supramolecular structures



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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 to 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 Ag NPs with monomodal distributions centered at 30–35 nm Ag NPs.

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1. 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 and 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 (>10⁵) 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 electron 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,

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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.

2. Materials and methods

The following chemicals were used as received: silver nitrate (AgNO_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 AgNO_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 H₂O, MD, and KOH(aq) had a pH 12.5. To this stirring clear solution, the 0.1 mol L⁻¹ AgNO_3 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”.

2.1. 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.

2.2. 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).

2.3. Small-angle X-ray scattering spectroscopy (SAXS)

SAXS studies were performed on a Bruker NANOSTAR instrument equipped with a microfocus Cu source and a 400 μm beam definition pinhole. Identical concentrations as for Raman were used for SAXS analysis, allowing for a direct comparison of their data. 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 AgNO_3 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].

2.4. 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.

2.5. Viscosity

Shear rate sweeps of MD solutions at pH 12.2 were measured using a ramp from 1 to 1000 s⁻¹ over 120 s, a dwell at 1000 s⁻¹ for 60 s, and a ramp from 1000 to 1 s⁻¹ over 120 s. 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.

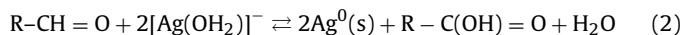
3. Results and discussion

3.1. 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 Ag_2O [40]. Therefore, the initial addition of reactants was expected to precipitate Ag_2O (Eq. (1)).



The solubility minimum for Ag_2O is pH 12, with solubility levels increasing both at lower pH (*via* Ag^+ ions) and at higher pH (as the $[\text{Ag}(\text{OH})_2]^-$ ion) [40]. Increasing alkalinity above pH 12 favors the solubility of the $[\text{Ag}(\text{OH})_2]^-$ 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 Ag_2O phase and the final Ag NPs material. Within the MD SMS, the $[\text{Ag}(\text{OH})_2]^-$ 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 Ag_2O precipitates in alkaline conditions within the MD SMS would supply new $[\text{Ag}(\text{OH})_2]^-$ 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.

3.1.1. 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 SI Figs. S1–S5 for PXRD, TEM, and UV–VIS, respectively). For the representative synthesis, the addition of AgNO_3 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 Section 2. The sample was destabilized with excess acetone and centrifuged to yield a black powder for characterization.

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