

Completely "Green" Synthesis and Stabilization of Metal Nanoparticles

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Over the past decade there has been an increased emphasis on the topic of "green" chemistry and chemical processes.^{1–5} These efforts aim at the total elimination or at least the minimization of generated waste and the implementation of sustainable processes through the adoption of 12 fundamental principles.¹ Any attempt at meeting these goals must comprehensively address these principles in the design of a synthetic route, chemical analysis, or chemical process.^{1,3} Utilization of nontoxic chemicals, environmentally benign solvents, and renewable materials are some of the key issues that merit important consideration in a green synthetic strategy. In the present work, we present a totally green approach toward the synthesis and stabilization of metal nanoparticles.

Metal and semiconductor nanoparticles are of importance due to their potential applications in emerging areas of nanoscience and technology.^{6–16} Size, shape, and surface morphology play pivotal roles in controlling the physical, chemical, optical, and electronic properties of these nanoscopic materials. Preparation of nanoparticles generally involves the reduction of metal ions in solutions or in high temperature gaseous environments. The high surface energy of these particles makes them extremely reactive, and most systems undergo aggregation without protection or passivation of their surfaces.^{12–16} Some of the commonly used methods for surface passivation include protection by self-assembled monolayers, the most popular being thiol-functionalized organics;¹³ encapsulation in the H₂O pools of reverse microemulsions;¹⁷ and dispersion in polymeric matrixes.¹⁸

The three main steps in the preparation of nanoparticles that should be evaluated from a green chemistry perspective are the choice of the solvent medium used for the synthesis, the choice of an environmentally benign reducing agent, and the choice of a nontoxic material for the stabilization of the nanoparticles. Most of the synthetic methods reported to date rely heavily on organic solvents. This is mainly due to the hydrophobicity of the capping agents used. There have been approaches reported¹⁹ for the synthesis of H₂O-soluble metal nanoparticles; however, to date a unified green chemistry approach to the overall process of nanoparticle production has not been reported.

In the present approach, H₂O is utilized as the environmentally benign solvent throughout the preparation. Although the use of alternative solvents such as supercritical CO₂ has been successful for the synthesis of nanoparticles,^{20,21} the use of CO₂-philic surfactants presents difficulty in isolation and recovery of the nanoparticles. There are also questions regarding the toxicity of the microemulsion components.²² The second concern in a green nanoparticle preparation method is the choice of the reducing agent. The majority of methods reported to date use reducing agents such as hydrazine, sodium borohydride (NaBH₄), and dimethyl formamide (DMF). All of these are highly reactive chemicals and pose potential environmental and biological risks. In the present method, the reducing sugar, β -D-glucose, is used as the reducing agent. With

gentle heating, this system is a mild, renewable, inexpensive, and nontoxic reducing agent.

The final, and perhaps most important, issue in the preparation of nanoparticles is the choice of the capping material used to protect or passivate the nanoparticle surface. There are several issues that should guide the choice of the capping agent, and these vary significantly from the required size ranges and morphologies of the nanoparticles to the targeted application. In the present preparation method, starch is selected as the protecting agent for several reasons.

It is well known that solutions of polymeric materials contain size-confined, nanosized pools of inter- and intramolecular origin, which can be used for the synthesis of nanoparticles. Linear¹⁸ as well as dendritic²³ polymers have been successfully used for nanoparticle synthesis. Polyhydroxylated macromolecules present interesting dynamic supramolecular associations facilitated by inter- and intramolecular hydrogen bonding resulting in molecular level capsules, which can act as templates for nanoparticle growth. Starch and, in particular, amylose form a wide range of inclusion complexes with numerous guest molecules.^{24,25} Amylose is a renewable polymer formed by the α -1,4 linkages between D-glucose units and adopts a left-handed helical conformation in aqueous solution. Starch was recently shown to allow the dissolution of single-walled carbon nanotubes in aqueous media.²⁶ The extensive number of hydroxyl groups present in starch can, in the present case, facilitate the complexation of silver ions to the molecular matrix. Analogously, it is plausible that silver ions can play a significant role in guiding the supramolecular organization among starch molecules. In addition to these criteria for the use of starch in the solution mixture, there are several key advantages to the use of this renewable material as the protecting agent. First, it is possible to form a dispersion of starch in H₂O, and so one can completely avoid the use of organic solvents. Second, the binding interaction between starch and the metal nanoparticles is relatively weak as compared to the interaction between the nanoparticles and typical thiol-based protecting groups. This implies that the protection should be easily reversible at relatively higher temperatures, enabling the separation of these particles. Additionally, it is possible that the use of place exchange reactions¹⁹ could be used to easily functionalize the nanoparticles. Finally, and perhaps most importantly, starch-protected nanoparticles can be readily integrated into systems relevant for pharmaceutical and biomedical applications.

The preparation of starched silver nanoparticles is quite straightforward. In a typical preparation, a 100 μ L aliquot of a 0.10 M solution of AgNO₃ was added to 6.0 mL of a 0.17% (wt) aqueous solution of soluble starch (Sigma). After complete dissolution of these components, a 150 μ L aliquot of a 0.10 M aqueous solution of β -D-glucose (Sigma) was added and further stirred. The mixture was heated to 40 °C and was maintained at this temperature for 20 h. All solution components were purged with argon before use, and reduction proceeded in the presence of argon to eliminate

oxygen. The solution turned light yellow after 1 h, indicating the initial formation of silver nanoparticles. The UV-vis absorption spectrum of the sample after 20 h, showing the surface plasmon absorption of these Ag(0) particles, is presented in Figure 1.

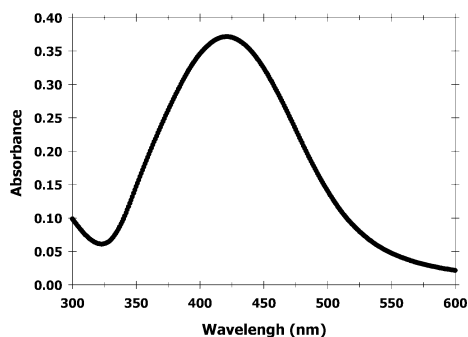


Figure 1. The surface-plasmon absorbance spectrum of silver nanoparticles formed in the aqueous starch dispersion ($\lambda_{\text{max}} = 419$ nm).

A typical transmission electron microscope (TEM) image of the nanoparticles formed is presented in Figure 2. In general, the particles are isotropic (i.e., low aspect ratio) in shape. These results illustrate the synthesis of Ag(0) nanoparticles through reduction of Ag^+ inside the nanoscopic starch templates. The hydroxyl groups act as passivation contacts for the stabilization of the nanoparticles formed inside these templates.

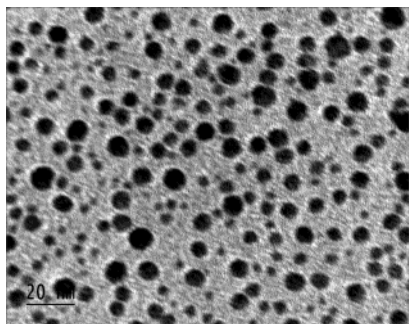


Figure 2. Typical TEM image of starched silver nanoparticles. The scale bar corresponds to 20 nm.

Figure 3 presents a histogram of the particle size distribution with the mean particle diameter = 5.3 nm and a $\sigma = 2.6$ nm. More than 90% of the particles are in the size range from 1 to 8 nm, indicating the possible size selectivity of the starch solution templates (a few particles were also observed in the 20 nm range). While these preliminary results demonstrate the proof of concept, it may be possible that better control of the particle size and polydispersity are achievable through the proper choice of the many reducing and protecting carbohydrates available as well as thermodynamic conditions. The solutions of dispersed silver nanoparticles in starch are highly stable and show no signs of aggregation even after 2 months of storage.

In conclusion, we have demonstrated the first comprehensive application of green chemistry principles in the synthesis of metallic nanoparticles.

The particles produced are stable and comparable in size and polydispersity to those produced using typical methods. The use of environmentally benign and renewable materials as the respective reducing and protecting agents, glucose and starch, as well as a benign solvent medium, offers numerous benefits ranging from environmental safety to ready integration of these nanomaterials

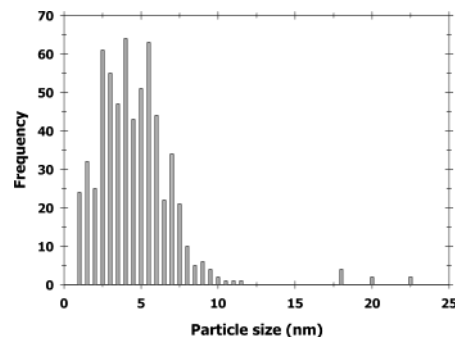


Figure 3. Histogram showing the size distribution of the silver nanoparticles (the average particle size = 5.3 nm and $\sigma = 2.6$ nm). The total number of particles counted for the histogram is 624.

to biologically relevant systems. This combination of solvent and renewable reactants presents a wide range of possibilities for the further development of green nanoparticle syntheses.

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Supporting Information Available: TEM image (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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