

Glutathione promoted expeditious green synthesis of silver nanoparticles in water using microwaves

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Received 2nd February 2009, Accepted 27th April 2009

First published as an Advance Article on the web 5th May 2009

DOI: 10.1039/b902184a

Silver nanoparticles ranging from 5–10 nm in size have been synthesized under microwave irradiation conditions using glutathione, an absolutely benign antioxidant that serves as the reducing as well as capping agent in aqueous medium. This rapid protocol yields the nanoparticles within 30–60 s at a power level as low as 50 W. The effect of microwave power on the morphology of ensuing silver nanoparticles is investigated for this green and sustainable procedure which is adaptable for the synthesis of palladium, platinum and gold nanoparticles.

Introduction

Over the past decade, the increased emphasis on developing green and sustainable chemical processes has led to numerous efforts toward the elimination or at least minimization of waste generation. Implementing sustainable methodologies in almost all areas of chemistry, including nanomaterial synthesis¹ entails eliminating toxic reagents and solvents. The choice of an environmentally benign solvent, the use of a multipurpose agent that serves the purpose of a reducing, capping and dispersing agent are some of the key issues that may be addressed in green synthesis of nanomaterials.¹

Synthesis of silver nanoparticles is of much interest to the scientific community because of their wide range of applications in catalysis,² electronics,³ photonics,⁴ optoelectronics,⁵ sensing,⁶ and pharmaceuticals.⁷ Specifically, these nanoparticles are strong candidates for Surface Enhanced Raman Spectroscopic (SERS) studies⁸ that yet again prompts the interest of the scientific community to develop newer green synthetic methods for obtaining these nanoparticles.

Numerous pathways have been employed for the synthesis of silver nanoparticles with different morphologies as well as size distributions including NaBH₄ reduction,⁹ polyol process,^{10–12} use of plant extracts,^{13,14} photoreduction¹⁵ *etc.* Most of these proceed *via* wet chemistry methods with the use of highly reactive reducing agents such as sodium borohydride, hydrazine *etc.* that are not environmentally friendly. Some of them use noxious and highly volatile organic solvents. To eliminate the use of toxic reducing agents, the use of amino acids,¹⁶ vitamins,¹⁷ and other eco-friendly biological agents in the synthesis of metal nanoparticles have been reported.^{18–20} In conjunction with the use of these

eco-friendly reducing agents and solvents, microwave irradiation (MW) is emerging as a rapid and environment friendly mode of heating for the generation of nanomaterials. It offers a rapid and volumetric heating of solvents, reagents, and intermediates, that provides uniform nucleation and growth conditions for nanomaterial synthesis.^{21–25}

Engaged in the development of greener and sustainable pathways for organic synthesis and nanomaterials,^{26–33} herein we report an easy and rapid synthesis of silver nanoparticles using glutathione as a reducing as well as capping agent under MW irradiation conditions in pure aqueous medium. To the best of our knowledge, glutathione has not been reported for the synthesis of silver nanoparticles.

The choice of glutathione (Fig. 1, GHS), as a reducing agent was made because of its benign nature and the presence of a highly reactive thiol group that can be used to reduce the metal salts. GHS is a tripeptide consisting of glutamic acid, cysteine and glycine units and is an ubiquitous antioxidant present in human and plant cells. Besides the thiol group, each GSH molecule also contains amine and carboxylate functionalities that provide coupling possibilities for further cross-linking to other molecules of biological or sensing interest.

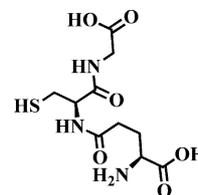


Fig. 1 Molecular structure of glutathione, GSH (reduced).

Results and discussions

The first step in developing this protocol, was the optimization of MW power, exposure time and glutathione concentration. Reactions were conducted at three different power levels *i.e.* 50, 75 and 100 W for 30, 45 and 60 s (Table 1).

Under all of the above reaction conditions (Table 1), silver nanoparticles with spherical morphology in the size range 5–50 nm were obtained. At lower power levels (50 W) and shorter reaction times (30 s), mostly unreacted silver nitrate remained in the reaction mixture. With increase in reaction time to 60 s, nanoparticles of 5–10 nm size with spherical morphology was observed (Fig. 2). At higher power levels (75 and 100 W) with 30 s reaction times, nanoparticles of 4–10 nm were obtained (Fig. 3a, b). However, with longer reaction times (60 s), increased

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Table 1 Effect of MW power and glutathione concentration on Ag nanoparticle formation

| Entry | MW power/W | Time/S | Temperature/°C | Pressure/Psi |
|-------|------------|--------|----------------|--------------|
| 1 | 50 | 30 | 34 | 28 |
| 2 | 50 | 45 | 41 | 33 |
| 3 | 50 | 60 | 47 | 54 |
| 4 | 75 | 30 | 39 | 47 |
| 5 | 75 | 45 | 51 | 56 |
| 6 | 75 | 60 | 62 | 130 |
| 7 | 100 | 30 | 42 | 60 |
| 8 | 100 | 45 | 56 | 128 |
| 9 | 100 | 60 | 61 | 148 |

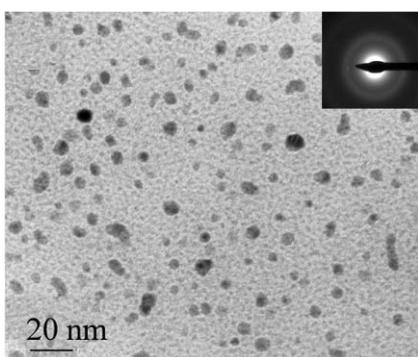


Fig. 2 TEM micrographs of the as-synthesized nanoparticles at 50 W for 60 s with a silver nitrate to glutathione mole ratio of 1.0 : 0.15. Inset is the electron diffraction pattern for the corresponding nanoparticles.

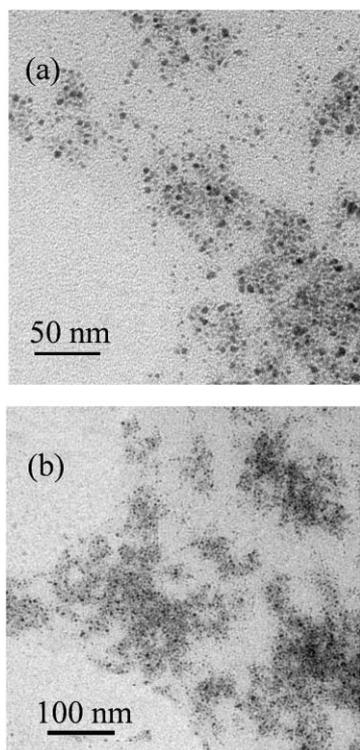


Fig. 3 TEM micrographs of the as synthesized nanoparticles at (a) 75 W and (b) 100 W for 30 s with a silver nitrate to glutathione mole ratio of 1.0 : 0.15.

size and agglomeration of the particles were observed (Fig. 4a, b). When the ratio of silver nitrate to glutathione was less than 1.0 : 0.15, incomplete reduction of silver nitrate occurred as seen in the UV-Visible spectrum. No particle formation was discerned in the absence of glutathione. Increasing the silver nitrate to glutathione mole ratio to 1.0 : 0.30 did not produce particles at 50 W and 60 s, but very small particles in the size range 2–6 nm were obtained when the power was increased to 75 W. Fig. 5 shows the TEM micrograph of the particles synthesized at 75 W for 60 s with a silver nitrate to glutathione mole ratio of 1 : 0.30. Reactions performed under conventional heating at 60 °C, keeping all other conditions intact, did not yield any particles even after 24 h. Thus, the optimized reaction conditions were 50 W power level, 45–60 s exposure time and 1 : 0.15 silver nitrate to glutathione mole ratio, to get uniformly distributed particles in the size range

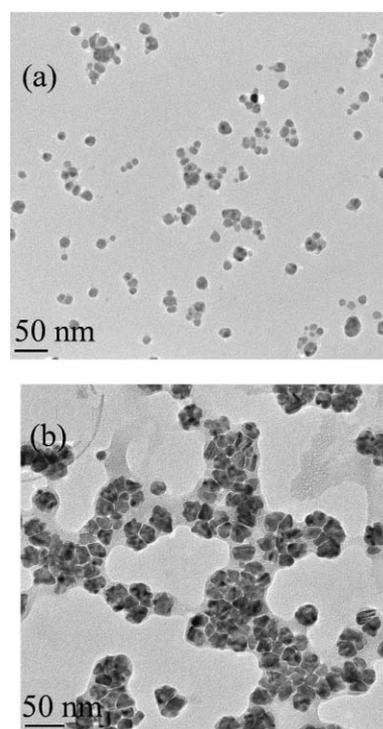


Fig. 4 TEM micrographs of the as-synthesized nanoparticles at (a) 75 W and (b) 100 W for 60 s with a silver nitrate to glutathione mole ratio of 1.0 : 0.15.

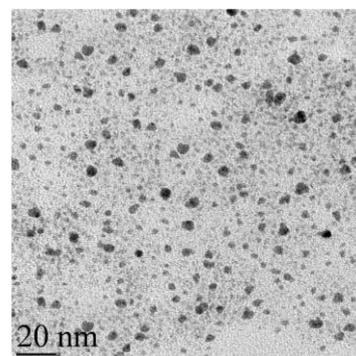


Fig. 5 TEM micrographs of the as synthesized nanoparticles at 75 W for 60 s with a silver nitrate to glutathione mole ratio of 1.0 : 0.30.

5–10 nm. The dispersion of the particles was quite stable and did not result in precipitation even after several weeks of storage under ambient conditions.

The formation of dendritic nanostructures (Fig. 6) on the TEM grid was observed when the reaction mixtures without complete conversion of silver nitrate were loaded on the TEM grid prior to the washing procedure. This was observed in our earlier studies related to the formation of silver trees and was attributed to the fact that the copper and carbon present in the TEM grid is responsible for catalyzing the reaction.³⁴ It was independently verified by separate reactions using copper turnings and activated carbon which generates similar dendritic structures thus raising the concern about the conclusions derived solely on the basis of TEM studies.³⁴

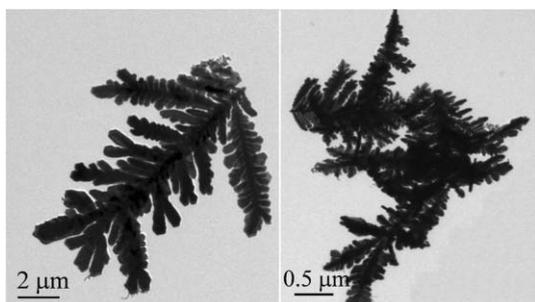


Fig. 6 TEM micrographs of the dendritic nanostructures.

It can be seen from the UV-Vis spectrum (Fig. 7) of the reaction mixtures at different reaction conditions, that heating silver nitrate alone in the MW oven have not resulted in any change in the silver nitrate absorption peak at 300 nm. However, when glutathione was added to the reaction mixture, no silver nitrate peak was observed and the silver plasmon peak appeared in the wavelength range 350–450 nm. The peak shifting towards red was observed with an increase in the amount of glutathione.

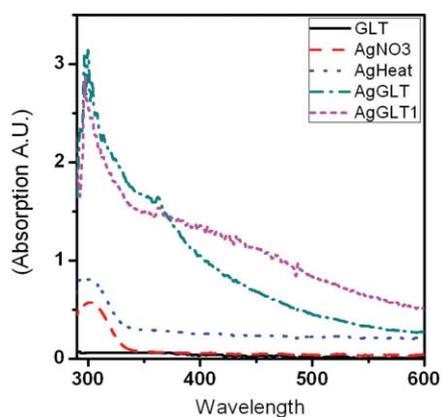


Fig. 7 UV-visible plots of silver nitrate, glutathione (GSH) and silver nanoparticles synthesized with glutathione.

X-ray diffraction pattern confirms the formation of only silver nanoparticles. Fig. 8 is the corresponding X-ray diffraction pattern for the nanoparticles synthesized at 75 W power level for 60 s. The diffraction pattern has some background noise that might be caused by the very small crystallite sizes as well as the organic coating on the as-synthesized nanoparticles. Electron

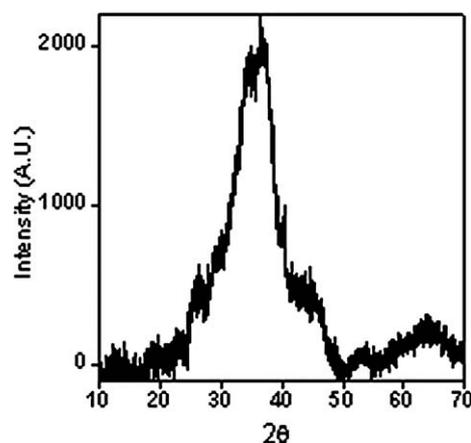


Fig. 8 X-ray diffraction pattern of the as-synthesized Ag nanoparticles at 75 W power level for 60 s.

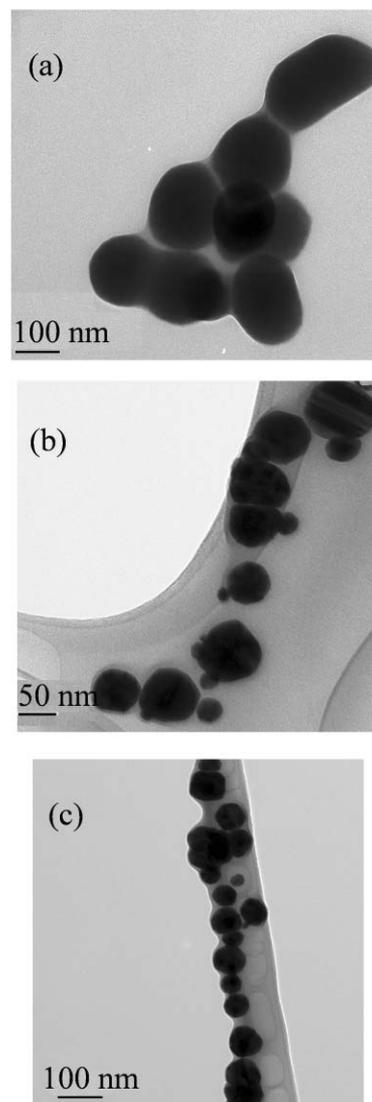


Fig. 9 TEM of the as-synthesized (a) Au, (b) Pt, and (c) Pd nanoparticles.

dispersive X-ray analysis (EDAX) studies of these nanoparticles confirmed the results of X-ray diffraction.

This developed protocol is far superior and sustainable compared to recently reported MW-protocol using amino acids.¹⁶ The main difference is, their protocol needs starch as a coating agent in addition to L-lysine, however, in our protocol, glutathione is acting as both reducing as well as coating agent. In addition, reaction temperature is as high as 150 °C as compared to our protocol, which is very modest, 45–50 °C.

This green and sustainable synthesis procedure could also be adopted for the synthesis of other noble metal nanoparticles such as palladium, platinum and gold. In the case of these noble metals however, bigger particle sizes in the range 100–120 nm were observed. Fig. 9(a–c) shows the TEM micrographs for the as-synthesized gold, platinum and palladium nanoparticles, respectively.

Conclusions

In conclusion, we have developed a rapid and green protocol for the synthesis of silver nanoparticles as well as other noble metals using glutathione, a benign antioxidant, that serves as both a reducing and capping agent. The entire process was carried out in pure water without using any toxic reagents or organic solvents. The effect of MW power on the morphology of silver nanoparticles was investigated. The method could be further exploited for the large scale and continuous synthesis of these nanoparticles.

Experimental

Chemicals

AgNO₃, Na₂PdCl₄, Na₂PtCl₆·6H₂O and Glutathione (reduced form) were purchased from Aldrich Chemicals and used as received.

Synthesis of silver nanoparticles

In a typical synthesis procedure, 1 mmol of silver nitrate was dissolved in 5 mL of distilled water. To this 0.046 g of glutathione (reduced), dissolved in 2 mL of water was added. The mixture was then transferred to a 10 mL crimp sealed thick walled glass tube equipped with a pressure sensor and magnetic bar. The tube was then placed inside the cavity of a CEM Discover focused MW synthesis system for 30–60 s operated at a power of 50 W. The reaction was performed at different power levels to optimize the reaction conditions. Formation of the particles could be observed from the change of color of the reaction mixture. The colorless solution turns reddish brown at the end of the reaction. After completion of the reaction, the tube was rapidly cooled to room temperature, particles centrifuged, and dispersed in water. The dispersion and centrifugation process was repeated twice to remove any unreacted silver nitrate or glutathione from the final product. These nanoparticles were then used for further characterizations.

Synthesis of Pd, Pt and Au nanoparticles

In a typical procedure, 0.05 mmol of Na₂PdCl₄ (for Pd) was dissolved in 5 mL water in a crimp sealed thick walled glass

tube equipped with a pressure sensor and magnetic bar. 2 mL of water containing 0.046 g glutathione was added to it. The slight brownish Na₂PdCl₄ solution instantly became bright orange as soon as glutathione was added to it. The mixture was then subjected to MW irradiation for 45–60 s at 75 W power. The color of the solution becomes dark brown at the end of the reaction. After completion of the reaction, the tube was rapidly cooled to room temperature, particles centrifuged, and dispersed in water. The dispersion and centrifugation process was repeated twice to remove any unreacted silver nitrate or glutathione from the final product. These nanoparticles were then used for further characterizations.

The same procedure was adopted for the synthesis of platinum nanoparticles using Na₂PtCl₆·6H₂O as the source of platinum.

For the synthesis of Au nanoparticles, 5 mL of 3 mM solution of HAuCl₄ was used as the precursor.

Characterizations

The phase of the as-synthesized metal nanoparticles was determined by X-ray diffraction in an MMS X-ray diffractometer with a Cu K α source in the 2 θ range 10 to 70. The data were collected with a step of 1° min⁻¹. A few drops of the as-synthesized nanoparticles were added to a quartz plate and dried at room temperature before recording the X-ray pattern. TEM micrographs were recorded on a Phillips CM 20 TEM microscope at an operating voltage of 200 kV. A drop of the as-synthesized nanoparticles was loaded on a carbon coated copper grid and then allowed to dry at room temperature before recording the micrographs. The UV-Visible spectra were recorded in a Hewlett and Packard 845X UV-Visible system.

Acknowledgements

Babita Baruwati and Vivek Polshettiwar were supported, in part, by the Postgraduate Research Program at the National Risk Management Research Laboratory administered by the Oak Ridge Institute for Science and Education through an interagency agreement between the U.S. Department of Energy and the U.S. Environmental Protection Agency.

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