Microwave synthesis of polymer coated silver nanoparticles by glucose as reducing agent

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Silver nanoparticles have been prepared by the reduction of silver nitrate using glucose as reducing agent and polyvinylpyrrolidine as stabilizing agent and characterized by transmission electron microscopy and UV-visible spectroscopy. TEM images show the average size of silver nanoparticles to be 11 nm. Various optimizing parameters such as effects of silver nitrate concentration, glucose concentration and microwave irradiation time are also described.

Keywords: Silver nanoparticles, Microwave synthesis, Glucose, Nanoparticles, Polyvinylpyrrolidone, Polymer coated nanoparticles

Nanoparticles of metals have been investigated extensively in recent years due to their novel material properties which differ greatly from the bulk substances. As is well known, due to the rapid development of nanoscience every year, millions of tons of nanomaterials are being synthesized. Though the nanomaterials have been shown to have extensive applications, they are also known to adversely affect the environment. Hence, the strategies for synthesis of these materials should be considered prudentially so as to reduce environmental pollution. From the view of green chemistry, all the reagents including reducing reagent, reaction medium and capping reagent should be environmental benign. Novel metal nanocrystallites such as silver and gold provide interesting areas of research field due to their close-lying conduction and valence bands in which electrons move freely. The free electrons give rise to a surface plasmon absorption band, which depends on both the particle size and chemical surroundings.

The processing of nanosized silver particles can be briefly classified into several regimes: (a) chemical reduction of silver ions generally in the presence of stabilizing agents, (b) thermal decomposition in organic solvents, (c) reversed micelle processes, (d) photoreaction, (e) co-γ-irradiation and (f) microwave irradiation. Among these methods, silver nanoparticles with spherical, nanowire or nanoprin shapes and with tuneable sizes have been manufactured but, in most cases, only with a low concentration of silver colloids (several millimoles per litre or less) in the presence of suitable stabilizers. The stabilizers such as surfactants and ionic polymers cannot be easily removed from the surfaces of the formed silver colloids, which unavoidably affect the physiochemical properties of the resulting nanoparticles. The most widely used substances for the stabilization of metal nanoparticles are ligands and polymers, (specially natural or synthetic polymers with a certain affinity toward metals), which are soluble in suitable solvents. Such substances can also control the reduction rate of the metal ions and the aggregation process of zero valent metal atoms. It has been reported that the preparation of polymer stabilized nanoparticles (through chemical methods) basically involves two processes: reduction of metal ions into neutral atoms and coordination of the polymer to the metal nanoparticles. The polymers also control the aggregation of metal atoms in solution.

Microwave irradiation is one of the novel techniques developed recently for the synthesis of solid materials. The main advantage of microwave irradiation is that it produces a uniform heating of the solution so that a more homogeneous nucleation is obtained as well as a shorter crystallization time, as compared to conventional heating and is therefore very useful for the formation of monodisperse metal colloids. Further advantages are short thermal induction period, absence of convection processes, easy control, and low cost.

Herein, we present a green method to synthesize silver nanoparticles. We describe in detail the preparation of silver nanoparticles by reduction of silver nitrate (AgNO₃) using glucose, in the presence of polyvinylpyrrolidone (PVP) and irradiating the solution under microwave. Silver nanoparticles have been characterized by transmission electron microscopy (TEM) and UV-visible spectroscopy. Various optimizing parameters such as effect of AgNO₃ concentration, effect of glucose concentration...
and effect of microwave irradiation time, etc., are also described.

**Experimental**

All chemicals and reagents used were of analytical grade (Molychem/Himedia/Merck). All aqueous solutions were prepared in triply distilled water. \( \text{AgNO}_3 (1.0 \times 10^{-4} \text{ mol L}^{-1}) \), glucose (0.5 mol L\(^{-1}\)) and PVP 1% (w/v) were used.

A Samsung CE2877 domestic microwave oven (850W) (Samsung India Electronics Ltd. New Delhi, India) was employed for irradiating the solutions. The particle size and morphology of the silver nanoparticles were characterized by Morgagni 268D transmission electron microscope operating at 80 kV (Mega view III Camera CCD) at the All India Institute of Medical Sciences (AIIMS), New Delhi. Perkin-Elmer Lambda20 UV-visible spectrophotometer was used for spectral studies.

In a typical procedure, the reaction solution were prepared by dissolving in a 50 mL Pyrex flask, glucose (0.5 mol L\(^{-1}\)), \( \text{AgNO}_3 (1.0 \times 10^{-4} \text{ mol L}^{-1}) \) and PVP 1% in triply distilled water to obtain a homogeneous reaction mixture. The mixture was irradiated in the microwave oven at a power of 300 watt for the duration of the reaction discontinuously to prevent an increase of pressure. After irradiation, the pale yellow coloured dilute colloidal solution was cooled to room temperature for characterization.

**Results and discussion**

It is interesting to find that silver nanoparticles can be synthesized with PVP, glucose and \( \text{AgNO}_3 \) promoted by microwave irradiation. The UV-visible spectrum of the prepared silver nanoparticles was recorded. The colloidal silver solution thus formed exhibits a strong absorption at 420 nm. The yellow colour of the colloidal silver sample provides clear evidence of the formation of silver nanoparticles. According to Mie’s theory, small spherical nanocrystals should exhibit a single surface plasmon band, whereas anisotropic particles should exhibit two or three bands, depending on their shape. Absorption spectra of larger metal colloidal dispersions can exhibit broad or additional bands in the UV-visible range due to the excitation of plasma resonances or quadrupole and higher multipole plasmon excitation.

TEM image was further used to characterize the formed silver particles. Figure 1 shows the TEM image and the corresponding particle size distribution histogram of the silver colloidal solution. The TEM image shows that most of the particles are nearly spherical, while the size distribution histogram reveals that such silver particles range from 6-15 nm in size. About 30 % of these nanoparticles consist of particles with 10 nm dia., 20 % particles were of 14 nm dia. and size of the remaining particles was in the range of 6-9, 11-13 and 15 nm dia. It may be noted that all these particles are well separated from each other. Silver nanoparticles thus formed were free from

![Fig. 1](image-url)
flocculation or aggregation for several months, suggesting that the polymer serves as a very effective protective agent for silver nanoparticles.

The effect of AgNO$_3$ concentration was studied in the range of 0.0001-0.1 $M$. Figure 2 shows a slight red-shift of the UV-visible spectra with increase in AgNO$_3$ concentration, indicating that higher the AgNO$_3$ concentration, larger is the particle size and broader is the size distribution of silver nanoparticles$^{31,32}$. It was observed that with increasing concentration of AgNO$_3$ the colour of resulting solution changed from light blackish turbid solution to brownish to white yellowish to pale yellow colour at constant irradiation time. The reason may be the changing morphology of the formed nanoparticles with larger size at higher concentration of AgNO$_3$ in solution.

The UV-visible spectra of silver nanoparticles prepared with varying glucose concentration (0.1-0.5 $M$) have been shown in Fig. 3. It can be observed that the increase in glucose concentration leads to faster reaction at a constant AgNO$_3$ concentration of 0.0001 $M$. It was observed that at constant irradiation time the resulting solutions changed from colourless solution (0.1 $M$) to white yellowish (0.2 $M$) to very light yellow (0.4 $M$) to pale yellow (0.5 $M$) at increasing concentration of the reducing agent. The changes in shape of the absorption spectra were obvious during the entire reaction process. This may be due to the changing morphology of the formed nanoparticles with smaller size at higher concentration of glucose in solution.

The position and shape of plasmon absorption of noble metal nanoclusters are strongly dependent on particle size, dielectric medium and surface-adsorbed species.$^{33,34}$ The formation process and the optical properties of the silver nanoparticles can also be identified from the colour change as well as the UV-visible spectra of the solutions. The UV-visible absorption spectra of the aqueous solutions containing prepared silver nanoparticles with 4, 8, 12 and 16 min heating time and 300 W are shown in Fig. 4. The solution was observed to change from colourless to transparent yellow (4 min) to dark yellow (8, 12, 16 min) indicating formation of larger number of nanoparticles with increased heating time. There is only one symmetric absorption peak at 420 nm which is the characteristic surface plasmon resonance of spherical silver nanoparticles$^{35}$. According to Mie’s theory, small spherical nanocrystals should exhibit a single surface plasmon band, whereas anisotropic particles should exhibit two or three bands, depending on their shape. Absorption spectra of larger metal colloidal dispersions can exhibit broad or additional absorption bands in the visible region.

![Fig. 2— UV-visible spectra of the silver nanoparticles prepared with varying concentrations of AgNO$_3$. (Conc. of AgNO$_3$/ colour: 1, 0.0001 $M$/ pale yellow; 2, 0.001 $M$/ light yellow; 3, 0.01 $M$/ brownish; 4, 0.1 $M$/ blackish/turbid).](image1)

![Fig. 3— UV-visible spectra of the silver nanoparticles prepared with varying concentrations of glucose. (Conc. of glucose/ colour: 1, 0.1 $M$/ colourless; 2, 0.2 $M$/ whitish yellow; 3, 0.3 $M$/ whitish yellow; 4, 0.4 $M$/ very light yellow; 0.5 $M$/ pale yellow).](image2)

![Fig. 4— UV-visible spectra of silver nanoparticles at different time under microwave irradiation at 300 W. (1, 4 min/ pale yellow; 2, 8 min/ darker yellow; 3, 12 min/ darker yellow; 4, 16 min/ darker yellow).](image3)
bands in the UV-visible range due to the excitation of plasma resonances or quadrupole and higher multipole plasmon excitation. It is well known that the shape and size of inorganic nanocrystals control their widely varying electrical, optical and catalytic properties. All of these silver colloidal aggregates were stable for several months.

In the present study silver nanoparticles have been synthesized rapidly in chemically green conditions from AgNO$_3$ employing glucose as the reducing agent and PVP as the stabilizing agent. Not only is the heating faster through microwave radiation, but the temperature distribution of the solution is also more uniform. This has led to faster reaction and narrow size distribution of the silver nanoparticles in the current study. The UV-visible spectra show that these synthesized samples have absorbance peak at 420 nm, while the average size of silver nanoparticles is shown to be about 11 nm by the TEM images.

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References