

One Pot Synthesis of Crystalline Silver Nanoparticles

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Abstract This paper describes a simple and convenient procedure for the preparation of crystalline silver nanoparticles. One pot synthesis of silver nanoparticles free from stabilizing agent has been investigated. Aqueous solution of AgNO₃ has been reduced by N₂H₄.H₂O in presence of CH₃COONa. The aggregation of silver nanoparticles were prevented by CH₃COONa in chemical bath and then washed away, leaving crystalline silver nanoparticles. The whole experiment has been carried out at room temperature, using water as solvent and also within very less time. The particles synthesized were characterized by UV-Visible, FTIR, TGA, TEM & X-ray diffraction studies.

Keywords: silver nanopartilces, electron microscopy, x-ray diffraction, thermo gravimetric analysis (TGA)

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1. Introduction

Metal nanoparticles have been extensively investigated because of their unique electronic and optical properties that are substantially different from bulk materials [1]. A lot of efforts have been devoted to the synthesis and characterization of silver, gold, and other noble metals nanoparticles [2]. These nano particles are useful in a broad range of areas, such as catalysis [3], photonics [4], optoelectronics [5] and surface-enhanced Raman scattering (SERS) detection [6]. In particular silver nanoparticle is a versatile element with applications in the field of semiconductor, biological sensors, antiviral, etc.

A number of methods have been demonstrated in the past for preparing these nanoparticles; notable examples include condensation in the vapor phase [7], chemical reduction in the solution phase [8], photon or ultrasound-induced reduction in solutions or reverse micelles [9] and thermal decomposition of precursors in solvents, sol-gel matrixes, and polymer films [10]. It has been shown that the size, morphology, stability, and properties (chemical or physical) of these nanoparticles have a strong dependence on the specificity of the preparation method and the experimental conditions [10]. During synthesis of metal nanoparticles a wide variety of capping agents are frequently used to prevent aggregation of nanoparticles. Besides inhibition of nanoparticle overgrowth, capping agents on nanoparticle surface unveils various favorable [11,12] and adverse [13,14] behaviors in catalytic application of metal nanoparticles. In many cases capping agents act as a barrier to expose metal surface to reactants for catalytic activities and more exposure of catalytic surface takes place with nanoparticles free from capping agents [15,16]. Therefore we have made an attempt to synthesize surface clean silver nanoparticles. Here we

report a simple and convenient one pot route for synthesis of crystalline silver nanoparticles of 100-150 nm size based on chemical reduction at room temperature. N₂H₄.H₂O has been used as reducing agent and Sodium acetate has been used as stabilizing agent for silver nanoparticles. The method produces crystalline silver nanoparticles free from stabilizing agent.

2. Materials and Methods

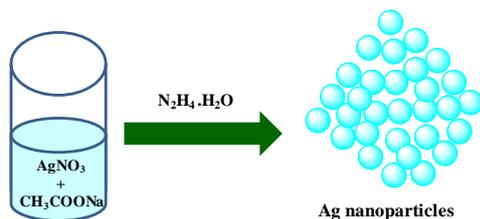
2.1. Materials

AgNO₃ was procured from Merck. CH₃COONa and N₂H₄.H₂O were obtained from Fluka Chemie. All reagents were of analytical Grade and used as received. Millipore water (>18.0M Ω), purified using the Millipore Milli-Q gradient system, was used in whole experiment. Prior to experiments, all glass wares were washed thoroughly with aqua regia and rinsed with Millipore water.

2.2. Preparation of Silver Nanoparticles

As illustrated by [scheme 1](#), silver nanoparticles were prepared through a very simple chemical reduction route by using N₂H₄.H₂O as reducing agent. To 40 ml of 4.3mM aqueous solution of AgNO₃, 0.05M (0.2721gm) of sodium acetate was added and stirred simultaneously. Then 0.02ml of N₂H₄.H₂O (98%) was added to the above mixture and was allowed to stir vigorously. Immediately after addition of N₂H₄.H₂O the solution turned black, confirming the reduction of silver ions. Then the solution was allowed to stir for 2-3 hours at room temperature. After stirring for 2-3 hours the solution turned transparent and very fine shining silver particles appeared inside the flask. The product was separated from the solution

through filtration. The solid particles obtained were then washed by water and dried in air. The same experiment was carried out in absence of sodium acetate but instead of fine particles big particles of silver were appeared inside flask and also a thin film of silver gets deposited inside the wall of the reaction vessel. This indicates aggregation of silver particles in absence of sodium acetate.



Scheme 1. Schematic Illustration of Synthesis of Silver Nanoparticles

2.3. Characterization

The UV-Vis spectra were recorded on a Varian Cary 100 dual beam spectrophotometer. Transmission Electron Microscopy (TEM) images were taken on Philips Morgagni 268, 200 KV electron microscopes by using carbon coated copper grids as substrates. For TEM analysis a drop of silver particles dispersed in water was put onto a carbon coated copper grid and dried naturally. The X-ray diffraction measurements were carried out by Rigaku RU 200 B X-ray Diffractometer using Ni filtered $\text{CuK}\alpha$ radiation. FTIR spectra were recorded at room temperature on Perkin Elmer FTIR Spectrophotometer Spectrum 2000 in the scan range of $400\text{--}4000\text{ cm}^{-1}$.

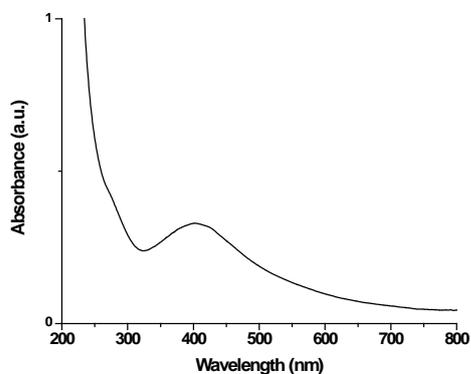


Figure 1. UV-Visible Absorption spectra of Silver Nanoparticle

3.1. UV-Visible Spectroscopy

The solid crystalline powder of silver was dispersed in water and UV-Visible spectra were recorded. A peak at wavelength 405 nm was observed in UV-Visible absorption spectra as shown in Figure 1, signifying the surface plasmon resonance (SPR) band of silver nanoparticles [17,18].

3.2. FTIR Study

In order to ensure the presence of acetate as an integral part of silver particles, FTIR spectra have been recorded. Figure 2 (a) and Figure 2 (b) represents the IR spectra of crystalline silver nanoparticle and that of sodium acetate respectively. IR spectra of sodium acetate shows 2 peaks at 1560 cm^{-1} and 1413 cm^{-1} corresponding to the stretching frequency of carbonyl, however in the IR spectra of silver nanoparticle it is clearly observed that there is no peak at the carbonyl frequency region. This confirms that acetate is not present with silver particles. Absence of acetate with silver particle is also been supported by thermal analysis. TGA profile does not show any step corresponding to decomposition of acetate. This indicates, the acetate is not adsorbed to silver particle as happens usually in other capping agents. Again the experiment conducted without addition of acetate led to aggregation of particles to big particles of silver metal, instead of crystalline powders, confirms the role of acetate as stabilizing agent. But FTIR and TGA analysis provides no clue on the presence of acetate with silver particles. It can be inferred, that the acetate is playing as a role of stabilizer, preventing the aggregation of silver particles, only in the chemical bath and gets removed through washing. In chemical bath, addition of reducing agent, hydrazine hydrate into the aqueous solution containing both silver and acetate ions, leads to formation of small silver metallic particles. These particles are surrounded by acetate ions present in solution. Due to ionization of acetate in water, there is an electrostatic repulsion between adjacent acetate ions that keeps silver particles separated and prevents from aggregation, which is happening otherwise in absence of acetate. However the acetate is not bound to silver and ultimately washed away, leaving silver powders only. Unlike other stabilizing agents, here acetate does not remain an integral part of silver nanoparticles. This report provides a simple and convenient route for one pot synthesis of crystalline silver nanoparticles free from stabilizing agent.

3. Results and Discussion

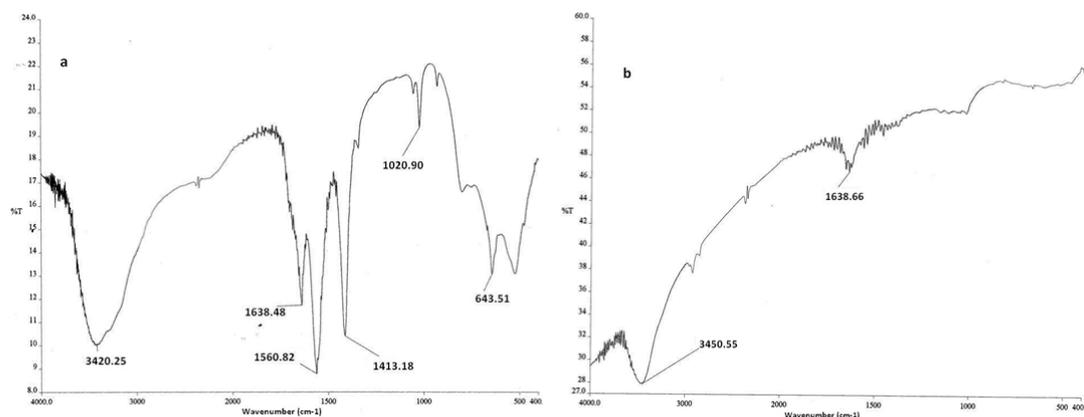


Figure 2. (a) FTIR Spectra of Sodium acetate, (b) FTIR Spectra of Crystalline Silver Nanoparticles

3.3. X-Ray Diffraction Studies

Figure 3 shows the X-ray diffraction pattern of synthesized crystalline silver nanoparticles. The diffraction pattern shows four sharp and well defined diffraction lines at $2\theta = 38.15^\circ$, 44.34° , 64.5° and 77.46° , which can be assigned to the (111), (200), (220) and (311) reflections of the face centered cubic (fcc) structure of metallic silver, respectively. The lattice parameter calculated from XRD pattern is $a = b = c = 4.082975 \text{ \AA}$ in agreement with the literature value $a = 4.086 \text{ \AA}$. The diffraction pattern is in well agreement with the literature report JCPDS File No. 04-0783. The well defined intense peaks in diffraction pattern confirm excellent crystallinity of silver nanoparticles.

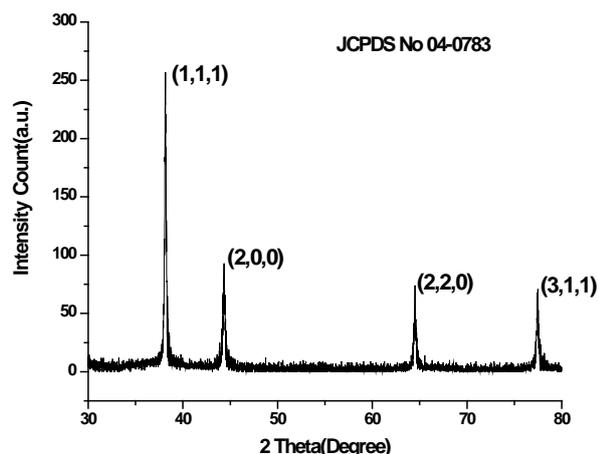


Figure 3. X-ray Diffraction pattern of crystalline silver nanoparticle

3.4. Thermogravimetric Analysis (TGA)

Figure 4 illustrates the TGA profile of silver nanoparticles. TGA profile reveals that, there is no mass loss and confirms the absence of acetate as an integral part of silver nanoparticles.

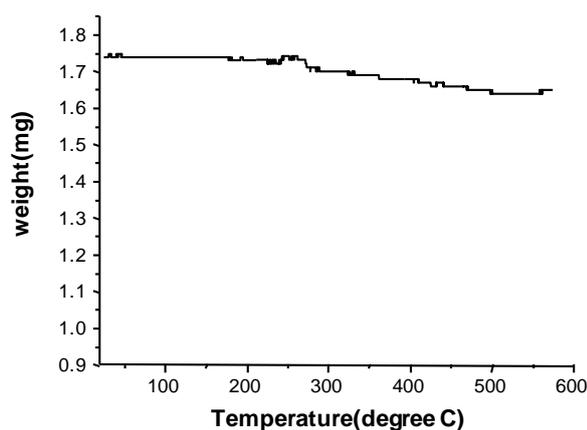


Figure 4. TGA profile of crystalline silver nanoparticles

3.5. Transmission Electron Microscopy (TEM)

Figure 5 shows the Transmission electron micrograph of silver nanoparticles. The average particle size is found as 100 to 150 nm. As shown from the TEM image the particles are well separated from the neighboring nanoparticles. Also it is clearly visible in TEM image that, the particles are cubic in shape. This is also supported by

the observation made from XRD pattern, which suggests the FCC pattern of silver particles.

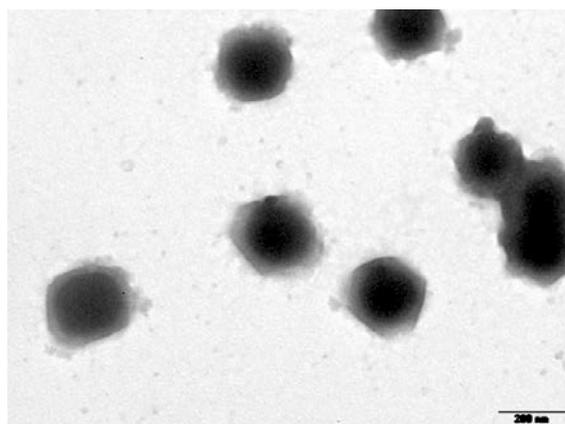


Figure 5. Transmission Electron Micrograph of crystalline silver particles. Scale bar corresponds to 200 nm

4. Conclusions

We have reported a simple, convenient and cost effective route to synthesize crystalline silver nanoparticles free from stabilizing agent. The particles were of cubic shape with well defined crystalline nature. This method was less time taking and reproducible. The reaction gets completed at room temperature condition and water was used as solvent. This technique finds an excellent scope for large scale production of silver nano crystals, which will have applications in electronics and catalysis.

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