SYNTHESIS AND CHARACTERIZATION OF β-CYCLODEXTRIN CAPPED SILVER NANOPARTICLES

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Abstract
The present study deals with the synthesis of silver nanoparticles (AgNPs) using β-Cyclodextrin as the reducing agent. The typical synthesis of gold and silver nanoparticles incorporates contaminants that could pose problems. Here we describe cost effective and environment friendly techniques for green synthesis of silver nanoparticles from AgNO₃ solution and β-Cyclodextrin as reducing as well as capping agent. Thermal treatment has been used to intensify the reduction. The optimum condition for obtaining silver nanoparticles was at pH 11. The formation of AgNPs was confirmed by UV-Visible Spectroscopy, X-Ray Diffraction (XRD) pattern and Transmission Electron Microscopy (TEM). The synthesized AgNPs were predominately spherical in shape and poly dispersed. The particles were stable for at least 4 months at a temperature of 25°C.

Keywords: Silver nanoparticles, β-Cyclodextrin, TEM and XRD

1. Introduction
The field of nanotechnology is one of the most active areas in science. Over the past decade, silver nanoparticles have stimulated great interest because of their applications in biomedicine, sensing and catalysis. Some biomolecules have been introduced as environmentally friendly reducing and capping agents for the synthesis of noble metal nanoparticles. Wallen and co-workers [1] have successfully synthesized starched silver nanoparticles in the size range of 1-8 nm by gently heating an aqueous solution of silver nitrate, soluble starch and glucose, where glucose served as an environmentally benign reducing agent and starch provided stable surface passivation or protection. Nanoparticles of metals play important roles in different fields. They have been investigated extensively in recent years due to their properties which differ from the bulk substances [2]. Nanoparticles possess a very high surface to volume ratio. This can be utilized in areas where high surface areas are critical for success. The applications of nanoscale materials like solar energy conversion, catalysis, medicine and water treatment are depending on their size, shape and chemical surroundings [3]. The noble metals, especially silver and gold, have attracted great attention due to their innumerable applications, which are useful in areas of photography, catalysis, biological labeling, photonics, and optoelectronics and as antimicrobial agents. Metal nanoparticles can be synthesized and stabilized through chemical and mechanical methods [4, 5], electrochemical techniques [6], photochemical reactions in reverse micelles [7] and nowadays via green chemistry method [8]. Synthesis of metal nanoparticles and study of their size and properties are of fundamental importance in the advancement of recent research [9]. Recently, gold nanoparticles with size of 10 nm have been successfully synthesized by employing D-glucose as both reducing agent and capping agent under controlled pH environments [10]. Stabilization using β-Cyclodextrin in the synthesis of mono and bimetallic nanoparticles in alkaline solution has been explored [11]. However, it remains a challenge to develop facile and environmentally friendly methods for the feasible synthesis of silver nanoparticles with controlled size, shape and surface functionality. The nanoscale materials of platinum, palladium, gold and silver can be used in the development of a new generation catalytic and sensing devices. Of great environmental concern is the fact that nanoparticles can enter human body through lungs and
intestinal tract and to a lesser extent through skin and are likely to be a health issue, although the seriousness of the effects is inconclusive. Hence it becomes more imminent to synthesize nanomaterials through greener and less hazardous methods. One such method for the synthesis of metal nano particle is the simple reduction of metal chlorides and nitrates in to metal nanoparticles by aminoc acids in the presence of aqueous β-Cyclodextrin(CD) as capping agent[12]. This method is not only simple but also eco-friendly as it is devoid of any hazardous reducing agents and their disposal. As a class of water-soluble and nontoxic cyclic oligosaccharides with a hydrophilic exterior and a hydrophobic interior, cyclodextrins (CDs) have been extensively investigated in host-guest chemistry. They can form inclusion complexes incorporating various molecular guests within their hollow, truncated cone-shaped cavity structure, enabling them to be used as drug carriers, enzyme mimics and for construction of versatile supramolecular aggregations owing to their special hydrophobic cavities [13, 14]. CDs too induce nanoparticle assembly via host-guest interactions because of their relatively weak capping ability for metal nanoparticles. Although the hydroxylic groups are poor electron donor ligands to silver, in relatively high concentrations, β-cyclodextrin is able to stabilize AgNPs. Herein, we report the controlled synthesis of silver nanoparticles by directly reducing silver nitrate with β-CD in an alkaline aqueous solution. The bio reduction behavior of β-CD in the synthesis of silver nanoparticles was investigated employing UV/visible Spectrophotometry, X-ray diffraction (XRD), and transmission electron microscopy (TEM).

2. Materials and Methods

2.1 Materials.

Silver nitrate (Merck) and β- Cyclodextrin (Himedia) were the chemicals purchased of high purity grade. All the samples were used without any further treatment. All solutions were freshly prepared each time, using doubly distilled water.

2.2 Synthesis of β-CD-Capped Ag Nanoparticles.

The synthesis of β-CD-capped Ag nanoparticles was simply achieved by the reduction of silver nitrate with β-CD in alkaline aqueous solution. Working solution of silver nitrate with concentration 10^{-3} M was prepared from stock solution of 10^{-3} M in doubly distilled water. An aqueous solution of β- Cyclodextrin was prepared such that its concentration was about 15 times higher than silver nitrate solution which was added and stirred for about 10min. Then sodium hydroxide solution was added and magnetically stirred continuously until silver ions were reduced to silver metal in nano dimensional range. During reduction process the temp was kept at 30–35°C.

2.3 Sample Characterization

The products were characterized by X-ray diffraction (Rigaku Dmax-2000, Ni-filtered Cu KR radiation), UV-visible Spectrophotometry with Jasco -550 double-beam spectrophotometer and Transmission electron microscope (TEM Philips CM20).

3. Results and Discussion

3.1 X-Ray Diffraction Studies

X-ray diffraction is one of the most important characterization tools used in Solid State Chemistry and Material Science. XRD is an easy tool to determine the size and the shape of the unit cell for any compound. The dried mixture of AgNPs was collected for the determination of the formation of AgNPs by an X-ray diffractometer. The crystallite domain size was calculated from the width of the XRD peaks, assuming that they are free from non-uniform strains, using the Scherer’s formula:

\[ D = \frac{0.94 \lambda}{\beta \cos \theta} \]

Where D is the average crystallite domain size perpendicular to the reflecting planes, \( \lambda \) is the X-ray wavelength, \( \beta \) is the full width at half maximum (FWHM) and \( \theta \) is the diffraction angle. To eliminate additional instrumental broadening, the FWHM was corrected using the FWHM from a large grained Si sample:

\[ \beta \text{corrected} = (\text{FWHM}_{\text{sample}} - \text{FWHM}_{\text{Si}})^{1/2} \]

This modified formula is valid only when the crystallite size is smaller than 100 nm[15]. The XRD study indicates that the resultant particles are (FCC) silver Nanopowder. The obtained results illustrate that silver ions had indeed been reduced to Ag⁺ by β- Cyclodextrin under reaction conditions. A number of Bragg reflections corresponding to the (111), (200), and (220) sets of lattice planes are observed which may be indexed based on the face centered cubic (FCC) structures of silver. Peaks were also observed suggesting that the crystallization of bio-organic phase occurs on the surface of the silver nanoparticles[16].

Particle Size Calculation

From this study, considering the peak at degrees, average particle size has been estimated by using Debye-Scherrer formula

\[ D = \frac{K \lambda}{\beta \cos \theta} \]

Where ‘\( \lambda \)’ is wave length of X-Ray (0.1541 nm), ‘\( \beta \)’ is FWHM (full width at half maximum), ‘\( \theta \)’ is the diffraction angle and ‘D’ is particle diameter size. The calculated particle size details are in Table.1. The particle size is less than 50 nm.

Table1: The grain size of silver nanopowder

<table>
<thead>
<tr>
<th>( \theta ) of the intense peak (deg)</th>
<th>hkl</th>
<th>( \theta ) of the intense peak (deg)</th>
<th>FWHM of Intense peak (( \beta )) radians</th>
<th>Size of the particle (D) nm</th>
<th>d-spacing nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>38</td>
<td>111</td>
<td>19</td>
<td>0.0035</td>
<td>43.9</td>
<td>0.2368</td>
</tr>
<tr>
<td>44.21</td>
<td>200</td>
<td>22.105</td>
<td>0.0033</td>
<td>46</td>
<td>0.2049</td>
</tr>
<tr>
<td>64.3</td>
<td>220</td>
<td>32.15</td>
<td>0.0052</td>
<td>36</td>
<td>0.1447</td>
</tr>
</tbody>
</table>
The formation of cyclodextrin capped silver nano particles is confirmed by X-ray diffractometry. The X-ray spectrum of the cyclodextrin capped silver nano particle shown in Fig.1b was evidently different from that of β-CD monomer itself shown in Fig.1a. The difference between both spectra of β-CD and capped nanoparticle is due to the interaction of β-CD with silver nanoparticle. X-ray diffraction showed the presence of the peaks at 2θ values of 38°, 44.21° and 64.3° corresponding to cubic phase of silver metal.

Figure 1. XRD pattern of (a) β-CD and (b) silver nanoparticles

3.2 UV/Vis Spectroscopy analysis
UV-visible spectroscopy is one of the most widely used techniques for structural characterization of silver nanoparticles. The absorption spectrum (Fig. 2) of the pale yellow-brown silver colloid prepared by β-CD reduction showed a surface Plasmon absorption band with a maximum of 420 nm indicating the presence of spherical or roughly spherical Ag nanoparticles and TEM imaging confirmed this. In metal nanoparticle such as silver, the conduction band and valence band lie very close to each other. The reaction mixture, showed color change from yellowish brown to reddish brown which indicated the formation of silver nano particles. The absorption peak obtained in the visible range 420 nm wavelength is a clear evidence of formation of silver nanoparticles from the metal nitrate solution. The frequency and width of the surface Plasmon absorption depends on the size and shape of the metal nanoparticles as well as on the dielectric constant of the metal itself and the surrounding medium [17-19].

3.3 TEM imaging of the sample
A drop of the dilute suspension was placed on a copper grid. The grid was allowed to dry under ambient condition for 24 hours and then vacuum dried. The samples were imaged on a transmission electron microscope. The size and shape of the aggregates were characterized by electron microscopy. Fig 3 shows the TEM micrographs of silver nanoparticles. In presence of β-CD, silver nanoparticles are nearly spherical and their average size is about 50 nm. Yet there are a few silver crystallites of size 100 nm and 200 nm, visible in the sample. These images suggest that the particles are poly disperse and are mostly spherical in shape. Hence it may be understood that the experimental conditions (viz., pH, temperature and the optimum concentration of Ag+ etc.) influence dispersity and shape. A few agglomerated nanoparticles were also observed in some places, thereby indicating possible sedimentation at a later time. It is evident that there is variation in particle sizes and the average size estimated was 50 nm for AgNPs.

Figure 2. UV-visible absorption spectrum of silver nanoparticles

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The biological molecules could possibly perform dual functions of formation and stabilization of silver and gold nanoparticles in the aqueous medium. In this work β-CD was used as the bio-substitute for proteins. This simple procedure for the biosynthesis of silver nanoparticles has several advantages such as cost-effectiveness, compatibility for biomedical and pharmaceutical applications etc.

4. Conclusions

The stabilization of metal Nanoparticles is a challenging issue as the high surface energy of the metal nanoparticle tends to aggregate them into bigger clusters. The consecutive particle growth due to the mutual coalescence between nanoclusters and their neighboring free silver atoms was limited in the presence of CDs. This work offers a reliable protocol for the synthesis of Cyclodextrin capped silver nanoparticles. Characterization using various techniques such as TEM, X-ray diffraction and UV-visible spectrophotometry also provide valuable information about the nanoparticles synthesized by this 'Green' facile method. XRD study showed the face-centered cubic lattice of AgNPs. The average crystal size of AgNPs was also found to be 50 nm. TEM analysis of the nanoparticles showed spherical clusters with diameter 50 nm. TEM analysis revealed that the synthesized nanoparticles were stable in solution over a period of 1 month at room temperature. The UV-Visible spectrum reveals the formation of silver nanoparticles by showing surface Plasmon resonance at 420 nm. The significant reduction in reaction time with β-CD is an important result and will enable nanoparticle biosynthesis methods to compete with other routes for the formation of nanoparticles that are currently much more rapid and reproducible. This result provides a very simple and “green” route to uniform CD functionalized Ag nanoparticles, which is potentially extendable to the controlled synthesis of other kinds of metal nanoparticles with specific surface functionality. The obtained uniform Ag nanoparticles functionalized by CD molecules would find a wide range of biomedical applications by virtue of the biologically compatible characteristic as well as the special inclusion ability of the CD molecules. Cyclodextrins synthesized from starch are proved to be the ‘Green Alternatives’ for polymers which are the commonly used as capping agents in nanoparticle synthesis. Cyclodextrins, harmless and easily disposable, play a dual role in this method as reducing agent and capping agent.

5. References

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