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Chemical Synthesis of Silver Nanostructure: Size Dependent Electronic Properties

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Abstract

Synthesis of nanoparticles has been the subject of a lot of studies due to its commercial demands and wide applicability in various fields such as chemistry, physics, biology, material science, engineering, medicine etc. Silver nanoparticles can be synthesized by using number of methods such as chemical, physical, green methods etc. This paper reports the chemical synthesis of silver nanostructure. For synthesis silver nitrate solution is used as a metal precursor and sodium borohydride is used as a reducing agent. Four different sets of samples were synthesized by varying the amount of silver precursor. The formation of nanostructure was confirmed by presence of surface Plasmon resonance in absorption spectra. Electronic properties and optical band gap calculation was done by using absorption spectroscopy. Absorption spectroscopy showed that the maximum absorption was red shifted when the amount of silver precursor added was increased, indicating the increasing of size. Similarly, it was found that the optical band gap was decrease with increasing the amount of silver precursor. Moreover, the antimicrobial activity of synthesized silver nanoparticles was studied against both the gram positive as well as gram negative bacteria such as Staphylococcus aureus, E. coli and Pseudomonas respectively.

Keywords: *Silver Nanoparticle, electronic and optical property, Antibacterial activity.*

Introduction

Nanotechnology has great importance in the field of science and technology to produce the nanomaterials[1]. Nowadays, because of the versatile and advantageous properties of nanoparticles such as unique chemical, optical, magnetic, mechanical and electronic properties, the synthesis and study of nanoparticles has become great interest[2,3]. Therefore, they are also used as catalysis, electronics and photonics. The study and preparation of nano-size material is interest in research and technology because of their increasing applications in electronic study medical science and partly because of their increasing unique properties differing from the bulk state of those[4].Silver has the highest electrical conductivity (6.3x 10^7 S/m) among all the metals, so that silver nanowires are also considered as very promising candidates in flexible electronics[5].

There are various methods reported for the synthesis of silver nanoparticles such as chemical method[6], electrochemical reduction[7], sonoelectrochemical[8], laser ablation, Green synthesis[9, 10]etc. Among them,

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chemical reduction and green synthesis are mostly used. This paper reports the chemical reduction method in which metal salt i.e. silver nitrate is used as a metal precursor and sodium borohydride is used as a reducing agent. The samples were characterized by powder X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Energy Dispersive Spectroscopy (EDS) and Scanning Electron Microscopy (SEM). The electronic and optical properties of nanoparticles are dependent upon the shape of size of the particles. The formation of the size of the nanoparticles is dependent upon different experimental conditions eg. pH of solution, reaction time, conc. of metal precursor etc. This paper reports the size dependent electronic and optical properties of nanoparticles. The size of nanoparticles was varied by changing the conc. of metal precursor.

Silver nanoparticles prevent the growth of both Gram positive and Gram negative bacteria at a very low concentration than antibiotics without any side effects. Therefore, in developing routes of synthesis, an emphasis was made to control the size of silver nanoparticles. There are different mechanisms have been proposed for the antibacterial activity of silver nanoparticles but exact mechanism is not known till [11].

Because of the antibacterial property of silver nanoparticles, it has been used in consumer, health related and industrial products. Moreover, due to its potential application to biological functions such as cancer therapy and imaging, AgNP biosynthesis has recently attracted considerable attraction of researchers interested in the field[12].

Experimental Methods

Synthesis of Silver Nanostructure

Sodium borohydride (10 mM 30 mL) solution was heated with stirring. When the solution was about to boil then silver nitrate solution (5 mM) was added dropwise. Then the solution was turned to brown color solution from dark pink color which indicates the formation of silver nanoparticles. Our study in this paper is to study the electronic properties on different sizes of nanoparticles. The size was varied by varying the amount of silver precursor i.e. silver nitrate. Four different samples were prepared with different amount of silver nitrate solution of same strength (5mM)

Sample C1: 30 mL 10 mM sodium borohydride solution+ 2.5 mL 5 mM silver nitrate solution.
Sample C2: 30 mL 10 mM sodium borohydride solution + 5 mL 5 mM silver nitrate solution.
Sample C3: 30 mL 10 mM sodium borohydride solution + 7.5 mL 5mM silver nitrate solution.
Sample C4: 30 mL 10 mM sodium borohydride solution + 10 mL 5 mM silver nitrate solution.

Measurements

The UV-Vis spectra in solution was carried out in USB2000, Photonics in range 300-1100 nm. The EDX measurement was done on Horiba Model EMAX 7593-H. The surface morphology of the samples was investigated by using scanning electron microscope (SEM, HITACHI, S-4300). Powder X-ray diffraction (XRD, HITACHI, S- 4300) was used to study the crystallinity of sample.

Antimicrobial test

Antimicrobial study of both synthesized nanoparticles were studied by Agar Diffusion Test or Muller-Hinton Agar (MHA) test against one gram positive bacteria *S. aureus* and two gram-negative bacteria *E. coli* and *pseudomonas aeruginosa*. The MHA plates were left overnight at room temperature to check for any contamination to appear. The bacteria test organisms were grown in nutrient broth. Standard organisms were swabbed on MHA plates. Then made the holes with the help of borer for putting the sample in each bacteria. Filter discs were impregnated with synthesized silver nanoparticles and placed on the plates. Antibiotic chloramphenicol served as the standard for measuring the antibacterial activity. The plates were then incubated at 37degree Celsius for 24 hours and the zone of inhibition was measured in mm with the help of ruler.

Results and Discussion

Formation of silver nanoparticles

During the chemical synthesis of silver nanoparticles, sodium borohydride acts as a reducing agent and silver nitrate was the main reactant and the source of silver. When silver nitrate was added to heated sodium borohydride solution, initially the solution was colorless, after some time color started to change indicating that formation of silver nanoparticles begins. Different color was obtained in different samples contain different amount of silver precursor showing different size of nanoparticles was formed. This was monitored by UV-VIS spectroscopy.

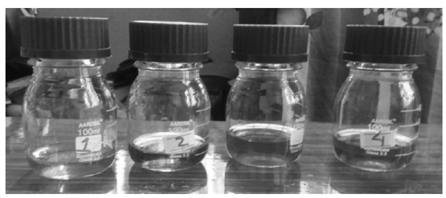

Figure 1: *silver nanoparticles samples C1, C2, C3 and C4 (From left to right).*

Electronic Spectral Analysis

Electronic properties were studied by UV-VIS absorption spectroscopy. Absorption spectra of the Ag nanoparticles, recorded for different amounts of salt are shown in fig a-d. This figure depicts the variation of absorption spectra in different conditions (amounts in case of chemical synthesis and heating periods in case of green synthesis). This figure also demonstrates that each absorption spectrum consists of a peak that corresponds to characteristic Surface Plasmon Resonance peak of Ag nanoparticles. The detail analysis shows that the maximum absorbance corresponding to silver nanoparticle, prepared with different amount are 420, 433, 437 and 440 nm respectively (in fig2).

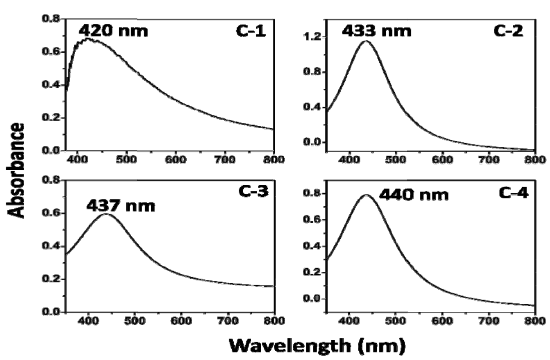

Figure 2: *UV-Vis spectra of chemically synthesized silver nanostructures.*

Optical Band Gap Calculation

The gap between the valence band and conduction band is known as band gap. The band gap is different in conductor, semiconductor and insulator. The band gap is changed with size for the same matter. There is relationship between the optical absorption spectrum of metal nanoparticles by surface Plasmon absorption and their sizes. The band gap of silver nanoparticles was calculated on the basis of formula as given below:

Band gap (BG) = 1240/maximum absorbance (ev)[5].

Table 1: *electronic spectrum observed and band gap of synthesized silver nanoparticles*

Samples	Band gap(ev)
Sample C1	2.95
Sample C2	2.86
Sample C3	2.83
Sample C4	2.81

This table shows the band gaps of different samples of silver nanoparticles. There are various factors affecting the band gap such as temperature, concentration of metal precursor etc. In the above case, the band gap decreases with the increase in concentration of silver nitrate salt for chemical synthesis and decrease with increase in temperature for green synthesis.

The UV-Vis spectroscopy shows that as the amount increases the size of nanoparticles also increases but the band gap decreases.

Energy Diffraction X-ray Spectroscopy (EDX) Analysis

Energy Dispersive Spectroscopy (EDS) analysis was carried out to investigate the chemical characterization of sample and the EDS spectrum of sample having 48% metallic silver was obtained.

Powder X-ray Diffraction (XRD) Analysis

The figure below shows the XRD pattern of silver nanoparticles synthesized from chemical reduction method synthesis. Size of the particles has been calculated using Debye Scherrer formula which is given by $\mathbf{D=0.94\ \lambda / \beta\ Cos\theta}$; Where D is the size of the particle, λ is the wavelength of X-ray, β (expressed in radian) is the full width at half maximum (FWHM) after correcting the instrument peak broadening and θ is the Bragg's angle[5]. The average size of the nanoparticles is found in the range of 10-11nm.

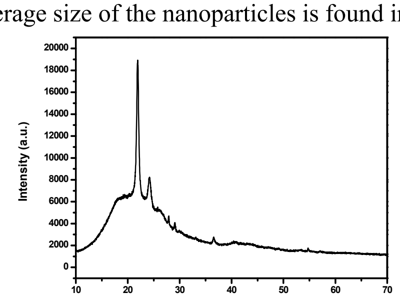

Figure 3: *XRD of chemically synthesized silver nanostructures.*

Narrow peak of XRD results show that all the synthesized silver nanoparticles are crystalline in nature.

Scanning Electron Microscopy

The morphology of the silver nanoparticles is characterized by using a scanning electron microscope with an acceleration voltage of 15kv. The figure below shows that the synthesized silver nanoparticles are rod shaped.

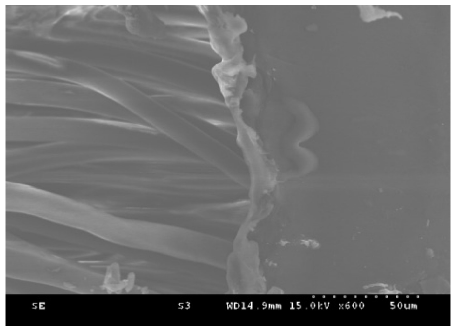

Figure 4: *SEM of chemically synthesized silver nanoparticles.*

Antimicrobial analysis

The synthesized silver nanoparticles were examined against 3 different types of bacteria samples;

a) Staphylococcus aureus(SA)- gram positive
b) Escherichia coli(EC)- gram negative
c) Pseudomonas bacillus(PB)- gram negative

The zone of inhibition is shown in the figure below.

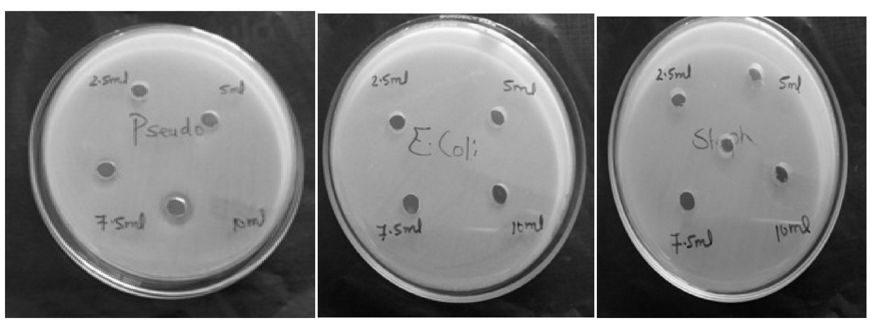

Figure 5: *synthesized silver nanoparticles against P. aeruginosa, E. Coli and S. aureus.*

It is clear from the above figure that synthesized silver nanoparticles have shown greater antimicrobial activity against *P. aeruginosa*. The variation in sensitivity to both Gram positive and gram negative bacteria could be due to the different cell structure, physiology, metabolism or degree of contact of organisms with nanoparticles.

Conclusions

Due to the wide applicability and commercial demands, the synthesis of silver nanoparticles has been increased. It can be synthesized through physical, chemical and biological methods. Among them chemical and green synthesis are the best methods because of its accuracy and good product yield and green synthesis is economical and eco-friendly.

In chemical method, sodium borohydride ($NaBH_4$) is used as a reducing agent and silver nitrate ($AgNO_3$) as a metal precursor. The characterization techniques such as UV-Vis, EDX, FTIR, SEM and XRD characterizes the synthesized silver nanoparticles. The UV-Vis spectroscopy shows that the shift of band to a higher along with increase in concentration and it also shows the increase in size of silver nanoparticles. The EDX shows the maximum presence of element is silver i.e. 48%.

The SEM shows the synthesized silver nanoparticles are rod shaped XRD shows the average size of synthesized silver nanoparticles is about11nm.The antimicrobial activity of chemically synthesized silver nanoparticles against both Gram positive as well as gram negative bacteria have been studied and it gives the better results for gram negative bacteria *pseudomonas aeruginosa*.

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