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Size Dependent Optical Properties of Silver Nanoparticles Synthesized from Fruit Extract of *Malus pumila*

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Abstract

Synthesis of nanoparticles by green method is regarded as a safe and non-toxic process, whereas conventional synthesis produces toxic substance. In this paper, - silver nanoparticles was synthesized by using fruit exact of Malus pumila and characterized by UV-VIS, FTIR, and EDS measurements. Progress of the reaction has been monitored by surface plasmon resonance of AgNPs. Optical band gap was calculated from UV-VIS absorption. It is found that band gap decreases with increasing the reaction time suggesting increase of size of nanoparticles with reaction time. The IR spectrum shows the different biomolecules responsible for reducing the silver precursor to silver. The EDS data shows the presence of metallic silver.

Keywords: *Silver nanoparticle, green method, optical properties*

Introduction

Nanotechnology is a broad interdisciplinary area of research, development and industrial activity which has grown very rapidly all over the world for the last decade. Metallic nanoparticles of different shape and size are explored for various applications. Silver nanoparticles (AgNPs) are very important among the most widely used metal nanoparticles.

Silver nanoparticles have applications in different fields such as: in cotton fabric as an antibacterial textile[1], to make highly stretchable electric circuits[2], to fabricate the transparent conducting films[3], in therapeutic applications[4], in nanomedicine[5], catalysts when combined with polymers[6], for clinical diagostic[7], etc.

They can be synthesized using different methods including physical and chemical methods[8,9], electrochemical reduction[10], photochemical reduction[11], heat evaporation[12] etc. Most of the methods reported in the literature involve the use of toxic, hazardous chemicals which may pose potential environmental and biological risks. Because of the increasing environmental concerns by chemical synthesis routes, an environmentally sustainable synthesis process has led to biometric approaches, which refers to applying biological principles in materials formation.

Biological methods of nanoparticles synthesis using microorganisms, enzymes, fungus, plants or plant extracts have been suggested as possible ecofriendly alternatives to chemical and physical methods. Also, the processes are readily scalable and less expensive.

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Plant extracts may act both as reducing agents and stabilizing agents in the synthesis of nanoparticles. Different part of the plant extract can be used for synthesis of silver nanoparticles. such as leaf extract of *Calotropis gigantean*[13], *Terminalia catappa*[14], flower extract of *Rhododendron dauricum*[15], *Calotropis procera*[16], seed extract of *Syzygium cumini*[17], fruit extract of *Emblica Officinalis*[18], fruit extract of *Malus pumila* for antibacterial for antibacterial study[19], etc.

This paper reports the synthesis of Silver nanoparticles by using fruit extract of *Malus pumila* and study of its size dependent optical properties.

There is growing interest in utilizing the optical properties of silver nanoparticles as the functional component in various products and sensors. Silver nanoparticles are extraordinarily efficient at absorbing and scattering light and, unlike many dyes and pigments, have a color that depends upon the size and the shape of the particle. The strong interaction of the silver nanoparticles with light occurs because the conduction electrons on the metal surface undergo a collective oscillation when excited by light at specific wavelength known as a surface Plasmon resonance (SPR), this oscillation results in unusually strong scattering and absorption properties[20].

A unique property of spherical silver nanoparticles is that Surface Plasmon Resonance (SPR) peak wavelength can be tuned from 400 nm (violet light) to 530 nm (green light) by changing the particle size and the local refractive index near the particle surface. Even larger shifts of the SPR peak wavelength out into the infrared region of the electromagnetic spectrum can be achieved by producing silver nanoparticles with rod or plate shape[20].

Experimental Methods

Preparation of Extract

The extraction of fruit was done in water. For this, 100 g of the small pieces of apples was put in 200 mL of deionized water, which was heated for 1 hour at 80 °C. Then whole mixture was filtered. Then the filtrate was used as reducing agent for preparation of silver nanoparticles.

Preparation of Silver Nanoparticles

The preparation of AgNPs was carried out by using 20 mL of the apple extract in 180 mL of 0.1 M aqueous $AgNO_3$ solution. The mixture was heated with stirring at 80 °C at different time interval. The UV-VIS spectrum is used for monitoring the formation of nanoparticle. The electronic spectra were recorded in time interval of 15 mins. Initially, it was colorless, and then color changed from yellow to wine red after one hour heating. UV-VIS spectroscopy was used to monitor the color changes of the mixture after 15, 30, 45 and 60 minutes.

Characterization

The synthesized Silver Nanostructure was studied and characterized by different spectral methods. UV-VIS spectra in solution were carried out in USB2000 Photonics in range 300-1100 nm. IR was recorded in solution form in IRTracer-100 Shimadzu, in range 400-4000 cm^{-1}. Energy dispersive spectroscopy measurement was carried out in EDS 8000.

Results and Discussion

Formation of Silver Nanoparticles

The fruit extract appears to be a potential source of water-soluble hydrocarbons, proteins those are found to be efficient reducing agent.

When apple (*Malus pumila)* extract was added to silver nitrate solution, initially the solution was colorless i. e no formation of silver nanoparticles. When this was heated, the color starts to change after 15 mins. After 15 mins color change to light yellow, which showed that formation of silver nanoparticles was started. The color became darker and darker after 60 mins. The change in color at different time interval is due to different in size of the nanoparticles. This was studied by UV-VIS spectroscopy. It was emphasized from previous studies that the color of nanoparticles originates from excitation of the SPR peak. The SPR peak is strong for noble nanoparticles such as gold and silver. The band intensity of SPR and wavelength depends on the type of metal, particle shape and size, composition of dielectric constant of surrounding medium shown theoretically by Mie theory[21].

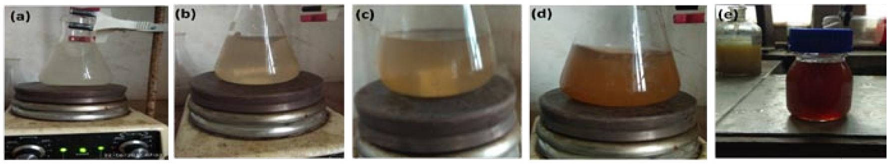

Figure 1*: Formation of silver nanoparticles (a) o min (b) 15 mins (c) 30 mins (d) 45mins (e) 60 mins.*

Optical Properties

Figure 2 showed the UV-VIS absorption spectra of silver nanoparticles. The UV-VIS spectroscopy revealed the formation of silver nanoparticles by exhibiting the typical Surface Plasmon Resonance absorption. The spectra were taken at different time interval of reaction time. Four different UV-VIS absorption were taken at four different interval of reaction time. They are after 15 mins, after 30 mins, after 45 mins and after 60 mins.

The spectra showed λ_{max} = 404 nm for sample after 15 mins; λ_{max} = 412 nm for sample after 30 mins; λ_{max} = 415 nm for sample after 45 mins; λ_{max} = 432 nm for sample after 60 mins. It is clear from the absorption spectra that the maximum absorbance wavelengths (λ_{max}) red shifted from 404 to 432 nm by increasing the reaction time. This showed that this red shifting may due to the increasing in size of the nanoparticles by increasing the reaction time[22]. The increase in size may be due to agglomeration of Ag nanoparticles to form larger nanoparticles. A tail in the longer wavelength region of the absorption spectra corresponds to the size and shape distribution of the Ag nanoparticles. The maximum absorbance wavelength is associated with the conduction band energy according to quantum theory of metal nanoparticles[23-25].

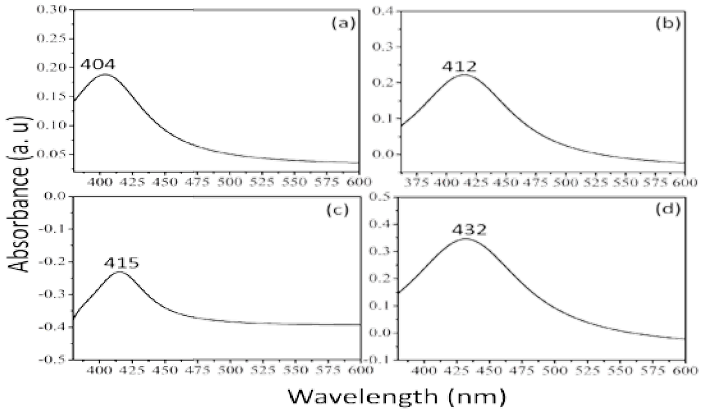

Figure 2: *UV-VIS Absorption Spectra of Silver Nanoparticle Samples (a) after 15 mins (b) after 30 mins (c) after 45 mins (d) after 60 mins*

Optical Band Gap Study

The gap between valence band and conduction band is called band gap. The band gap is different in conductor, semiconductor and insulator. In the same matter band gap is changed with change in size.

The band gap of silver nanoparticles was calculated from absorption spectra and by using Einstein Photo Energy relation.

$$Eg = \frac{hc}{\lambda\text{max}}$$

$$Eg = 1240 / \lambda \text{ (eV)}$$

Table 1 showed that the band gap decreasing in order with increasing the reaction time. This showed that the size of nanoparticles increase with increase of reaction time.

Table 1: *Band Gap of Silver Nanoparticles*

Sample	Band Gap(eV)
Sample (after15 mins rxn)	3.06
Sample (after30 mins rxn)	3.00
Sample (after45 mins rxn)	2.98
Sample (after60 mins rxn)	2.87

The change in band gap can be explained as follows. There is relationship between the optical absorption spectrum of metal nanoparticles caused by surface plasmon absorption and their sizes. The surface plasmon resonance is the coherent excitation of all the `free' electrons within the conduction band. Gustav Mie[21] in 1908 was first to introduce the optical absorption of metal nanoparticles as localized surface Plasmon resonance. The absorption of light in metal nanoparticles can be described as intra-band excitations of conduction electrons[6] from the lowest energy state to higher energy states near the Fermi level of the conduction band upon receiving photon energy having the maximum absorbance wavelengths (λ_{max}). Smaller particle size contains, fewer numbers of atoms and reduces the potential attraction between the conduction electrons and metal ions of the particle. Due to this, the conduction band energy increases for the smaller particle. But for larger particle size contains large numbers of atoms, thus increasing the potential attraction between conduction electrons and metal ions and therefore reduces the conduction band energy of the metal nanoparticles[23].

Infrared Spectral Studies

FTIR measurement was carried out to identify the possible biomolecules responsible for reducing agent for the formation of AgNPs. Two obvious infrared bands(figure 3) are observed at 3300 and 1630 cm^{-1}.The intense broad band appearing around 3300 cm^{-1} is due to N—H and O—H stretching mode in the linkage of the proteins. The medium intense band at 1630 cm^{-1} from the CHO stretching mode in amine group which is commonly found in the protein[26].

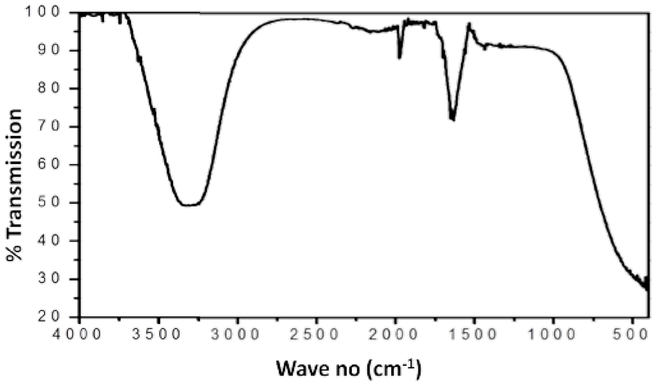

***Figure 3**: Infrared Spectrum of Silver Nanoparticle*

Energy Dispersive Spectroscopy

Energy dispersive spectroscopy (EDS) is used for the elemental analysis or chemical characterization of a sample. Energy dispersive spectroscopy (EDS) confirms the nature of elements present in the samples. Its characterization capability is due to its fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its x-ray emission spectrum. The EDS analysis shows that the sample contains about 21 % of metallic silver.

Conclusions

Silver nanoparticles were synthesized by green method. The formation of nanoparticles was monitored by UV-VIS spectroscopy. UV-VIS spectra revealed that the SPR band red shifted with increasing the reaction time. This observation suggested the increase in size with reaction time. Again the optical band gap was calculated by absorption spectra, which was found to be decreasing with increasing the reaction time indicating the size of nanoparticles increasing with increasing the reaction time. IR was used to identify the possible biomolecules responsible for reducing agent. EDS shows the amount of metallic silver in the sample, which confirms the presence of element silver in prepared samples.

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