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Research Article

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Green Engineering of Optical Band Gap in Plasmonic Silver Quantum Dots using Elettaria Cardamom Extract

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Abstract
Silver quantum dots are prepared from aqueous $AgNO_3$ solution by employing biological reduction using Elletaria Cardamom extract under different compositions. The prepared quantum dots were analyzed experimentally by employing UV-visible Spectroscopy, HRTEM and FTIR techniques. The observed change in colour of mixture with composition is analyzed in detail. UV-vis experimental data was employed to calculate the optical band gap of different samples. Effective engineering of optical band gap is achieved by method of green synthesis. HRTEM analysis clearly indicated the formation of quantum dots through particles of spherical shape with average size of 10 nm. Crystallization of the obtained particles is confirmed as FCC of silver. FTIR measurements were carried out to identify the possible biomolecules responsible for capping and efficient stabilization of the Ag metal nanoparticles in the present study.

Keywords: Green Engineering, Band Gap, Biological Reduction

Introduction

Green engineering of optical band gap of metal nanoparticles have significant importance because of its applications in various fields including water purification, photocatalysis and anti-microbial activity. Traditional, physical and chemical methods of synthesis of metal nanoparticles have increased environmental concerns due to the addition of toxic compounds for stability, and formation of dangerous byproducts. While chemical and physical methods require high temperature and pressure, nanoparticle synthesis by biological methods can be done at room temperature and pressure [1-3]. Synthesis using bio-organisms is compatible with the green chemistry principles. “Green synthesis” of nanoparticles makes use of environmental friendly, non-toxic and safe reagents [4]. Nanoparticles synthesized using biological techniques or green technology have diverse natures, with greater stability and appropriate dimensions since they are synthesized using a one-step procedure [5].

A better platform for the synthesis of nanoparticles is provided by plants as the green synthesis, which offer an environmentally friendly, economical, reproducible and simple approach. Metal nanoparticles have wide range of applications in which biological routes play an important role in the synthesis. In these routes, plants, fungi and microbes, can be employed in more environmentally sound production of silver nanoparticles. Considering the vast potentiality of plants as sources, this work aims to apply a biological technique for the synthesis of silver nanoparticles as an alternative to conventional technique. Cardamom extract was used for the bioconversion of silver ions to nanoparticles. Silver nanoparrticles can be produced at different concentrations of the extract without using any additional harmful chemical/physical reagents [6-7].

In the present study, the synthesis of AgQDs is done using aquous $AgNO_3$ and cardamom extract as precursers. The variation in the optical band gap values of QDs as a function of precursor volumes is analyzed. Cardamom extract and AgNO3 solution in different compositions are taken. The prepared nanoparticles were characterized by UV-Vis spectroscopy, HRTEM, GI XRD, and FT-IR spectroscopy.

Materials and Methods

0.03 kg of cardamom is taken and washed in distilled water for several times. After cleaning it, it is boiled for 30 minutes in 1L distilled water in a thoroughly cleaned large beaker. It is allowed to cool for one hour and then the extract is very well filtered out. 0.01 N aqueous solution of $AgNO_3$ is prepared. For that 0.3397 g of $AgNO_3$ is dissolved in 200 ml distilled water in a beaker and thoroughly stirred. The cardamom extract is mixed and thoroughly stirred for 45 minutes each with aqueous solution of 0.01N AgNO3 in five different volumes and are named as C_1, C_2, C_3, C_4 and C_5.

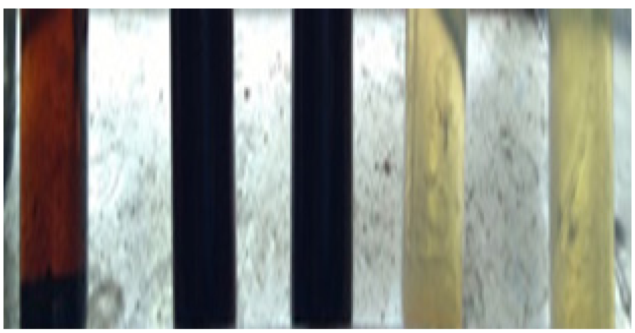
Table 1: The different compositions and their representations

Sample	Cardamom extract(ml)	Volume of $AgNO_3$ solution (ml)
C1	2.5	20
C2	5	20
C3	10	20
C4	20	20
C5	30	20

The obtained samples are subjected to UV-Visible spectroscopy in the range 200 to 900 nm using Jasco made UV Visible Spectro Photo Meter. Crystalline and morphological studies are conducted using HR TEM analysis. For understanding the involvement of different functional groups in the reduction process, FTIR spectroscopy is also conducted.

Results and Discussion

UV Visible Spectroscopy Analysis and Color Change



C1 **C2** **C3** **C4** **C5**

Figure 1: Colour change between different samples

A colour change with varying compositions are observed as shown in the figure 1. The liquid mixtures appear in different colors for different compositions. The obtained colour change is attributed to the reduction of Ag+ ions to Ag atoms further leading to the formation of Ag quantum dots. The change in color may be due to excitation of surface plasmon resonance due to these nanoparticles [8].

$$Ag^{+} + \text{reducing agent} \longrightarrow Ag^{0}$$

The free electrons present in QDs give rise to the localized surface Plasmon resonance. The absorbance is due to the combined vibration of electrons of the metal NPs in resonance with the light waves. The different colours are attributed to difference in size and shape, for which the specific oscillations depend on it. As a general rule, smaller particles will have a higher percentage of their extinction due to absorption. The direct method to investigate the band structure of materials by studying its absorption spectra [9].

Figure 2. shows the optical absorption spectrum of different samples. Maximum optical absorption is observed to be blue shifted from 450 to 430 nm with increase in volume of the plant extract taken for the reduction reaction. Also optical absorption is found to be decreasing with increasing volume of cardamom extract in the liquid composition. Composition with higher volume of cardamom extract not exhibited optical absorption (sample C5). Gaussian shaped single absorption peaks indicates plasmonic resonance from spherical shaped Ag nanoparticles [10].

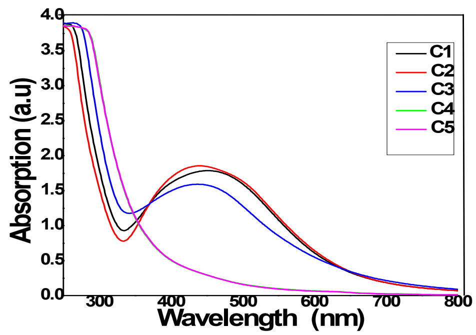
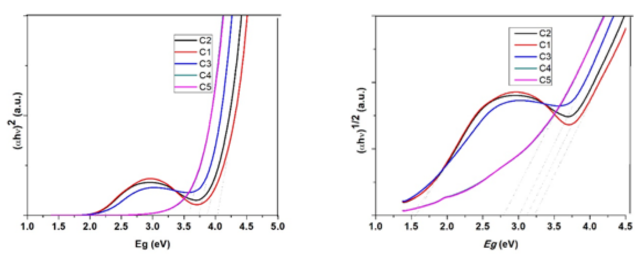


Figure 2: Absorption Spectrum of different samples

Fundamental absorption refers to band to band excitation transition. The sudden rise in absorption, at the fundamental absorption edge, can be used to determine the optical band gap. The absorption coefficient α is related to the energy of the incident photon as [11]

$$(\alpha h\nu)= \beta\, (h\nu- E_g)^{\,r} \qquad (1)$$

α is proportional to the optical absorption A, E_g is the optical energy gap, $h\nu$ is the energy of the incident photon, β is a constant, and r is the exponent that takes the value 1, 2, 3,1/2 and 3/2, depending on the nature of the electron transitions responsible for the optical absorption. The exponent r takes the value of 1/2 for direct and 2 for indirect electron transition. The fundamental band edge, corresponding to both direct and indirect transitions can be observed by plotting $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ versus photon energy $h\nu$.



(a) **(b)**

Figure 3: Tauc plot for (a) direct and (b) indirect optical band gaps of Ag nanoparticles

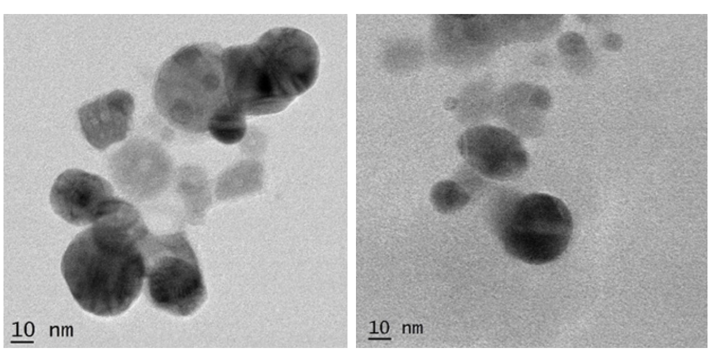
Table 2: The variation of optical band gap with different samples

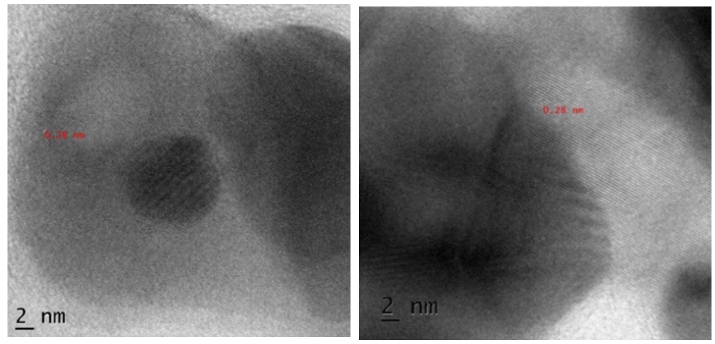
Sample Name	Optical band gap (eV)	
	Direct transitions	Indirect transitions
C1	4.26	3.23
C2	4.13	3.11
C3	3.91	2.98
C4	3.78	2.78
C5	3.78	2.78

The values of optical band gaps associated with direct and indirect transitions for different samples are given in Table 2. As the amount of plant extract increases in the mixture, the band gap is found to be decreased. The size of the Ag Nano particles produced, as a result of the reduction process, is a significant factor in tuning the value of the optical band gap. As the size decreases, the optical band gap increases due to quantum effects [12]. In the present study, the sample C1, of which minimum ratio of plant extract used, exhibited maximum optical band gap for both direct and indirect transitions. The reduced rate of reduction resulted in the minimum size of quantum dots of Ag nanoparticles.

HR TEM Analysis

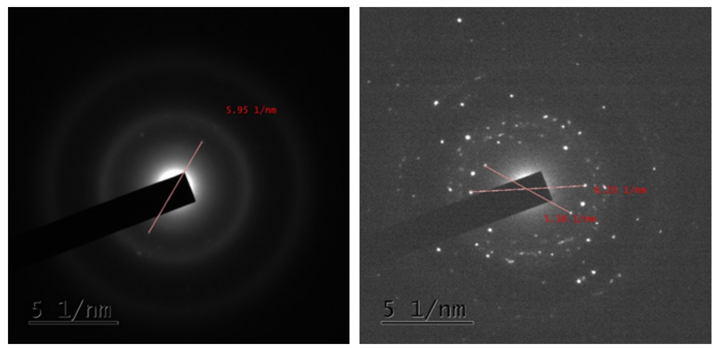
HRTEM is one of the most powerful tools which can give direct structural and size information of the nanostructures including quantum dots. In the present study, HR TEM analysis were conducted on the samples for different magnifications. Detailed investigations are done on the shape and size of AgNPs present in the samples. The TEM images of the so-formed AgNPs revealed that the NPs were spherical in shape, with a size range of 10 nm indicating existence of quantum dots. At higher magnification, the TEM micrograph revealed that Ag NPs were not in physical contact but separated by uniform distance with some deviations. Figure 4 (a) shows the obtained TEM images for sample C1. Discrete agglomeration of nanoparticles of average size 10 nm is observed. Figure 4b) shows the obtained images for sample C2 with different magnifications. It is observed that with increased volume of extract, agglomeration of nanoparticles of size about 10 nm is observed in certain directions. The capping of AgNPs has also been observed under TEM micrograph. This capping might be because of presence of phytochemicals compounds present in extract.





(a) (b)

Figure 4: HR TEM Image of samples (a) C1 and (b) C2 under different magnifications



(a) (b)

Figure 5: SAED Pattern of samples (a) C_1 and (b) C_2

Diffraction patterns of the nanoparticles were obtained by TEM and by SAED analysis. Figure 5 shows the ring diffraction patterns Ag Nano particles with crystalline structure. From SAED analysis, structural orientations of the obtained nanoparticles are elucidated as FCC structure of Ag.

FTIR Studies

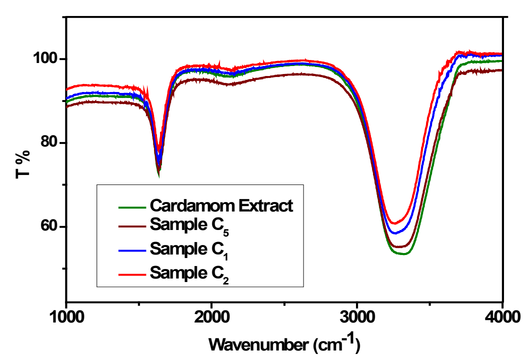


Figure 5: FT-IR Spectra of samples C1, C3, C5

FTIR measurements were carried out to identify the possible biomolecules responsible for capping and efficient stabilization of the metal nanoparticles synthesized by cardamom extract. The FTIR spectra of different samples with absorption peaks corresponding to OH and CO groups were observed. For the sample C2, a large shift in the absorbance peak of OH group was observed, from 3307 of the pure extract, to 3233 cm-1. The spectra obtained to characterize the interaction between $AgNO_3$ and extract has strong peak corresponding to the OH group (stretch H bonded, strong broad). The highest absorption peak at 3307 cm-1 reflects that the OH group might be responsible for the reducing property of the extract.

The absorbance band at 1649 cm-1 is associated with the bending vibration OH group, which confirms the presence of water. The band at 2112 cm-1 may be due to C=O stretching vibrations of the carbonyl functional group in ketones, aldehydes, and carboxylic acids. However, the exact procedures of bio-reduction are not fully comprehended. Also the precise direction in which the electrons are transported is a matter requiring investigation [13].

Conclusion

In the present study, tuning of the optical band gap associated with quantum dots of silver nanoparticles is successfully done by employing techniques of green synthesis. Cardamom extract and $AgNO_3$ solution in different volumes were treated and it resulted in the reduction of Ag^+ ions to Ag metal atoms, which further accumulated as Ag nano particles. The prepared nanoparticles were characterized by UV-vis spectroscopy, HRTEM, and FT-IR spectroscopy. UV-visible absorption gives absorption peaks at wavelength 450nm. Optical band gap is found to be much sensitive to particle size. The result from HRTEM revealed the size and shape of biosynthesized nanoparticles. Most of them are spherically symmetric with average size10 nm.

Through the data presented in this study we are offering a unique, eco- friendly; cost effective method of green engineering of optical band gap of metal nanoparticles having vast applications in many fields in present and future.

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