Fluorescence Study on Biological Synthesis of Cadmium Sulfide Nanoparticles by *Tinospora cordifolia*: A green perspective

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Abstract: Synthesis of CdS nanoparticles (CdS-NPs) was achieved by a simple green procedure using *Tinospora Cordifolia* leaf extract as stabilizer/reducing agents. CdS-NPs in the size range of 6-12 nm is obtained by the treatment of aqueous Cadmium & Sulfide ions with leaf extracts of *Tinospora Cordifolia*. This eco-friendly approach is simple, amenable for large scale commercial production and technical applications. Further, photoluminiscence studies of these CdS-NPs were recorded & suggested that the present particles were suitable for fluorescence emitting probes. These red emitting CdS-NPs exhibited distinct fluorescence properties.

Keywords: Fluorescence, Biological Synthesis, Cadmium Sulfide Nanoparticles, *Tinospora cordifolia*.

Introduction:

The field of nanotechnology has witnessed impressive advances in various aspects such as the synthesis of nanoscale matter and understanding/utilizing their exotic physicochemical and optoelectronic properties. Nano-sized colloids are characterized by excellent electrical, thermal, optical and catalytic properties. As such, they have attracted a considerable degree of attention over the recent past owing to their various potential applications as conductors, catalysts and chemical sensors. It has therefore become necessary to attempt to synthesise small-size and narrow-distribution colloidal metal dispersions. Of the various techniques explored to obtain such metal nano particles, at present, there is a greater need to develop safe, reliable, clean and eco-friendly methods for the preparation of these nanoparticles. Although many synthetic technologies are well documented, the search for suitable biomaterials for the biosynthesis of nanoparticles continues among researchers worldwide. The noble metal nanoparticles have several important applications in the field of biolabelling,1 sensors, drug delivery system,2 filters3and also possesses antimicrobial activity.4 These metal nanoparticles exhibit new physico-chemical properties.

In the last decade, the biosynthesis of nanoparticles, as a representative intersection of nanotechnology and biotechnology, has received increasing attention due to the growing need to develop environmentally benign technologies in material syntheses. Early this decade, the potential of various microbes and plant biomasses for the synthesis of nanometals was explored. Sastry and co-workers examined the possibility of using microbes and plant materials as nano-factories.5-10 Since then, various microorganisms and plants have
been employed for the synthesis of nanoparticles. In recent years, the biosynthetic method using plant extracts has received more attention than chemical and physical methods, and even than the use of microbes, for the nano-scale metal synthesis. Gardea-Torresdey et al.\textsuperscript{11,12} initially reported the possibility of using plant materials for the synthesis of nano-scale metals. Later, the bioreduction of various metals to nano-sizes of various shapes, capable of meeting the requirements of diverse industrial applications, was extensively studied.

\textit{Tinospora cordifolia} is an annual or perennial ayurvedic plant which is used in several traditional medicines to cure various diseases. Common names are amrita, gulbet, gurcha (hindi), gulvel (marathi), amudom, chindil (tamil), tippateega (telugu). This weed has been known to possess immunomodulatory, hypoglycaemic, jaundice, rheumatism, urinary diseases, anemia and for its anti-allergic and anti-inflammatory properties. The plant mainly contains alkaloids, glycosides, steroids, sesquiterpenoid, aliphatic compound, essential oils, mixture of fatty acids and polysaccharides. A wide range of chemical compounds including aporphine alkaloids, clerodanediterpenes, berberine, palmatine, tembertarine, magniflorine, choline, and tinosporin. The alkaloids like berberine, palmatine, tembetarine, magniflorine choline, tinosporin etc., glycoside like tinocordiside, tinocordifolioside etc., have been isolated from this plant. The trace element studies on the aqueous extract of these medicinal plants have been carried out using particle-induced X-ray emission technique for their medicinal uses. The aqueous extract of \textit{Tinospora cordifolia} roots shows a good hypolipidaemic activity. The alkaloids, glycosides, steroids, sesqui-terpenoid& aliphatic compound present in this plant may act as the reducing agents and by which the present reduction of CdS ions takes place. However, the ingredient responsible for the reduction of CdS ions needs further study.

\textbf{Experimental:}

Known weight (100 g) of \textit{Tinospora cordifolia} plant leaves powder is purchased from the local herbal market. \textit{Tinospora cordifolia} leaves powder (Figure-1) were taken in 250 ml capacity beaker having 200 mL of organic free water and was placed on boiling steam bath for 15 to 20 min till color of the water changes. The extract was cooled to room temperature, gently pressed and filtered firstly through sterile serene cloth. This solution was treated as source extract and was utilized in subsequent procedures.

Now, 40 mL of the above source extract was doubled in volume by adding 40 mL of sterile organicfree water. The synthesis of cadmium sulfide nanoparticles involves the reaction between cadmium chloride and sodium sulfide under the influence of prepared supernatant.

0.25 M concentration of cadmium chloride and sodium sulfide was used for the reaction to synthesize CdS. Cadmium chloride and sodium sulfide ranging 1:1 was taken for nanoparticle formation. A volume of 5ml of cadmium chloride and 5 ml of sodium sulfide corresponding to ratio 1:1 were added in a screw cap tube and allowed to react. This reaction produced an orange-yellow colour of cadmium sulfide suspension to which equal volume of supernatant was added to the tube and mixed thoroughly. The mixture was kept in water bath at 60°C for about 20 minutes until there was fluffy orange yellow deposition seen at the bottom, indicating the formation of nanoparticles. The suspension was left to cool and incubated at room temperature overnight. Following day, the solution was observed for coalescent orange yellow clusters deposited at the bottom of the tube. The sodium chloride formed from the reaction of cadmium chloride and sodium sulfide was removed without disturbing the CdS nanoparticle precipitate. The precipitate was washed with acetone and water to remove if any contaminants present and dried in hot air oven at 50°C.

Concurrently, UV-vis spectrophotometric study was perused in which extract of source was taken as blank. The deposition gets distinctly visible in the flask which was left for 1h-24h and subsequently filtered. The UV-visible spectra were recorded on a Schimadzu UV-vis spectrophotometer. The FTIR spectra were obtained on a Schimadzu FTIR spectrometer with the samples as KBr pellets. The formation of single-phase compound was checked by X-ray diffraction (XRD) technique. The XRD pattern was taken with X-ray diffractometer (XPERT-PRO) at room temperature, using CuK\textsubscript{α} radiation $\lambda=$1.5406 Å over a wide range of Bragg angles ($0^\circ \leq 2\theta \leq 85^\circ$). TEM micrograph of CdS-NPs was obtained at 20 K data were obtained on a F20 Tecnai High Resolution microscope (Philips, Netherlands). For TEM analysis, the specimen was suspended in distilled water, dispersed ultrasonically to separate individual particles, and one or two drop of the suspension deposited onto holey-carbon coated copper grids and dried under Infrared lamp.
Results and discussion:

Figure-2, shows the UV-vis spectra recorded from aqueous Tinospora cordifolia leaf extract-CdS (0.025 M) solution as a function of time of reaction. After addition of CdS solution to the extract, the color changes to orange yellow. At this stage, formation of metal nanoparticles due to reduction was followed by UV-vis spectroscopy. The generation of color is due to excitation of surface plasmons in metal nanoparticles. The CdS surface plasmon resonance was observed at 435 nm which steadily increases in intensity as a function of time of reaction without showing any shift of the wavelength maximum. This simply indicates longitudinal plasmon vibrations. Also, the plasmon bands are broadened with an absorption tail in the longer wavelengths, which may be due to the size distribution of the particles. The reduction of the CdS ions taking place at a faster rate and the saturation of data occurs at 360 min.

It seems that the present procedure of biosynthesis of CdS-NPs proceeds with a fairly faster pace and bio-reduction of Cadmium & Sulfide ions is complete within 12 h. In earlier studies on synthesis of CdS-NPs employing bacteria, fungi or plant extracts the time required for completion (i.e. complete reduction of CdS) range from 24 to 120 h, and are rather slow. Reduction may be accomplished due to phytochemicals (alkaloids, glycosides, steroids, sesquiterpenoid, aliphatic compound, essential oils, mixture of fatty acids and polysaccharides) present in Tinospora cordifolia.

UV-visible and TEM studies:

Figure 2 shows the UV-vis spectra of CdS-NPs colloid obtained. The surface Plasmon resonance (SPR) band is broad indicating poly-dispersed nanoparticles. A smooth and narrow absorption band at 435 nm is observed which is characteristic of mono-dispersed spherical nanoparticles. UV-visible spectroscopy is one of the most widely used techniques for structural characterization of metal nanoparticles. The surface plasmon resonance (SPR) band (\( \lambda_{\text{max}} \)) around 435 nm broadened and slightly moved to the long wavelength region, indicating the presence and formation of CdS nanoparticles. The optical absorption spectra of metal nanoparticles are dominated by surface Plasmon resonances (SPR), which shift to longer wavelengths with increasing particle size. The position and shape of plasmon absorption of CdS nanoclusters are strongly dependent on the particle size, dielectric medium, and surface-adsorbed species. The surface plasmon absorption of CdS nanoparticles have the short wavelength band in the visible region around 440 nm is due to the transverse electronic oscillation.

The TEM images obtained for colloid is shown in figure 3. It is clear from the TEM images in figures 3B and 3C, that the particle size, nearly spherical particles of average size 10nm is obtained. The typical high resolution TEM image (figure-3D) confirms the particles are spherical in shape.

The Scherrer rings, characteristic of fccCdS is clearly observed, showing that the structure seen in the TEM image are nano crystalline in nature. It is observed that the CdS nanoparticles are scattered over the surface and no aggregates are noticed under TEM. The difference in size is possibly due to the fact that the nanoparticles are being formed at different times.
Figure 2: UV-visible absorption spectra of CdS nanoparticles after 24 h of reaction.

Figure 3: SEM & TEM’s of the CdS nanoparticles used in this work. (A) SEM image of CdS (B) The bar marker represents 40 nm, (C) 5 nm & (D) HR-TEM micrograph at 2 nm showing spherical shape of CdS nanoparticles.

XRD and FTIR studies:

Figure-4 shows the XRD pattern of CdS nanoparticles obtained using *Tinospora cordifolia*. The diffraction peaks appeared at 25.31, 32.40, 38.10, 42.81, 46.44, and 59.40. The average crystallite size according to Scherrer’s equation calculated using the highest peak of the 38.10 is found to be 10.36 nm, nearly in agreement with the particle size obtained from TEM image.
FTIR measurement was carried out to identify the possible biomolecules responsible for capping and efficient stabilization of CdS nanoparticles synthesized using *Tinospora cordifolia*. Figure-5 shows the FTIR spectrum of CdS nanoparticles obtained in this study. In the IR spectrum of *Tinospora cordifolia* capped CdS nanoparticles, the spectrum showed absorptions at 3332.90 (OH), the band observed at 1620 arise C=O of -COOH, respectively. The band observed at 1319 cm\(^{-1}\) is due to C-O stretching mode. The very strong band at 1049 cm\(^{-1}\) arises from C-O-C symmetric stretching and C-O-H bending vibrations of protein in the *Tinospora cordifolia*.

![Figure 4](image1.png)

Figure 4: X-ray diffraction pattern of CdS-NP at room temperature synthesized by *Tinospora cordifolia* extract with CdS solution.

![Figure 5](image2.png)

Figure 5: FT-IR spectra of *Tinospora cordifolia* mediated CdS nanoparticles.

**EDX Studies:**

The elemental analysis of the CdS-NP was performed using the EDX spectrum of these spherical nanoparticles and were presented in Figure-6. Throughout the scanning range of binding energies, a clear peak indicating any impurity was not seen. The result indicates that the synthesized product is composed of high purity CdS-NP.
Figure 6: Energy-dispersive X-ray spectrum of the *Tinospora cordifolia* mediated CdS-NP.

**Photoluminescence Studies:**

The spectral analysis of CdS nanoparticles was performed at 0 h and 12 h. The 0 h spectra however showed an absorbance maximum but there was significant increase in the absorbance at 435 nm after 12 h of incubation period. The optical property of synthesized CdS nanoparticles was evaluated by recording photoluminescence spectra. Figure 7 & 8, shows photoluminescence spectra of CdS nanoparticles synthesized using leaf extract of *Tinospora cordifolia*. The excitation peak was found at 582 nm while emission peak was observed at 628 nm.
**Figure 7&8:** Absorption spectra and Photoluminescence Spectra of CdSe nanoparticles absorbing at 616 nm and emitting at 608 nm (which was excited at 476 nm).

**Conclusion:**

This work describes a green method for the synthesis of CdS-NPs. Further fluorescence studies were conducted to verify these particles as suitable bio markers. The results revealed describes these materials may act as fluorescent bio markers.

**References:**


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