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MICROBIAL BIOSYNTHESIS OF CADMIUM SULFIDE (CDS) NANOPARTICLES AND THEIR CHARACTERIZATION

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ABSTRACT

Green synthesis of the Cadmium Sulfide nanoparticles with novel, clean and biological transformation with unique properties, finding potential application in emerging field of nano-photonics & nanoelectronics has been carried out. The average particle size of cadmium sulphide (CdS) nanoparticles prepared by biological routes using immobilized microbes like *Pseudomonas aeruginos, Bacillus lichenisformis, Escherichia coli, Fusarium oxysporum & Aspergillus terrus,* was 17.86, 17.00, 17.86, 18.73 and 13.21 nm respectively. Variety of visual analysis techniques were performed like UV-vis optical absorption photoluminescence spectra and Atomic Force Microscopy (AFM) for structural characterization of the nanoparticles. The optical band gap of these materials has been determined in order to establish a relationship between energy band gap of bulk and nano materials. Change in the colour of Cadmium chloride and sodium sulfide solution indicates the synthesis of cadmium sulfide nanoparticle, the resultant shows the absorbance at characteristics peak for each CdS nanoparticle at 465, 459, 465, 468 and 428 nm respectively. Band of gap obtained for the microbes confirms the success full biosynthesis of nano particles with value for *Pseudomonas aeruginosa* (2.66eV), *Bacillus lichenisformis* (2.71eV), *Escherichia coli* (2.66eV), *Fusarium oxysporum* (2.64eV) & for *Aspergillus terrus* (2.90eV). The randomly selected nanoparticles obtained from microbes (*Pseudomonas Aeruginosa* and *Aspergillus terrus*) were subjected to 3D visualization and characterization by the use of AFM. Photo catalytic dye-degradation was also performed to all the biologically synthesised cadmium sulphide nanoparticles.

KEYWORDS: Nanoparticle's, Cadmium Sulfide, U.V, Band Gap, Photo Catalytic & AFM.

INTRODUCTION

Nano particles obtained from semiconductor material especially from group II to group VI are making their presence felt in the research and market due to their different unique and specific optic, electronic and catalytic properties and their high surface-to-volume ratio is responsible for all these properties.[1] CdS nanoparticles are used in zero dimensional quantum confined materials and optochemical and optoelectronic properties. CdS nanoparticles have their properties influenced by their size. Therefore, researchers are able to control and modify nanoparticles surface in order to control their properties, like by chemical methods.[1] Generally living organisms produce organic matter but there are various studies supporting that at intra-cellular as well as at extra-cellular level various organisms can produce inorganic substances too.[2-4] In order to fulfil the necessity and exponentially growing high-tech demand, there is an urgent need to thrive an eco-friendly commence for nanoparticles synthesis that is lack of expensive approach and using toxic chemicals in the synthesis procedure . Recently, microorganisms have been used as biofactories for the synthesis of both metallic nanoparticles including sulphides, gold and silver nanoparticles[5] and semiconductor. The cadmium sulfide (CdS) is an important II–VI semiconductor with many excellent physical and chemical properties, which has promising applications in research and multiple technical areas of including, gas sensor, solar cells, photochemical catalysis detectors for laser and infrared, nonlinear optical materials, various luminescence devices, optoelectronic devices and so on.[5-8] CdS can be obtained in thin film form, by various methods or in powdered form, by hydrothermal/solvo thermal methods, thermal decomposition etc. The formation of CdS nanoparticles can be analysed and detected with the help of spectroscopy. The quantum size effects make the visible absorption spectra different than that of bulk CdS nanoparticles.[9] Besides the chemical synthesis, different biological template such as peptides, fusion proteins and nucleotides can act as a capping to regulate the synthesis of CdS nanomaterial's.[10] They control the crystal structure and size under aqueous and ambient conditions.

EXPERIMENTAL SELECTION
MATERIAL AND METHODS

Nutrient Broth, Nitrate Broth and Potato Dextrose Broth were used for the preparation of supernatants. Cadmium chloride and sodium sulphide were used for making their solution. All chemicals were of analytical grade and were used without further purification. Double distilled water was used in all the experiments.

Microbes Used

Pseudomonas aeruginosa (MTCC NO-4673), *Bacillus lichenisformis* (MTCC NO-3127), *Escherichia coli* (MTCC-729), *Fusarium oxysporum* (MTCC NO-3656) & *Aspergillus terrus* (MTCC NO- 3374).

Preparation of Growth Media

I. Nitrate Broth was prepared by adding necessary ingredients:

Peptone: 5.00g/l, Meat Extract: 3.00g/l, Potassium Nitrate: 1.00g/l and pH 7 at 27ºC

II. Potato dextrose broth was prepared by adding the ingredients:

Potato dextrose 200g/l, dextrose 20g/l, pH 5.1 at 25ºC, 1litre double distilled water

Preparation of Cadmium chloride and sodium sulfide solution:

I. 100 ml of cadmium chloride and sodium sulfide salt solution were prepared.

Synthesis of Cadmium Sulfide nanoparticles using microbes

Synthesis from *Pseudomonas aeruginosa*

Pseudomonas was maintained in a nitrate broth by inoculating it in test tubes and allowed it to grow in a rotary shaker at 30° C for 24 h. Stock culture was maintained by sub-culturing. From an actively growing culture stock, 200µL of culture was re-suspended to a 100ml of fresh nitrate broth and allowed it to grow in the rotary shaker for 24 h. After 24 h the culture was centrifuged at 8000 rpm for 15 minutes. The pellets were discarded and the supernatant is re-suspended in a conical flask containing 50ml of 5Mm of cadmium chloride and sodium sulfide. The whole mixture was kept in the rotary shaker and allowed the reaction to occur for 24 h at 37° C. A change in color was observed and followed by centrifugation at 8000 rpm for 15 minutes, from which supernatant was collected for UV analysis.

Synthesis from *Bacillus lichenisformis*

Bacillus lichenisformis was maintained in a nitrate broth by inoculating it in test tubes and allowed it to grow in a rotary shaker at 30° C for 24 h. Stock culture was maintained by sub-culturing. From an actively growing culture stock, 200µL of culture was re-suspended to a 100ml of fresh nitrate broth and allowed it to grow in the rotary shaker for 24 h. After 24 h the culture was centrifuged at 8000rpm for 15min and harvested the pellet by discarding the supernatant. The pellet was washed with 2ml of Phosphate Buffer Saline .The harvested pellet is then re-suspended in a conical flask containing 25 ml of 5 Mm of cadmium chloride and sodium sulfide. The whole mixture was kept in the rotary shaker and allowed the reaction to occur for 24 h. A change in color was observed and followed by centrifugation at 8000 rpm for 15 minutes, from which supernatant was collected for UV analysis.

Synthesis from *E.coli*

E.coli was maintained in a nitrate broth by inoculating it in test tubes and allowed it to grow in a rotary shaker at 30° C for 24 h. Stock culture was maintained by sub-culturing. From an actively growing culture stock, 200µL of culture was re-suspended to a 100ml of fresh nitrate broth and allowed it to grow in the rotary shaker for 24 h. After 24 h the culture was centrifuged at 8000rpm for 15minutes The pellets were discarded and the supernatant is re-suspended in a conical flask containing 50ml of 5Mm of cadmium chloride and sodium sulfide. The whole mixture was kept in the rotary shaker and allowed the reaction to occur for 24 h at 37° C. A change in color was observed and followed by centrifugation at 8000 rpm for 15 minutes, from which supernatant was collected for UV analysis.

Synthesis from *Fusarium Oxysporum*

Fusarium oxysporum was maintained in a potato dextrose broth by inoculating it in test tubes and allowed it to grow in a rotary shaker at 30° C for 48 h. Stock culture was maintained by sub-culturing. From an actively growing culture stock, 200µL of culture was re-suspended to a 100ml of fresh potato dextrose broth and allowed it to grow in the rotary shaker for 72 h. After 72 h the culture was centrifuged at 4000rpm for 15min and harvested the pellet by discarding the supernatant. The pellet was washed with 2ml of Phosphate Buffer Saline. The harvested pellet is then re-suspended in a conical flask containing 25 ml of 5Mm of cadmium chloride and sodium sulfide. The whole mixture was kept in the rotary shaker and allowed the reaction to occur for 48 h. A change in color was observed and followed by centrifugation at 8000 rpm for 15 minutes, from which supernatant was collected for UV analysis.

Synthesis from *Aspergillus Terrus*

Aspergillus Terrus was maintained in a potato dextrose broth by inoculating it in test tubes and allowed it to grow in a rotary shaker at 30° C for 48 h. Stock culture was maintained by sub-culturing. From an actively growing culture stock, 200µL of culture was re-suspended to a 100ml of fresh potato dextrose broth and allowed it to grow in the rotary shaker for 72 h. After 72 h the culture was centrifuged at 4000rpm for 15min and harvested the pellet by discarding the supernatant. The pellet was washed with 2ml of Phosphate Buffer Saline. The harvested pellet is then re-suspended in a conical flask containing 25 ml of 5Mm of cadmium chloride and sodium sulfide. The whole mixture was kept in the rotary shaker and allowed the reaction to occur for 48 h. A change in color was observed and followed by

centrifugation at 8000 rpm for 15 minutes, from which supernatant was collected for UV analysis.

RESULT AND DISCUSSION

Visual Analysis

From the visual analysis we have seen there was change in the color of cadmium chloride and sodium sulfide solution, from yellow to dark yellow color which indicates the synthesis of cadmium sulfide nanoparticle. And we have observed with the increase in incubation time the color of the solution changed from light to more dark color. Concentration dependent reaction shows that $5*10^{-3}$mM concentration is the best option concentration for the synthesis of cadmium sulfide nanoparticles. The change in color occurs with the occurrence of the following reaction ($CdCl_2 + Na_2S \rightarrow CdS + 2NaCl$).

UV Spectral Analysis

The UV-vis absorption spectra of the cadmium sulfide nanoparticles solution were measured with Shimadzu-1800 UV-vis spectrophotometer. UV analysis of the synthesized cadmium sulfide nanoparticle from *E.Coli*, *B.Licheniformis*, *Pseudomonas Aeruginosa*, *F. oxysporum* and *A.Terrus* shows absorbance at 465 nm, 459nm, 465nm, 468nm and 428 nm respectively shows the characteristic peaks for CdS NP's (fig 1). This lambda maximum **(λ max)** is then further used for finding the band gap of CdS NPs synthesised from various microbes.

Band gap determination

To find the band gap the formula used was $E = hc/\lambda$ max, Where, h= Planck's constant, C= speed of light and λ= wavelength in nm. The band gap of CdS NP obtained from *Pseudomonas Aeruginosa*, *Bacillus Lichenisformis*, *E.Coli*, *Fusarium Oxysporum*, *Aspergillus Terrus* was *2.66ev*, *2.71ev*, *2.66ev*, *2.64ev*, *2.90ev* respectively.

Particle size determination

Particle size determination is another important aspect for analysing the nanoparticles synthesized. The formula used for the particle size determination was as per the protocol established by Winkelmann et al., (2007).[11] The particle sizes of different nanoparticles were provided in the table 2. The formula explained by them was.

$$E_g^{nano} = E_g^{bulk} + \frac{h^2}{8m_0r^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.8e^2}{4\pi\varepsilon\varepsilon_0 r}$$

Where, Eg = h c / λ; h = $6.626x10^{-34}$ Js, value of c = $2.998x10^{8}$ m/s; e = $1.602x10^{-19}$C; ε0 = $8.854x10^{-12}C^2/N/m^2$; m0 = $9.110x10^{-31}$ kg. For CdS, λbulk = 512 nm; ε = 5.7; me* = 0.19; mh* = 0.80. From the calculation the particle size of the nanoparticle obtained from *P.aeruginosa*, *B.licheniformis*, *E.Coli*, *F.oxysporum*, A.*terrus were* 17.86, 17.00, 17.86, 18.73, 13.21nm respectively.

Photo catalytic dye-degradation

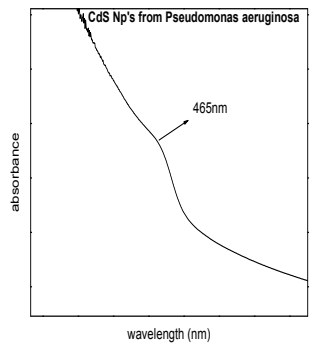
Photo-catalytic activity of CdS nanopowders was studied by degradation of synthetic methylene blue and crystal violet dyes in aqueous solution. 10 mg CdS nano particles were suspended in 50 ml solution of the dye in a reactor and exposed to light from top from a 160W mercury vapour lamp for durations ranging between 0 and 120 minutes. The contents in the reactor were continuously stirred using magnetic stirrer. The distance between light source and surface of the solutions was maintained at 15 cm to avoid excessive heating. Figure 2 shows the photo catalytic degradation of crystal violet dye by CdS nanoparticles obtained from *Fusarium oxysporum*.

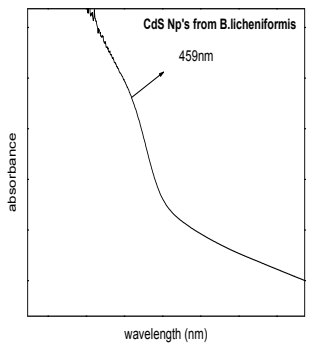
Atomic Force Microscopy study

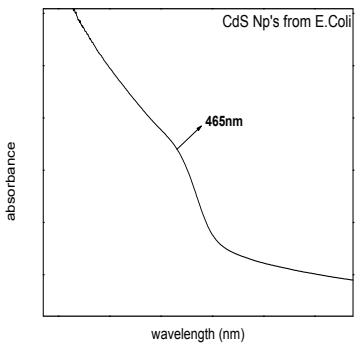
Using the atomic force microscope (AFM), individual particles and groups of particles can be visualized as it offers visualization in three dimensions. Thus we have characterized our sample with AFM and images below shows the AFM images of cadmium sulfide nanoparticles synthesized from *Pseudomonas Aeruginosa* and *Aspergillus terrus*.

Peak reading from AFM Analysis

From the figures and data obtained from atomic force spectroscopy of the CdS nanoparticles, the peak obtained from the AFM analysis are shown in figure 3 and 4.







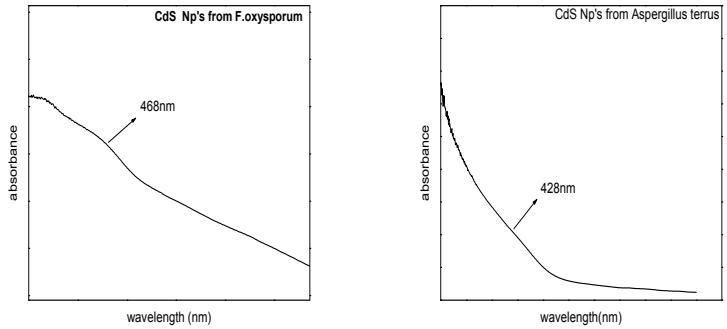


Figure 1:U.V-Visible spectra of CdS nanoparticles synthsized from different microbes respectively to find the *λ max*.

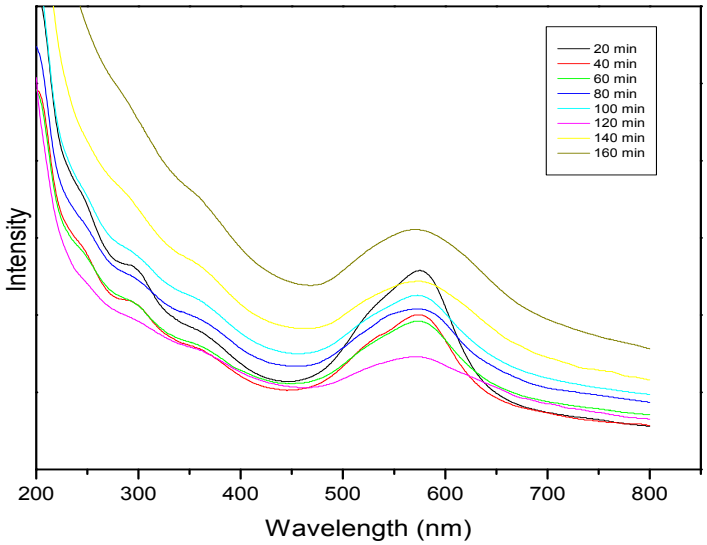


Figure 2*:* Photocatalytic degradation of crystal violet dye from *Fusarium oxysporum* cadmium Sulfide nanoparticles.

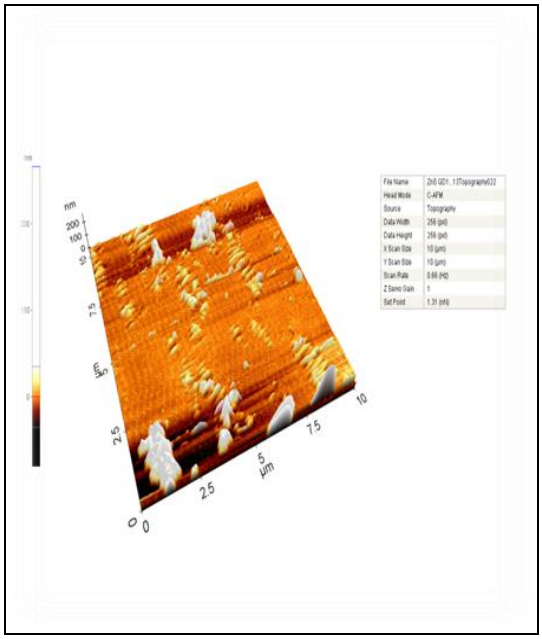


Figure 3(a)

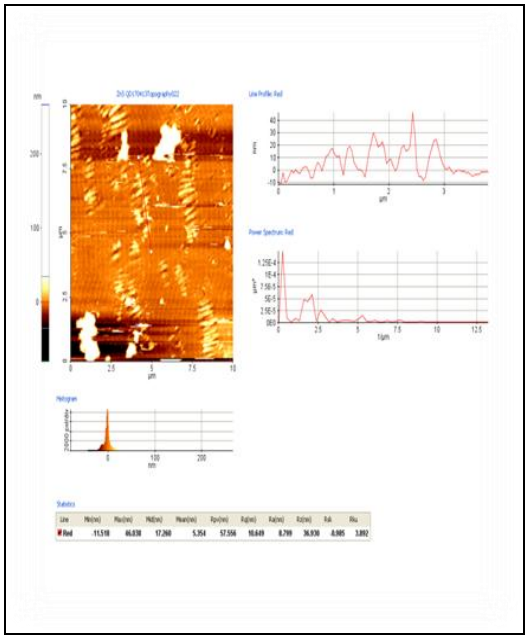


Figure 3(b)

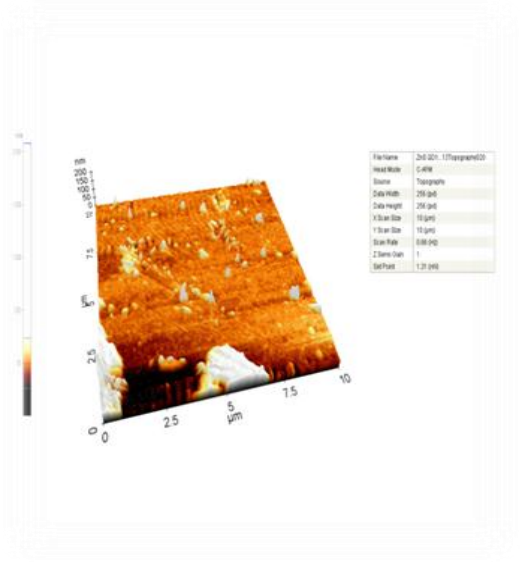


Figure 3(c)

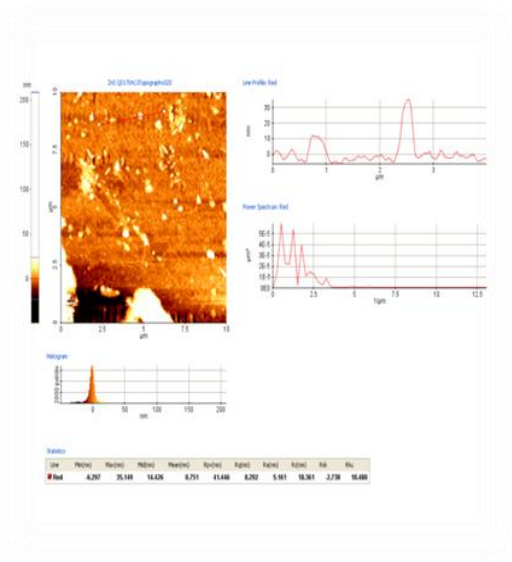


Figure 3(d)

Figure 3: AFM analysis of CdS nanoparticle produced from *Pseudomonas aeruginosa*, 3 (a) and (b), and from *Aspergillus Terrus* figure 3(c) and 3(d) respectively.

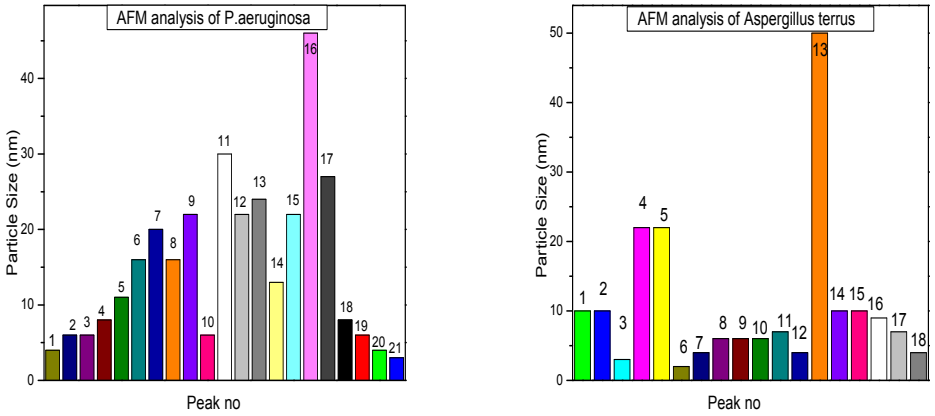


Figure 4: Graph showing the peak reading for corresponding particle sized nano particle prepared by *P. Aeruginosa* and *Aspergilus terrus*.

CONCLUSION

Cadmium Sulphide nanoparticles were synthesized using bacteria as well as fungus and were characterized using TEM microscopy, Atomic Force Microscopy, UV Spectroscopy and visual analysis. All the nanoparticles were in range from 5-30 nm and are monodispersed. Nanoparticles are capped with organic green matter and reduced by reducing enzymes which are either secreted extracellularly or bound to cell wall. These nanoparicles may find applications in photochemical catalysis, gas sensor, detectors for laser, infrared, solar cells, luminescence devices and optoelectronic devices etc.

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