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Biosynthesis and characterization of cadmium sulfide nanoparticles – An emphasis of zeta potential behavior due to capping

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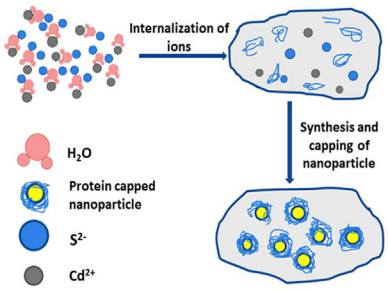
HIGHLIGHTS

- Synthesis of CdS NPs utilizing reproducible molecular machinery viz. *Escherichia coli* biomass.
- Uniform and Polydispersed NPs with high surface area and diameter well below 10 nm.
- Proteins play active roles in the formation and in capping of CdS NPs as confirmed.
- High ζ-potential with varying pH confers stability of aqueous CdS NP dispersion.
- Dispersion stability due to interplay between NP surface and adsorbed protein.

GRAPHICAL ABSTRACT



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ABSTRACT

Biological approaches have been amongst the most promising protocols for synthesis of nanomaterials. In this study, Cadmium sulfide nanoparticles (CdS NPs) were synthesized by incubating their precursor salts with *Escherichia coli* and zeta potential (ζ-potential) measurement with varying pH was carried out to evaluate stability of the colloidal dispersion. Formation of CdS NPs was studied in synchrony with microbial growth. TEM analysis confirmed the uniform distribution of NPs. Average size (5 ± 0.4 nm) and electron diffraction pattern revealed polycrystalline cubic crystal phase of these nanoparticles. X-ray diffractogram ascertained the formation of CdS nanoparticles with phase formation and particle size distribution in accordance with the particle size obtained from TEM. Absorption edge of biosynthesized CdS NPs showed a blue shift at ~400 nm in comparison to their bulk counterpart. A hump at 279 nm indicated presence of biomolecules in the solution in addition to the particles. FT-IR spectrum of capped CdS NPs showed peaks of protein. This confirms adsorption of protein molecules on nanoparticle surface. They act as a capping agent hence responsible for the stability of NPs. The enhanced stability of the particles was confirmed by Zeta potential analysis. The presence of charge on the surface of capped CdS NPs gave a detail understanding of dispersion mechanism and colloidal stability at the NP interface. This stability study of biosynthesized semiconductor nanoparticles utilizing microbial cells had not been done

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in the past by any research group providing an impetus for the same. Surface area of capped CdS NPs and bare CdS NPs were found to be 298 ± 2.65 m^2/g and 117 ± 2.41 m^2/g respectively. A possible mechanism is also proposed for the biosynthesis of CdS NPs.

1. Introduction

Cadmium Sulfide (CdS) is one of the most extensively studied semiconducting material belonging to II–VI group. It has unique optical and chemical properties owing to the quantum size effect [1]. The CdS NPs have promising application in several fields including nonlinear optics, photo-electrochemical cell, solar cell, single electron transistor and photo-catalysis [2–7]. The fundamental aspect concerning the field of Nanotechnology is the development of reliable and efficient synthesis method for these semiconducting nanomaterials. To obtain materials with desired properties, many parameters influencing growth of nanomaterials are manipulated. They include solvent, temperature, precursor molecules [8] and pH [9]. Particular attention has been focused on using different capping agents in an effort to stabilize, control shape, size and crystallinity of the developing nanocrystals [8,10]. However, at this point, it is still difficult to predict that how the physical properties of the resulting material would get affected by varying different parameters of nanomaterial synthesis, [8]. One-dimensional CdS has been prepared by utilizing a variety of methods like thermolysis [11,12], solvothermal (hydrothermal) process [13,14], Microwave-assisted synthesis [15], Chemical Vapor Deposition [16] and DC Electrochemical Deposition [17]. In recent times, momentum has shifted from physical and chemical processes towards biological processes; involving biological molecules as capping agents [18]. Living organisms have innate feature to exquisitely regulate synthesis of inorganic materials such as sea shells [19], bone, teeth, and even magnetite crystals [20–22]. Microorganisms such as bacteria and fungi play an important role in the remediation of toxic metals by reducing them under stress conditions. This forms the basis of using microorganisms in biosynthesis of nanoparticles [8,21,23]. Previous reported studies on microbial synthesis of CdS NP are for instance, Sweeney et al. [8]. reported intracellular formation of CdS nanocrystals by *E. coli*. They give the idea that nanocrystal formation depends on growth phase of cells. Bai et al. [24]. reported a simple biosynthetic method for NP formation utilizing bacteria. The determined bacterial protein is responsible for the same. Mi et al. also showed that by genetically engineering the genes responsible for CdS binding peptide, CdS quantum dots could be synthesized [25]. The microorganisms and biomolecules provide a large number of nucleation centers to direct shape and crystallinity of developing inorganic nanomaterial and establish conditions for obtaining highly stable and dispersed nanoparticle systems [21].

In a colloidal solution complex interfacial interactions occur between nanoparticle surface and the surrounding liquid. The electrolytic interactions, van der Waals forces, solvation forces, hydrophobic and steric interactions counteract to make a stable dispersion [26,27]. Important among these is the electrostatic repulsion which depends on the surface charge. Surface charge results into strong repulsive force among particles making a dispersion stable [28]. Brownian motion and van der walls attraction tend to aggregate particles, so a strong electrostatic repulsion is required to overcome the attraction forces and avoid agglomeration. Usually, the measurement of electrostatic potential acting on solid–liquid interface is carried out as an average potential, calculated in the *surface of shear*. An imaginary surface considered to lie near particle surface where the surrounding medium is considered stationary. This average potential is known as electro kinetic or zeta potential (ζ-potential) [29]. The zeta potential depends on chemical identity of the surfaces, pH of surrounding solvent medium and ions present in suspension [30]. The zeta potential of any colloidal solution is measured by varying the pH of aqueous solution which influences two mechanisms viz. dissociation of functional group(s) and adsorption of ions [27]. At a particular pH when colloidal particles in a solution carry no net charge (or are neutral), the inter-particle repulsive forces are absent leading to the colloidal solution to be least stable. This pH of dispersion medium is known as IEP (iso-electric point) [27,31]. This IEP is one of the basic characteristic of particles that carry charge (for example: biomolecules). This helps in determining sign of the net charge for different pH values [32]. Particles having high zeta potential value, either positive or negative, repel each other and avoid agglomeration. In case attraction exceeds repulsion then particles start agglomeration, eventually lowering the zeta potential values [33]. This makes zeta potential an important characterization tool for studying phenomena occurring at interface due to surface charge modifications [27].

Surface engineering and modification techniques have been used to disperse particles with high degree of stability and homogeneity. The proposed work is aimed at biosynthesizing semiconductor CdS nanoparticles by incubating precursor salts with *Escherichia coli*. Evaluation of stability of biosynthesized CdS NPs dispersion is carried out by zeta potential analysis. Additionally, a comparative study of change in zeta potential of biomolecule capped NPs and bare CdS NPs (without capping agent) at different pH was performed. The results suggest that biomolecular capping might lead to the stability and controlled growth of nanoparticles; intrinsic to microbial cells.

2. Materials and methods

2.1. Bacterial strain and chemical

The chemicals used in this experiment, cadmium chloride (purity > 99.9%) and sodium sulfide (purity > 98.0%), were purchased from Sigma Aldrich. Bacterial strain (*E. coli, MTCC 40*) was collected from Institute of Microbial Technology, Chandigarh, India. In all experiments deionized water was used with resistivity of the order of 18 MΩ cm (ELGA Purelab Flex).

2.2. Biosynthesis of cadmium NPs

Microbial cells from late logarithmic phase (*O.D. = 1.65*) were used for CdS NPs synthesis. The cells were in mature and high dividing stage of their life cycle [8]. Bacterial cells were centrifuged at 6000 rpm for 5 min followed by washing and re-suspending three times in 0.1 M phosphate-buffered saline (PBS, pH 7.4). This ensured removal of culture media. 200 mg of wet biomass was transferred in 50 ml de-ionized water. A 0.01 M $CdCl_2$ solution was mixed to this microbial cell filtrate. After 30 min 0.01 M Na_2S was

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