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Thermal and optical characterization of biologically synthesized ZnS nanoparticles synthesized from an endophytic fungus *Aspergillus flavus*: A colorimetric probe in metal detection

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ABSTRACT

Nanostructured semiconductor materials are of great importance for several technological applications due to their optical and thermal properties. The design and fabrication of metal sulfide nanoparticles with tunable properties for advanced applications have drawn a great deal of attention in the field of nanotechnology. ZnS is a potential II–IV group material which is used in hetero-junction solar cells, light emitting diodes, optoelectronic devices, electro luminescent devices and photovoltaic cells. Due to their multiple applications, there is a need to elucidate their thermal and optical properties. In the present study, thermal and optical properties of biologically synthesized ZnS nanoparticles are determined in detail with Thermal Gravimetric Analysis (TGA), Derivative Thermogravimetric Analysis (DTG), Differential Scanning Calorimeter (DSC), Diffuse Reflectance Spectroscopy (DRS), Photoluminescence (PL) and Raman spectroscopy. The results reveal that ZnS NPs exhibit a very strong quantum confinement with a significant increase in their optical band gap energy. These biologically synthesized ZnS NPs contain protein residues that can selectively bind with metal ions in aqueous solutions and can exhibit an aggregation-induced color change. This phenomenon is utilized to quantitatively measure the metal concentrations of Cu^{2+} and Mn^{2+} in this study. Further the stability of nanoparticles for the metal sensing process is accessed by UV–Vis spectrometer, zeta potential and cyclic voltammeter. The selectivity and sensitivity of ZnS NPs indicate its potential use as a sensor for metal detection in the ecosystem.

1. Introduction

Chalcogenides have gained significant interest among the researchers due to their prominent electroluminescence properties at nanoscale. In particular, research on ZnS which is a nontoxic semiconductor has traditionally shown remarkable fundamental properties and promising diverse applications, including light-emitting diodes, electroluminescence, flat panel displays, infrared windows, sensors, lasers and biodevices [1–7]. Additionally, ZnS finds prospects due to the presence of polar surfaces, excellent transport properties, good thermal stability and high electronic mobility [8,9]. Further, ZnS is a most suitable candidate because of its distinguishing chemical, optical and electronic properties of crystalline phosphor [2,5,10]. Since, these nanoparticles have huge applications biological synthesis methods are explored, where fungi are one of the sources exploited for synthesis. Chemically synthesized nanoparticles are highly unstable and tend to agglomerate in the absence of trapping media or encapsulation, whereas biological synthesis provides discrete particles through surface modification with protein capping [11]. Biologically synthesized nanoparticles have proven to possess long-term stability due to the presence of protein capping on them. Therefore, such encapsulation also improves the surface conditioning; having a significant influence on the optical, electronic properties and thermal stability of nanoparticles [12,13]. In this study, we have documented the properties of nanoparticles synthesized from an endophytic fungus *Aspergillus flavus* isolated from a medical plant *Nothapodytes foetida*. The endophytes associated with medicinal plants produce secondary metabolites, these bioactive metabolites originate from different biosynthetic pathways and belong to diverse structural groups such as terpenoids, steroids, quinones, phenols, and coumarins [14,15]. Thus, nanoparticles synthesized from endophytes might hold a great potential in enhancement of the luminescence property.

Copper and manganese occurs naturally in the environment and is toxic at elevated concentrations, which has been a challenging issue for environmental scientists. In the industrial and agricultural sector, it is observed that use of high concentration of copper can destroy biological reprocessing systems [16,17]. According to literature it has been reported that in some areas of Bangladesh, concentration of Mn was 2.0 mg/L, which is four-fold higher than WHO norms. In infant milk formulations the level of Mn is approximately 1.3 mg/L, which is much higher than the amount present in cows' milk. These concentrations of

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Mn cause neurological effects such as Parkinson syndrome. Also, production of homemade illicit drugs and contamination of food stuffs with the Mn containing fungicides in some countries are considered to be serious environmental threat [17,42]. Excess amounts of copper in drinking water is hazardous to human health and can cause Alzheimer's disease, inflammatory disorders and liver damage . Moreover, high concentrations of copper may destroy the biological reprocessing systems in water. Due to its role and effects in metabolic pathways, a simple, selective and sensitive method is essentially required for the quantification and detection of Cu^{2+} and Mn^{2+} in drinking water, industrial, environmental, and food samples [16,39].

Several methods have been developed for their detection, such as electrochemical analysis, atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) and molecular fluorescence spectroscopy [18,19]. Most of these methods are expensive, complicated and difficult for in-situ detection. Therefore, there is a need to develop a simple, quick and inexpensive method for detecting heavy metals in aqueous solutions. Herein, the emphasis will lie on the use of nanoparticles as biosensors based on optical sensing. The color change aids in the utilization of plausible absorption/interparticle surface plasmon coupling based on colorimetric sensing of any target analyte that induces nanoparticle aggregation [20].

This paper focuses on the optical, thermal and stability characterization of polycrystalline ZnS nanoparticles and their properties were determined in detail. TEM and DLS revealed the formation of spherical particles with an average diameter of about 18 nm and 58.9 nm respectively in our previous studies [21]. Subsequently, by the selective binding property of nanoparticles, metal detection has been carried out by UV –Vis spectroscopy.

2. Materials and Methods

2.1. Thermal Characterization

The thermal stability of the samples was studied using the thermal analysis technique, for the recording of Thermo-Gravimetry (TG), Derivative Thermogravimetric Analyzer (DTG) (Perkin Elmer, Diamond TG/DTG STA 6000, USA) and Differential Scanning Calorimeter (DSC) (Mettler Toledo DSC 822e, Canada) analyses under airflow. 35 mg of samples were heated at the heating rate of 10 °C/min in the temperature range of 35–800 °C in TGA-DTG and heating rate at room temperature to 700 °C in 7 min in case of DSC. Samples analyzed were contained within alumina crucibles and heated at a rate of 10 °C min^{-1} under flowing air flow.

2.2. Optical Characterization

For DRS experiments, UV–vis spectra were taken using (Varian, Cary 5000, USA) in a diffuse reflectance mode within a spectral range of 175–3300 nm. The optical band gap energy (E_g) is calculated by the Kubelka and Munk method [10] [22]. Photoluminescence spectra were achieved through fluorescence measurement (Fluorolog 3 TCSPC, Horiba, USA), xenon lamp as an excitation source and at an excitation wavelength of 315 nm and grating 1200 g/mm. All measurements were performed at room temperature. In order to investigate the crystallization, structural disorder and defects of the ZnS nanocrystallites Raman measurements were performed at room temperature. The instrument used for this spectroscopy was a Confocal RAMAN Imaging System (Alpha 300RA, WITec GmbH, Ulm, Germany). A fiber coupled DPSS laser 532 nm with maximum output power after single mode fiber coupling of 70 mW, grating 600 g/mm, an integration time of 10 s.

2.3. Stability Studies

Electrochemical workstation was employed for the electrochemical characterization of the ZnS nanoparticle sample (VERTEX Ivium I.A.E.I.S., Netherlands). It consists of 3 electrodes namely the working electrode (Pt electrode), the reference electrode (calomel electrode) and the counter electrode (Pt wire). The cyclic voltammetry curve was obtained by sweeping the potential at a rate of 25 mV/s between −2.5 V and 2.5 V [49]. For this zeta potential analyzer the temperature is set at 25 °C and at scattering angle equal to 90° (Horiba, nanopartica SZ-100). For the analysis, the nanoparticle sample of the desired concentration was flushed through a folded capillary cell and the measurement was carried out; a sufficient sample volume was used to completely cover the electrodes of the cell. To avoid air bubbles in the cell, the sample was injected slowly and analysis was only carried out if there were no visible air bubble inclusions present. Then the cell was placed in the sample holder and the corresponding zeta-potential measurements were taken [52].

2.4. Colorimetric Detection of Metal Ions

Colorimetric detection method follows liner correlation where two variables wavelength and intensity at various concentrations are considered [38]. Colorimetric detection was used to evaluate the detection concentration of metal ions of Cu^{2+} and Mn^{2+} with ZnS NPs. For copper ions detection, different concentrations of metal solutions (0.5, 1, 5, 10, 20 μM) were added to ZnS NPs (18 nm size, 2.6 mM concentration) solution at pH 9 [44] and stirred for 20 min. After thorough stirring, a color change was observed and the corresponding UV–vis absorption spectrum (Hitachi, U-2000, PM & E 101) was recorded. Similar procedure was adopted for Mn^{2+} metal ions detection.

3. Results and Discussion

3.1. Thermal Stability

To determine the crystalline conditions, TGA-DTG and DSC of ZnS nanoparticles were carried out. The specimens were heated from room temperature to 900 °C with an increment of 10 °C/min in air. Notably, in TGA data plots given in Fig. 1 revealed the weight loss of the nanoparticles upto 620 °C. The decomposition started around 100 °C and continued till 620 °C. The first weight loss was intense with approximately 72% mass change. In TGA-DTG maximum rate of decomposition was recorded at 292 °C and change of mass as a function of temperature was 53.86% as shown in Fig. 2. For the DSC curve (Fig. 3) exothermic peaks at 80 °C, 120 °C, 250 °C and endothermic peak at 280 °C were recorded, respectively [4,23]. These peaks can be attributed to the evaporation of water and decomposition of the proteins. A large exothermic peak was exhibited at 450 °C and this might be due to the crystallization of ZnS [24].

3.2. Optical Properties

The optical methods take advantage of observing the essential characteristics of the nanomaterials without significantly modifying or permanently damaging them due to their noncontact and noninvasive nature. Nanoparticles are ideal nanomaterials for ultrasensitive and multiple applications in optical sensing, so there is a need to explore the optical properties of these nanoparticles [25].

3.2.1. Photoluminescence Analysis

Photoluminescent spectrum is an effective tool to evaluate the defects and optical properties of ZnS NPs as a photonic material. Also, photoluminescence spectrum is sensitive to synthetic conditions, size, and shape of NPs. Broadening of the emission peak could be attributed to both size distribution and an increase in the surface states owing to