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Synthesis and characterization of biopolymer protected zinc sulphide nanoparticles

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ABSTRACT

Zinc sulphide (ZnS) nanoparticles are prepared by a simple, economic and green synthesis route. X-ray diffraction patterns confirm zinc blend structure. ZnS formation is confirmed through chemical analysis by energy dispersive analysis of X-rays. Transmission electron microscopy reveals formation of nanosize with dimension in the range of 8–2 nm. Band gap of the nanocrystals is found to lie in the range of 4.51–4.65 eV. Photoluminescence study indicate defect like vacancies. The growth mechanism of ZnS nanoparticles is discussed with the help of Fourier transform infrared spectroscopy and thermogravimetric analysis. The materials show high dielectric constant compared to its bulk counterpart. The dielectric loss of the samples shows anomalous behaviour. The frequency dependent A.C. conductivity of the samples is discussed both in high and low frequency regimes. Current–voltage (*I–V*) characteristic performed under dark and under illumination, shows excellent light response of the material.

1. Introduction

Semiconductor nanomaterials exhibit unique size-dependent physical and chemical properties that differ from those of the bulk systems. Among them, zinc sulphide (ZnS) has attracted much research interest because of its excellent properties which lead to wide range of applications. The band gap of its cubic phase at room temperature is 3.72 eV. Several preparation methods have been used to obtain ZnS nanoparticles [1,2]. Most of these methods are based on the use of toxic chemicals. These chemical based methods are also not cost effective, a major disadvantage for the synthesis of nanoparticles at the industrial scale. Additionally, the chemically fabricated nanoparticles are less biocompatible and their applications in biological and medical systems are restricted [3]. An appropriate alternative is the application of biological reagents including carbohydrate, peptide, nucleotides and fusion proteins [4]. It offers numerous of eco-friendliness and compatibility for pharmaceutical and biomedical applications as they do not use toxic chemicals in the synthesis protocols [5]. Green chemical route for the synthesis of ZnS nano have been in practice [6,7]. In some of our resent works also, we have reported on such preparations using edible mushrooms [8,9] and *Elaeocarpus floribundus* leaf extract [10].

The use of starch has recently become important in green synthesis methods of fabricating nonmaterial due to the fact that this biopolymer acts as an effective surfactant agent and is environment friendly. Moreover, the surface modification of fluorescent semiconductor nanostructures by biopolymer has added a new dimension to nanoparticles research with

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respect to their biological applications [11]. Starch molecules which contain anhydrous glucose unit may play an important role for the structural modification of composite nanomaterials [12]. Syntheses of CdS [13], CdSe [14] and ZnSe [15] nanoparticles have been reported using starch as capping agent. But to the best of our knowledge it has not been utilized for the synthesis of ZnS nanoparticles. So, we thought it is worthwhile to explore the properties of ZnS nanoparticles prepared using starch in order to strengthen our research on green chemical route.

The performance and efficiency of nanostructure based devices are determined by the optical, electrical and dielectric properties of the material. A study of these properties is very important as it helps in optimizing sample parameters for better device applications. The band gap of ZnS nanostructures could be extended via quantum confinement effect that makes it very promising for applications in photoconductors, nanophotodetectors, ultraviolet light sensors and photoconducting semiconductor switches [16]. A.C. conductivity is an important parameter used to characterize the dielectric and transport properties of the materials [17,18]. Knowledge of dielectric constant of the material is needed to properly design and apply instruments such as for making level controls using radar, RF admittance or capacitance technologies. High dielectric materials have recently become important mainly in three areas – memory cell dielectrics, gate dielectrics and passive components. Another important aspect comes from the electrical transport behaviour under light illumination. It has been observed that this type of semiconductors show enhanced conductivity through increase of current on illumination. This is called photocurrent and it arises due to generation of electron hole pairs because of the interaction of the photons with bound electrons of the lattice atoms. The conductivity of the materials depends upon the carrier density and complex process of generation, trapping and recombination of carriers. Photocurrent is also a function of temperature, applied field, intensity of light and energy of radiation [19].

In this work, we report the synthesis of ZnS nanoparticles through green chemical route using starch as capping agent and the investigation on structural, optical, thermal, dielectric and transport properties of the synthesized material.

2. Experimental

2.1. Materials

Materials used in the present work are $ZnCl_2$, Na_2S and starch. $ZnCl_2$ (Merck Specialities Pvt. Ltd.) and Na_2S (Qualigens fine chemicals) are used as zinc and sulphur source respectively. Starch is obtained from Aldrich. These are of high purity and used without any further purification.

2.2. Synthesis method

Solution of Na_2S (0.5 M) is added drop wise to the prepared solution of $ZnCl_2$ (0.5 M) and then aqueous solution of starch is added drop wise to the mixture. The mixture is set for continuous stirring and thereafter the resultant solution is kept overnight at room temperature to complete the reaction process resulting in the formation of ZnS colloid. Nanoparticles are collected by centrifugation at 2000 rpm for 15 min. Resultant product is dried at 120 °C for 2 h and then crushed to fine powder with the help of mortar and pestle. The process is carried out for four different concentrations (1, 2, 3 and 4 wt%) of starch. The four final products of ZnS nanoparticles are to be designated henceforth as I, II, III and IV respectively.

2.3. Characterization methods

Prepared ZnS nanoparticles are examined by X-ray diffraction (XRD) technique using an X-ray diffractometer (Philips X'pert-with Cu Kα radiation) of wavelength 0.154 nm over 2θ range of 20–70°. The purity and elemental analyses of the samples are examined by energy dispersive analysis of X-rays (EDAX) (Oxford, INCA-7587). Transmission electron microscopy (TEM) micrographs are obtained in JEOL JEM 2100 using an accelerating voltage of 200 kV. UV–Visible spectra are recorded in a Hitachi U-3210 spectrometer, Photoluminescence (PL) spectra are recorded by Hitachi F-2500 and Fourier transform infrared (FTIR) spectra are recorded by Perkin Elmer Spectrum RXI FTIR system, Thermogravimetric analysis (TGA) is performed using a Perkin–Elmer thermal analyzer, dielectric parameters are recorded by LCR Hitester HIOKI 3532 and current–voltage (I–V) characteristics are taken with the help of Keighley sourcemeter (model 2400).

3. Results and discussion

3.1. Structural study

Fig. 1 shows the XRD patterns of as prepared ZnS powdered samples. Three broad peaks are observed in the diffractrogram at around 2θ = 28.54°, 47.73°, 56.28° for Sample I, which are in good agreement with those of cubic lattice structure of ZnS (JCPDS card no. 77-2100). The three diffraction peaks correspond to (1 1 1), (2 2 0) and (3 1 1) planes of cubic ZnS polycrystalline structure [20]. For samples II, III and IV there is slight shift in the peak positions and increase in peak broadening. No diffraction peaks from other crystalline forms are detected, indicating high purity and well crystalline of the obtained ZnS nanoparticles. Also, the broadening of the XRD patterns indicates the nanocrystalline nature of the samples. The crystallite