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Synthesis and characterizations of ZnS nanoparticles on *E.coli* DNA skeleton

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Abstract : Bio-inspired nanoparticles syntheses have attracted considerable attention due to effective size control. In this paper we have synthesized Zinc Sulphide (ZnS) nanocrystals using *E. coli* genomic DNA as a templet. The XRD and UV-Vis results confirm the formation of ZnS nanoparticles with particle size ~2.2-2.5 nm. The TEM result shows the formation of nearly spherical ZnS nanoparticles over the strands of genomic DNA. The results show effective control of shape and size during synthesis process.

(**Keywords:** Bio-inspired, DNA, *E. coli*, Nanoparticles)

Introduction

Over the past few years, the synthesis of semiconductor nano-particles has attracted extensive interest because of their shape and size dependent properties and broad range of potential applications in optoelectronics[1], catalysis[2], solar energy conversion[3], photo induced energy transfers[4] metal-insulator transition[5-6] and water pollutant photo degradation[7]. A variety of semiconductor nanoparticles (NPs), such as CdS[8-9], CdSe[10], CdTe[11], ZnS[12], PbS[13] and PbSe[41] have been successfully synthesized using different methods. Among them, ZnS nanocrystals (NCs) have been extensively studied for a long time. It is a wide band gap (~ 3.6 eV) material with unique optical properties and has found important applications in various fields such as light-emitting diodes, lasers, chemo-sensor, and biomedical labeling[15-17]. These properties depend on the shape and size distribution of nano-particles. It is necessary to have a narrow size distribution and control on the shape of semiconductor particles for well-defined and optimized properties[18-19]. Many methods have been developed to prepare ZnS NPs, including the precipitation in homogeneous solution[20-21], reverse micelles[22-23], photochemical route[24] and solvothermal route[25-27] etc. However, the ZnS nano-particles (NPs) prepared by these methods usually aggregated into big clusters due to high surface energy, resulting in the reduction of the surface area and restricting control over the particle size distribution[28-29]. To overcome this problem, the way of using a matrix/template to synthesize ZnS nanoparticles has been developed. Using biomolecules as a template to synthesize inorganic nano-particles is an effective method to fabricate functional materials by providing such environment in which the NPs' morphology is highly controlled resulting in NPs formation with well-defined structure and controllable dimensions[30-35]. Among biological molecules, deoxyribonucleic acid (DNA) is one of the most interesting template systems because of its physicochemical stability, well-defined sequences of DNA base and a variety of super helix structures[36]. Therefore, precise control over the arrangement of DNA will provide the possibility for well templating the resulting nano-particles. In general, synthesis of nano-particles based on DNA templates have been performed by incubating metal ion coated DNA in a reduction agent solution. The ion-DNA complexes controlled the release of metal ions, slowing down

their reduction and effectively inhibited metal ions from growing into big clusters. The resulting NPs synchronously aligned on the DNA template and realized the synthesis and assembly in one step. Some nano-structures such as sliver[37] and Cu_2O[38] nano-particles have been synthesized by this method. When DNA networks were used as template, the synthesis of sliver nanoparticles, nano-rods and nano-wires were prepared in one step by changing the density of the DNA network template[37]. No reports of synthesis of ZnS nanoparticles on DNA templates are available to the best of our knowledge.

In the present work, ZnS nanoparticles have been successfully synthesized by using *E. coli* DNA networks as templates. The total DNA of *E. coli* has been isolated and then ZnS nanoparticles were synthesized over DNA skeleton by simple wet chemistry route under nitrogen environment. The method we report here is simple and reproducible. X-ray diffraction (XRD), UV-visible spectrometer and transmission electron microscopy (TEM) were carried out on the synthesized ZnS nanoparticles.

2 EXPERIMENTAL

2.1 Materials

Zinc acetate dehydrated [Zn $(CH_3COO)_2$. $2H_2O$], Sodium sulfide (Na2S) flakes and ethanol were procured from Merck India Limited, Mumbai, India. Tris HCl, disodium salt of Ethylenediaminetetraacetic acid (EDTA), Sodium Dodecyl Sulfate (SDS), Lysozyme, Pronase E, equilibrated phenol, Chloroform, Isoamyl alcohol, Sodium acetate, and RNase were procured from Himedia Laboratories. Pvt. Ltd were used for synthesis. Chemicals were used as purchased without further purification as all the chemicals were of molecular biology grade. All the solutions were made in sterile thrice distilled water. The *Escherichia coli* (*E. coli*) DH5-α cultures were obtained from National Collection of Industrial Microorganisms (NCIM), India. Ice bath, DNase free tips, some glass tubes, spooler, centrifuge cups, and eppendorf tubes (all equipment were made free from DNase) were employed for total genomic DNA isolation

2.2 Isolation of Total Genomic DNA From *E. coli*
The modified Marmur's procedure[39] was used for the total genomic isolation from *E. coli.*

2.3 Synthesis of ZnS Nanocrystals on DNA Skeleton

The ZnS nano-crystals on DNA skeleton were synthesized by wet chemical route under nitrogen environment. The reaction was performed in a three neck round bottom (RB) flask. All the solutions were kept under high vacuum for ½ hr before the synthesis to remove the air from the solutions. The DNA solution was first diluted to 40 ng/µl. 10 ml of zinc acetate solution (50 mM) and 10 ml of diluted DNA solution were completely mixed gently and the solution was kept for 15 min under gentle stirring, then Na2S solution was added drop by drop in to the Zn2+/ DNA solution, appearance of faint white colour in the vicinity of reaction mixture indicates the formation of ZnS nano-crystals. The liquid samples were used for TEM and UV-Vis measurements, while the precipitate were collected by centrifuging the sample at 3000 rpm at 4°C and then the sample were dried at 55°C under vacuum to perform XRD.

2.4 Characterizations

The prepared ZnS nano-crystals were characterized by UV- Visible Spectroscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM),. XRD was carried out using Rigaku D/max-2200 PC diffractometer operated at 40 kV/20 mA, with $CuK_{\alpha 1}$ radiation having wavelength of 1.54 Å from 10^0 to 70^0 on 2θ scale. The phase identification was carried out with the help of standard JCPDS database. The crystallite size was calculated using Scherrer's formula. Transmission electron microscope (model Technai 30 G^2 S-Twin) operated at 300 kV accelerating voltage was used to take TEM images. Sample for TEM was prepared by placing a drop of the as-

synthesized liquid sample on the surface of carbon coated copper grid and the grid was dried in air. UV- Visible Spectroscopy was performed on a Perkin Elmer lambda 35 UV/Vis spectroscopy using a Deuterium lamp for UV source and Tungsten lamp for visible source. All the measurements were carried out at room temperature.

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3.1

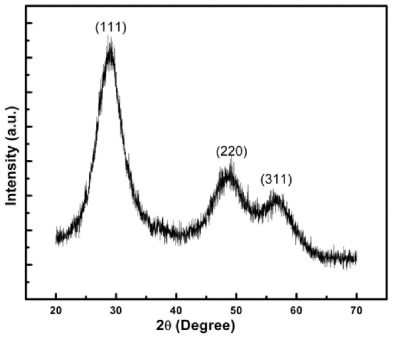

Figure 1: XRD Pattern of ZnS Nano-particles Grown on Skeleton of *E. coli* DNA.

Figure 1 shows the wide-angle X-ray diffraction (XRD) pattern of ZnS nano-crystals produced on DNA network templates. XRD spectrum show broad peaks corresponding to (111), (220) and (311) reflections, at 2θ positions of 28.63°, 47.87° and 56.47° for all the samples. Standard JCPDS file for cubic ZnS (JCPDS 77-2100) were used for indexing and XRD data of samples show good agreement with it. No peaks related to Zn, ZnO or other zinc compounds were observed, which clearly suggested that the produced ZnS nanoparticles were crystalline in nature without any impurities. The particle size, *d*, of nano-crystals were estimated by Debye-Scherrer's [40] formula.

$$d = \frac{0.9\lambda}{BCos\theta}$$

where, λ is the wavelength of used radiation, d is the particle size, B is the full width at half maxima (FWHM) on 2θ scale, and θ is the Bragg angle. The most prominent X-ray diffraction, corresponding to (111) peak at 28.63° was used for crystallite size determination and was found ~2.2 nm.

3.2 UV-Vis Spectroscopic analysis

The UV-Vis spectra of DNA/ZnS nano-particles are shown in figure 2. The spectra show a band centered at 285 nm. This absorption peak (285 nm) is strongly blue-Shifted as compared to cubic bulk ZnS (absorption peak at 338 nm)[41], indicating a smaller particle size. The particle size can be calculated from the empirical relationship between the average size of nanoparticles and the onset of UV absorption given by Banfield et al.[42], the estimated particle size is about 2.5 nm, which is in good agreement with XRD/TEM observations.

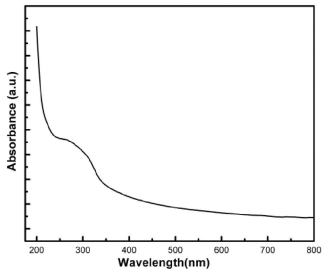

Figure 2: UV-Vis Spectra of ZnS nanoparticles grown on skeleton of *E. coli* DNA showing absorption peak at 285 nm.

3.3 TEM Analysis

Figure 3 shows the representative TEM images; (a) TEM at 200 nm scale, (b) TEM at 50 nm scale, (c) HRTEM and (d) SAED pattern of ZnS nanoparticles on DNA skeleton. TEM image gives a clear evidence of the formation of ZnS nanoparticles over the chain of DNA. The TEM image shows that the ZnS nano-particles grow over DNA skeleton and forms bead like structure and the particles are of spherical in nature. The high crystallinity of the ZnS NCs are clearly by HRTEM image (Fig 3c). The distances between the adjacent lattice fringes are measured to be about 0.31 nm, which is in good agreement with the standard value, 0.312 nm (JCPDS No. 77-2100).

Presence of high crystallinity and a cubic structure in ZnS NCs are also supported by Selected Area Electron Diffraction (SAED) pattern, shown in figure 3(d). In this the three diffraction rings are perfectly indexed to the same positions as those from bulk ZnS.

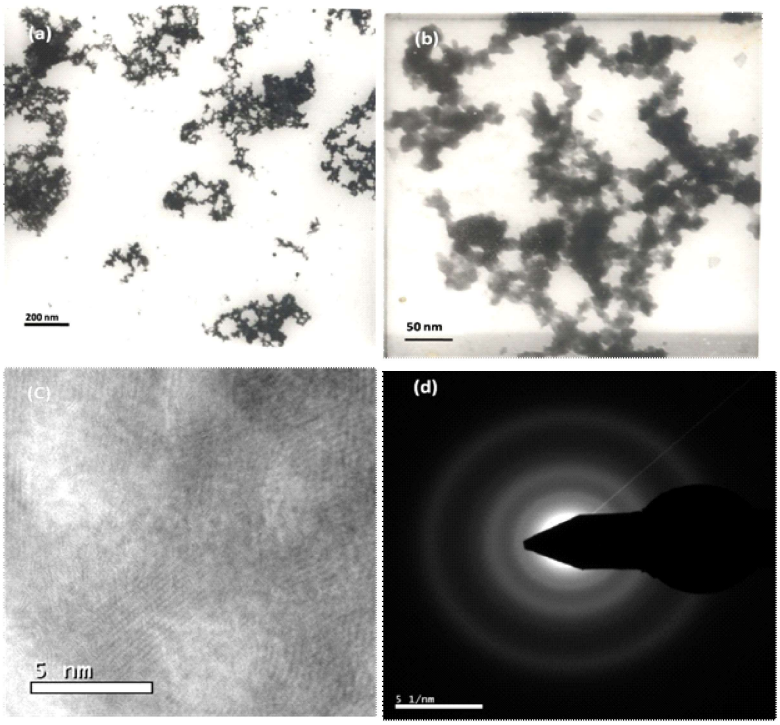

Figure 3: TEM Micrograph (a) TEM at 200 nm scale, (b) TEM at 50 nm scale, (c) HRTEM and (d) SAED pattern of ZnS nanoparticles grown on skeleton of *E. coli* DNA.

Conclusion

In summary, we have synthesized ZnS nanoparticles on *E. coli* DNA Skelton as templates by simple wet chemistry under nitrogen environment. The XRD and UV-Vis results confirm the formation of ZnS nanoparticles with particle size ~2.2-2.5 nm. The synthesized ZnS has good crystallinity and is spherical in nature. The size and assembly of ZnS nanoparticles could be controlled by using DNA. These results indicate that the approach is facile and effective for synthesizing and controlling ZnS nanoparticles.

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