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Structural and Morphological Studies of Electrospun Manganese-Doped Zinc Sulphide (ZnS: Mn) with Capping Agent L-citrulline/PVA Composite Nanofibers

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***Abstract* — Materials in the form of fibers are of great practical and fundamental importance. Combination of a high specific area, flexibility, and superior directional strength make nanofiber a preferred material for many fields such as biomedical applications including drug delivery as well as scaffold formation. Manganese doped Zinc Sulphide with capping agent L-citrulline is blended with high molecular weight Poly Vinyl Alcohol (PVA) and the resulting solution is electro-spun to get non-woven nanofibers. Structural Characterization has been done by X-ray diffraction (XRD) and Fourier Transform Infra-Red Spectroscopy (FTIR). The fiber obtained is of good crystallinity as evidenced by the intense XRD peaks. The morphology is analyzed using a Scanning Electron Micrograph (SEM). The SEM micrographs reveal smooth fibers with several millimeters in length and average diameters in the range of 645 nm. Studies point to the possibility of using the prepared fibers for bio-medical applications.**

Keywords* — *Nanofibers. Electrospinning, Zinc Sulphide Nano particles, Blended Fibers, Poly Vinyl Alcohol

I. Introduction

Research on semiconductor nanoparticles stimulated great interest in recent years because of their unique optical and electrical properties. Among the semiconductor nanoparticles, zinc sulfide as an important II–VI semiconductor has been researched extensively because of its broad spectrum of potential applications such as in catalysts, electronic and optoelectronic Nano devices [1]. Particularly, manganese-doped zinc sulfide (ZnS:Mn) is a favorable phosphor that exhibit excellent optical properties such as high luminescence intensity, narrow emission band etc. modification of these nanocrystals by suitable capping agent such as amino acid ligands makes the nanocrystals biocompatible. Here using the amino acid ligand, L-citrulline (LC).

As ZnS is toxic, capping with amino acids makes these nanocrystals more biocompatible and less toxic [2,3]. For this, highly luminescent manganese doped Zinc Sulfide (ZnS: Mn) nano crystals are modified by suitable amino acid capping agents such as L-citrulline [3]. These biocompatible capping agents bind to the surfaces of the nanoparticles during the synthesis of the chemical capping co-precipitation method [2,3].

In this study, we explore the structural and morphological properties of a novel composite material. This composite consists of manganese-doped zinc sulfide (ZnS:Mn) nanoparticles capped with L-citrulline and embedded in polyvinyl alcohol (PVA). It is electrospun for the production of nanofibers. Electrospinning is a versatile and efficient technique used to generate ultrafine fibers with diameters ranging from nanometers to micrometers, providing a promising platform for fabricating advanced materials with potential applications in biomedicine and optoelectronics [4,5].

II. Methodology

A. Synthesis of L-citrulline-capped ZnS:Mn nanoparticles

In the work, L-citrulline-capped ZnS nanoparticles were synthesized by a simple and cost-effective wet chemical co-precipitation method. The chemicals used were $Zn(CH_3COO)_2.2H_2O$ (>98%; Merck Specialities Private Mumbai, India), $Mn(CH_3COO)_2.4H_2O$ (>99.5%; Merck Specialities Private Limited), $Na_2S.9H_2O$ (98%; Merck Specialities Private Limited) and L-citrulline ($C_6H_{13}N_3O_2$) (99%; Loba Chemie Pvt, Ltd, Mumbai, India). In a typical experiment, 0.1M Zinc acetate, 0.01 M manganese acetate and 0.025M citrulline were mixed in 50 mL of distilled water to which 0.1 M aqueous solution of sodium sulphide was added dropwise to form L-citrulline capped ZnS:Mn nanoparticles.

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The mixture was kept under constant stirring for 1.5 hrs and then filtered and dried in the oven at 40˚C. A powder was obtained and used for further detailed studies [2,3].

B. Solution Preparation

In a typical procedure, PVA aqueous solution was prepared by dissolving PVA powder (2.2 g in 20 ml) in distilled water under magnetic stirring for 1.5 hrs at 65˚C, and then cooled to room temperature. The resultant solution was again subjected to stirring for another 12 hrs. After cooling, 0.06g of nanoparticles (3% of PVA) was added to the PVA solution with vigorous stirring. The stirring continued till complete dissolution took place [6,7]. A viscous solution of ZnS:Mn/PVA (with L-citrulline) was the result. The sample was held in a spinning nozzle with a tip diameter of 1 mm. A copper pin connected to the anode of a high-voltage generator was placed in the solution. A voltage of 15 kV was applied to the solution and dense webs of fibres were collected on an aluminium foil, at a distance of 12 cm from the tip of the nozzle. Finally, the film attached to the aluminium foil was separated from it and used for different characterizations.

III. Results and Discussion

A. Structural Characterization

a) X-Ray Diffraction

In order to understand the crystalline nature of nanoparticles and nanofiber, X-ray diffraction study has been performed using X-ray diffractometer equipped with CuKα radiation (λ=1.5406 A0) with 2Θ value varying from 100 to 750 for Nano particle and from 100 to 900 for Nanofiber. Figure1 shows the diffraction pattern of nanoparticles and nanofibers. Three prominent peaks corresponding to (111), (220) and (311) planes of ZnS were observed respectively at 2Θ values of 28.570, 47.820, and 57.190.

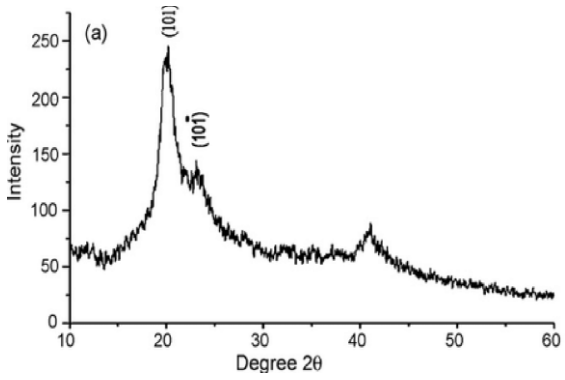
The diffraction peaks from (111), (220), and (311) planes have only appeared in the pattern and all other high angle peaks are submerged in the background due to the large line broadening, which is attributed to the nano size of the particles [8,9]. On comparing with the standard sample (JCPDS card no 050566), the X-ray diffractogram and 2Θ values of ZnS were found to be in fairly good agreement, thus confirming the zinc blend crystal structure having particle size 2.65 nm. The broadening in the diffraction peaks might be due to the size effect, ie, the crystallite size is in the nano- regime.

These nanocrystals have lesser lattice planes compared to bulk, which contributes to the broadening of the peaks in the diffraction pattern [10]. It could also arise due to lack of sufficient energy needed by an atom to move to a proper site in forming the crystallite diffraction plane. From the X-ray diffraction peaks the particle size is determined from the full width at half maximum (FWHM) of the diffraction peaks using the Debye-Scherrer formula

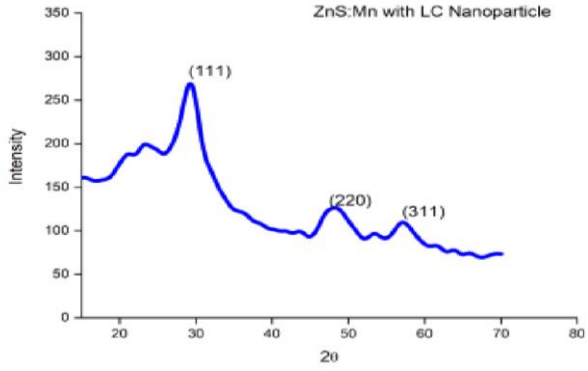
$$D = 0.9\,\lambda / \beta \cos\Theta$$

were D, λ, β and Θ are the average particle size, wavelength of the CuKα radiation, full width at half maximum of the sample, and the diffraction angle respectively.

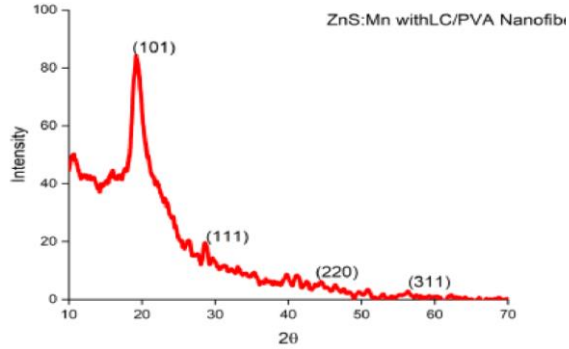
The major peaks in the XRD pattern of L-citrulline capped ZnS:Mn nanoparticles are broadened due to a decrease in particle size upon capping. The X-ray patterns of the LC capped ZnS:Mn/PVA nanofibers are presented in figure1. The peak at 2θ=20° corresponds to the (101) plane of crystalline PVA in the ZnS:Mn/PVA nanofibers. The diffraction angles at 2θ=28.080, 48.360 and 57.430 can be assigned to (111), (220), and (311) planes of the cubic structure of ZnS, respectively.



(a)



(b)



(c)

Fig. 1. (a) XRD pattern of PVA particles, (b) XRD pattern of LC capped ZnS: Mn nano particles, (c) LC capped ZnS:Mn/PVA composite Nanofiber

(b) IR Spectrum

The FTIR spectrum of the ZnS:Mn nanocrystals the peaks at 3243/cm is assigned to be the O-H stretching vibrations and the peaks at 1626 /cm corresponds to O-H bending. The peaks observed at 2915 /cm and 2815 /cm are due to the presence of

carbon and which is an instrumental image. The band centered at the 1415/cm is attributed to the stretching vibrations of the C=C groups in the acetate species used to synthesis ZnS. From the IR spectrums, it is clear that the functional groups present in the Nanofiber is a combination of the groups present in the PVA and the solutions.

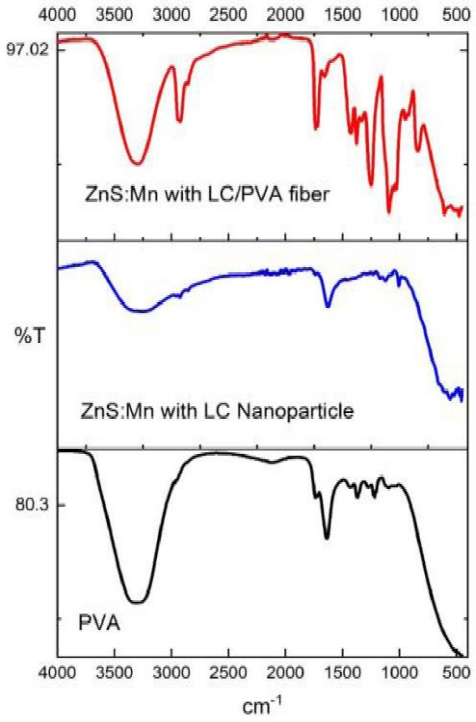


Fig. 2. FTIR spectrum of PVA, LC capped ZnS: Mn Nano particles and LC capped ZnS: Mn/PVA Nanofiber

B. Morphological Studies

The SEM image of the electrospinning ZnS:Mn with L-citrulline/ PVA is in Figure 3.

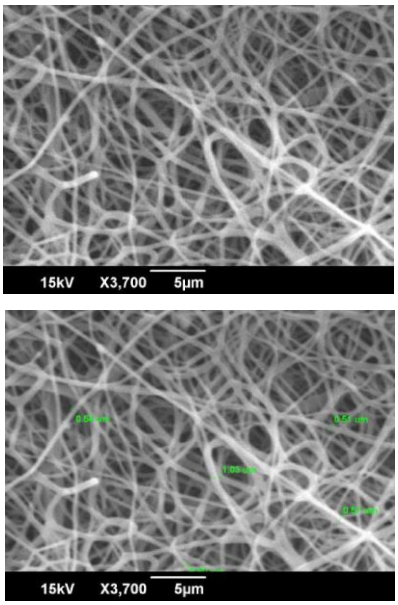


Fig. 3. SEM images of LC capped ZnS:Mn/PVA composite Nanofibers

The fibers appear smooth, without significant roughness or surface irregularities. This suggests that the polymer solution was well prepared, with proper solvent evaporation and solidification during the electrospinning process. In this work no beads or "bead-on-string" structures are visible, which is a good indicator of a well-controlled electrospinning process. Beads typically form when the polymer concentration is too low, or the solution's surface tension isn't optimized.
The fibers appear to be randomly oriented, which is typical in many electrospun nanofiber mats. Random orientation can be useful in applications like filtration or scaffolds where isotropic properties are needed. They are longer than several millimetres, with diameters about 645 nm.

IV. Conclusion

The nanoparticles of ZnS doped with manganese capped with L-citrulline, have been successfully synthesized using a well-known chemical precipitation method in water medium. These nanoparticles were characterized structurally by XRD and found to have cubic crystal structure with the diffraction planes (111), (220), and (311). The crystallite sizes of the nanoparticles have been calculated using Debye Scherrer's equation. Nanoparticles dissolved in PVA and by using the electrospinning technique, nanofibers are formed with diameters 645 nm.

Electro spinning is a very simple process, requiring just simple laboratory equipment to yield fibres down to the nanoscale, the science behind it is not simple at all. Electrospinning process involves the understanding of electrostatics, fluid rheology and polymer solution properties such as rate of solvent evaporation, surface tension and solution conductivity. These fundamental properties are constantly interacting and influencing each other during the electrospinning process. The versatility of electrospinning also meant that fibres of different morphology and made of different materials can be made directly or indirectly from electrospinning. Therefore, different polymers, blends, mixtures or precursors can be used to make fibres to suit specific applications. Understanding the basics behind the materials and the fundamentals that affect electrospinning will open new avenues and applications for electrospun fibres.

XRD spectrum of the fibre agreed with the same three peaks corresponding to the nanoparticles and there are one extra peaks corresponding to the angle $2\Theta=20°$ which corresponding to the PVA solution. IR spectrum of the fibre compared with the IR spectrum of the Nano particle and the IR spectrum of the PVA. From these it is clear that the groups present in the fibres are a combination of the two.

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