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Structural Characterization of PVA Assisted ZnS Nanocrystals

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Abstract: ***Polymer nanoparticles have attracted the interest of a number of researchers, due to their synergistic and hybrid properties derived from several components. ZnS has been used widely as an important phosphor for photoluminescence, electroluminescence and cathodoluminescence devices due to its better chemical stability compared to other chalcogenides such as ZnSe. Cubic ZnS with a bulk band gap of 3.7 eV is a common and attractive choice as a host semiconductor for doping to produce nanophosphors in EL applications due to its stability, low cost and low toxicity. PVA has excellent film forming, emulsifying and adhesive properties. PVA assisted ZnS nanoparticles have been prepared at room temperature. The structural studies have been carried out on PVA assisted ZnS nanoparticles. The average size of the particle is found to be less than 25 nm from the structural measurements. The lattice parameter is evaluated in the range of 5.38 – 5.45 A^0.***

Keywords: ZnS Nano crystals, Structure, PVA.

1. Introduction

During the past two decades, the small particle research has become quite popular in various fields of chemistry and physics. Nanoparticles or quantum dots are defined as small particles with 1 to100 nm in diameter at least in one dimension. The small particles now we call nanostructured materials are very interesting materials both for scientific reason and practical application. Semiconductor nanocrystals represent a class of materials that have hybrid molecular and bulk properties. They have attracted much attention over the past few years because of their novel properties which originate from quantum confinement effect [1, 2]. When the particle radius falls below the exciton Bohr radius, the band gap energy is widened, leading to a blue shift in the band gap, emission spectra, etc. On the other hand, the surface states will play a more important role in the nanoparticles, due to their large surface to volume ratio with a decrease in particle size. Transition from bulk to nanoparticles lead to the display of quantum mechanical properties and an increased dominance of surface atoms which increases the chemical reactivity of a material. Notable examples include the tunable band gap and catalytic behavior [3] of nanoparticles. For nanocrystals prepared by solution based chemical methods, a capping agent who adsorbs the nanocrystal surface, generally is added both to control the size of nanocrystals and to prevent agglomeration of synthesized nanocrystals.

Polymers are chosen as good host materials because they usually exhibit long term stability and possess flexible reprocess ability. In addition, the small size and high optical activity of ZnS nanoparticles make them interesting for optoelectronic applications operating in the ultraviolet region. In the case of semiconductor nanoparticles, radiative or nonradiative recombination of an exciton at the surface states becomes dominant in its optical properties with a decrease of particle size. These size dependent optical properties have many potential applications in the areas of solar energy conversion, light-emitting devices, chemical sensors, biological sensors and photo catalysis [4]. Wide band gap II-VI semiconductors are expected to be the novel materials for the optoelectronic devices. ZnS, which is an important member of this family, has been extensively investigated as it has numerous applications to its credit. ZnS has been used widely as an important phosphor for photoluminescence, electroluminescence and cathodoluminescence devices due to its better chemical stability compared to other chalcogenides such as ZnSe. Cubic ZnS with a bulk band gap of 3.7 eV is a common and attractive choice as a host semiconductor for doping to produce nanophosphors in EL applications due to its stability, low cost and low toxicity. ZnS nanoparticles could be used as good photo catalysts due to rapid generation of the electron-hole pairs by photo-excitation and highly negative reduction potentials of excited electrons; as conduction band position of ZnS in aqueous solution is higher than that of other semiconductors such as TiO_2 and ZnO. Since, a larger ratio of surface to volume of a catalyst would facilitate a better catalytic activity; the size controlled synthesis of ZnS nanostructures to produce a larger ratio of surface to volume is of great importance. The enhanced surface to volume ratio causes increase of surface states, which change the activity of electrons and holes, affecting the chemical reaction dynamics. The size quantization increases the band gap of photo catalysts to enhance the redox potential of conduction band electrons and valence band holes [5]. A number of metal ions, such as Mn^{2+}, Cu^{+}, Pb^{2+}, Ag^{+} and Eu^{2+}, have been successfully doped into ZnS to produce PL or EL emission in different regions of the visible spectrum. Compared to bulk or micrometer scale powders, these nanoscale materials are anticipated to have some unique properties that are potentially useful to improve their AC EL performance. In EL applications, AC is preferred since the AC voltage required is usually 2 orders of magnitude lower than for DC voltages. In optoelectronics, it finds use as light-emitting diode, reflector, dielectric filter, and window material.

Polyvinyl alcohol (PVA) is produced commercially from polyvinyl acetate, usually by a continuous process. PVA has excellent film forming, emulsifying and adhesive properties.

It is also resistant to oil, grease and solvent. It is nontoxic. It has high tensile strength and flexibility, as well as high oxygen and aroma barrier properties. However these properties are dependent on humidity, in other words, with higher humidity more water is absorbed. The water, which acts as a plasticizer will then reduce its tensile strength but increase its elongation and tear strength.

2. Experimental

Zinc chloride ($ZnCl_2$) 99 mM of 4 mL is added to 2.2 g PVA (13,000 g/mol). The volume of solution is made up to 50 mL by bi-distilled water and the solution is left for 24 hours at room temperature to swell. After that the solution is warmed up to 80^{o}C and stirred for 4 hours until viscous transparent solution is obtained. One milliliter of Sodium Sulphide (50 mM) is dropped into the solution with gentle stirring. Solution is casted on flat glass plate dishes. After the solvent evaporation, a thin film containing PVA assisted ZnS nanocrystals are obtained. The film is washed with de-ionized water to remove other soluble salts before measurements [6].

3. Results and Discussion

The XRD pattern of PVA assisted ZnS nanocrystals are recorded on PANalytical XPert Pro X-ray powder difractometer using CuK$_\alpha$ (1.54060 A^0) radiation. The XRD is used to determine the degree of crystallinity of PVA assisted ZnS nanocrystals using Debye-Scherrer's equation [7] to estimate the crystal size of the ZnS nanocrystals. depending on the full-width at half-maximum of diffraction peaks. As the crystal size increases the broadening increases. The average size of the crystal is measured by using Scherrer's formula with the full width at half maximum intensity of the pattern.

$$\mathbf{t = 0.9\ \lambda / \beta Cos\theta}$$

Where't' is the thickness, 'λ' is the wavelength of the radiation, 'β' is the full width at half maximum intensity (FWHM) and 'θ' is the angle measured. The average size of the crystal is found to be less than 25 nm. The lattice parameter (a) of the unit cells is calculated according to the relation:

$$1/d^2 = 1/a^2\ (h^2 + k^2 + l^2)$$

Where, d is the interplaner spacing of the atomic planes as determined from the position of the peak (111), lattice parameter is estimated in the range of 5.38 – 5.45 A^0. These values are smaller compared to the bulk value of 5.48 A^0. As already mentioned the XRD peak broadening could also be due to the strain in addition to the crystalline size of the crystal.

4. Conclusion

ZnS nanoparticles could be used as good photo catalysts. PVA assisted ZnS nanocrystals have been prepared at room temperature. The structural studies have been carried out on PVA assisted ZnS nanocrystals. The XRD studies revealed that the average size of the crystal is found to be less than 25 nm. The lattice parameter is evaluated in the range of 5.38 – 5.45 A^0.

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