STRUCTURAL AND OPTICAL PROPERTIES OF ZnS NANOCRYSTALS EMBEDDED IN POLYACRYLAMIDE

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ZnS quantum dots (QDs) incorporated in polyacrylamide were synthesized by adding aqueous suspension of ZnS Sol in acrylamide:bisacrylamide copolymer. X-ray Diffraction supports the zinc blend structure of the samples. Optical properties of ZnS nanocrystals were carried by UV-Vis spectroscopy. The size estimated by the effective mass approximation and ranges between 4-6.5 nm. Size calculated by XRD data also shows good correlation with optical data.

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1. Introduction

Semiconductor nanocrystals have gained tremendous attraction during the last many decades [1,2]. These interesting materials has not only showed many physical phenomenon but also expressed novel optical and transport properties, which are potentially useful for technological point of view [3], like in light emitting diodes, piezoelectric devices and photodetectors [4,5].Blue shift in the optical absorption spectrum, size dependent luminescence, enhance oscillator strength, non-linear optical effects, geometrical structure, chemical bonds, ionization potential, mechanical strength, melting point etc. are all affected by particle size. The change in the properties of nanoparticles is driven mainly by two factors, namely the increase in the surface to volume ratio and change in the electronic structure of the material due to quantum confinement effects. The above properties is mostly exhibited by Zinc Sulfide (ZnS), which having wide energy gap of 3.7 eV at room temperature. However there are lot of reports of fabrication of nano structure of this material involving one method or other and is reflected in the increasing interests and publications on ZnS research [6].

The present paper deals with synthesize of ZnS quantum dots (QDs) incorporated in polyacrylamide, in which electrons are confined in all spatial directions. However, due to the enhancement of quantum confinement, these QDs show new physical properties that are strongly dependent upon nano size of the ZnS materials. The sizes of the particles were calculated by the effective mass model approximation [7-8].

2. Experimental details

The starting chemicals used in the present work were acrylamide 99.9% (Bio-Rad), bisacrylamide 98% (Loba), ZnS (Loba), ammonium persulfate 98% (Loba), and TEMED (N,N,N',N'-tetramethylenediamine) 99% (Sigma).

The gel material was prepared with aqueous suspension of Zinc sulfide in acrylamide:bisacrylamide copolymer. The ZnS suspension was prepared using double distilled water with concentration of 1.0×10^4 , 3.0×10^4 , 20.0×10^4 and 40.0×10^4 mol/L. At room temperature, magnetic stirrer stirred this suspension for 1hour so that the solution becomes homogenous. For

the copolymerization reaction, 10 mL of a mixture containing 0.098 g of acrylamide and 3.6g of bisacrylamide was prepared. The ZnS solution was added slowly to the jelly monomer mixture. Ammonium persulfate (10%) and TEMED were added to the jelly matrix, allowing the copolymerization reaction to take place at room temperature. The polymerization was carried at presence of light at room temperature. The final precipitate was stored at room temperature to dry (to form stable gel of the compositions) for 5 days (120h).

These ZnS/polymer compositions were characterized by X-ray diffraction studies with Cu K α radiation (λ =1.5418 Å) using Rigaku Rotating Anode (H-3R) diffractometer surface morphologies The morphology and the size of the products was carried out using high resolution FE-SEM (FEI NOVA NANOSEM-600). The Optical Absorption (OA) of the samples was studied using Perkin Elimer λ -12 spectrometer. This Optical Absorption (OA), of the (gel material) was done just after the polymerization and after 24, 48, and 120h to observe the stability of the synthesized material.

Drying time (hrs)	Band gap of nanoparticles(eV)	Particle size (nm)	Absorption peak (nm)
120	4.3	5.14	265.1
48	3.9	5.63	272.3
24	3.7	7.86	281.4

Table 1 Optical parameters of ZnS/Polymer nanoparticle compositions.

The size of the particles was estimated from the width of first peak using Debye Scherrer formula [9].

However, using the values of OA the nanoparticules sizes were also determined from the absorption onset by the effective mass model approximation (Brus equation)

$$E = E_{Bulk} + \hbar^2 \pi^2 / 2 e r^2 (1/m_e m_o + 1/m_h m_o)$$
(1)

where *E* is the band gap of the nanoparticles, E_{bulk} is the bandgap of the bulk material, r is the particle radius, m_e and m_h are effective masses of the electrons and holes, respectively, and m_0 is the free electron mass.

3. Results and discussion

(a) Structural study

Fig.(1), shows the X-ray diffraction patterns of ZnS QD (for 120h composition with ZnS concentration of 3.0×10^4 mol/L, basically this molar concentration shows the best results) at room temperature. The obtained peak positions (111), (220) and (311) correspond to the Bragg angles 29.5°, 48.7° and 56.5° and were very broad which show the zinc blend structure of the sample [10]. The lattice parameter has been computed as 5.29 Å (for 120h composition), which is very close to the standard value (5.42 Å). The broad peak indicates nanocrystalline behavior of the particles. The size of the particles has been computed from the width of first peak using Debye Scherrer formula [9].

$$L = [0.9\lambda] / \beta Cos\theta$$
⁽²⁾

where L is the coherence length, β is full width at half maximum (in radian) of the XRD peaks, θ is the diffraction angle and λ is the wavelength of X-ray used. In addition, the diameter of crystallite is given by

D = (4/3) LThe primary crystallites size using Scherer formula is about 4.3 nm.



Fig. 1. X-ray diffractogram of gel polyacrylamide doped with ZnS (3.0x10⁴ mol/L) nanoparticules after 120 h drying time.

Similarly, XRD data of other compositions kept for 48h and 24h, show reduced lattice parameter (5.28 Å and 5.29 Å) and crystallites size was calculated of order of 5.45nm and 6.12nm respectively.

(b) Optical study

Fig.(2) shows UV-visible spectra of ZnS nanoparticles embedded in polymer compositions with different drying time. The spectrum of ZnS/polymer system shows the absorbance in the range of 240-310 nm. The absorption peak at 310 nm is blue shifted compared to the bulk ZnS for which the absorption peak is at 345 nm. The blue-shifted absorption edge is due to the quantum confinement of the excitons present in the broadening of the absorption spectrum is mainly due to the quantum confinement of the size of the crystallites. As the size of the particles decreases, the degree of confinement and its effect increases. The confinement in a nanocrystalline size permits the energy transfer efficiently to the atom. The addition of polymer host/environment to ZnS nanoparticles causes the decrease in particle size as well as the shifting of absorption peaks from 290 to 309 nm indicating that system forms a new energy level in the band structure of ZnS.

Further, UV-Vis absorption data was used to analyze size of ZnS QDs by using equation (1). Since, the peaks positions can be related with the mean diameter of particles, smaller diameter meaning lower wavelength. Results obtained from these analysis (see Table 1), shows the effect of quantum confinement (quantum size effect, QSE). The QSE in direct-gap semiconductors nanocrystals determines a shift of the optical absorption edge to higher energies with decreasing size, which can explain the UV-Vis blue-shift effect [11-13]. The average size of the nanoparticle estimated from the optical data analysis is in good agreement with that calculated from that of XRD data.

(3)



Fig. 2. Absorption spectra of gel polyacrylamide doped with ZnS (3.0x10⁴ mol/L) nanoparticules after (a) 24 h; (b) 48 h and (c) 120 h.

(c) Morphological study

The surface morphology of the prepared sample can be studied by SEM and the picture is shown in Fig.(3), (120h drying time and with $3.0x10^4$ mol/L). The grain sizes of the samples estimated from the SEM picture is much larger than that obtained from XRD data and optical data. The possible reason may be the advantage of one technique over other.



Fig. 3. SEM image of gel polyacrylamide doped with ZnS ($3.0x10^4$ mol/L) nanoparticules after 120 h drying time.

4. Conclusion

We prepared ZnS quantum dots (QDs) incorporated in polyacrylamide by adding aqueous suspension of ZnS Sol in acrylamide:bisacrylamide copolymer. Structural study carried by X-ray Diffraction supports the zinc blend structure. An optical property of ZnS nanocrystals shows blue shift in band edge and shows quantum confinement effect. The size estimated by the effective mass approximation and ranges between 4-6.5 nm. Size calculated by both techniques shows good correlation with each other.

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References

- [1] W.Q. Peng, G. W. Cong, S. C.; Qu, Wang, Z.G. Opt. Mater., 29(2-3), 313 (2006)
- [2] Bouvy, C.; Piret, F.; Marine, W.; Su, B.L. Chem. Phys. Lett., 433(4-6), 350 (2007)
- [3] Son, D.; Jung, D.R.; Kim, J., Moon, T.; Kim, C.; Park, B Appl. Phys. Lett. 90, 101910 (2007)

- [4] X.Wang, Y. Ding, C.J. Summers, Z.L.Wang, (2004) J. Phys. Chem. B 108 8773.
- [5] A. Narayanaswamy, H.F. Xu, N. Pradhan, M. Kim, X. Peng, J. Am. Chem. Soc. 128, 10310 (2006).
- [6] C. R. Gorla, N.W. Emanetoglu, S. Liang, W.E. Mayo, Y. Lu, M.Wraback, H. Shen, (1999) J.Appl. Phys. 85, 2595.
- [7] N. O. Dantas, A. F. G. Monte, W. A. Cardoso, A. G. Brito-Madurro, J. M. Madurro, P. C. Morais, Microelectron. J. 36, 234 (2005).
- [8] W. Dong, C. Zhu. Optic. Mater. 22, 227. (2003)
- [9] D. Xu, G. Guo, L. Gui, Y. Tang, Z. Shi, Z. Jin, Z. Gu, W. Liu, X. Li, G. Zhang, Appl. Phys. Lett. 75, 481 (1999).
- [10] T.A. Kennedy, E.R. Glaser, P.B. Klein, and R.N. Bhargava, Phys. Rev. B 52, R14 356 (1995)
- [11] Y. L. Li, Y. H. Wang, J. Yun, Guang Pu Xue Yu Guang Pu Fen XiAppl.Phys.Lett. 27, 1890 (2007)
- [12] X. W. Zhao, S. Komuro, S. Fujita, H. Isshiki, Y. Aoyagi, T. Sugano, Mat. Sci. Eng. B 51, 154 (1998).
- [13] J. Borah, J. Barman, K. C. Sarma, (2008) Chalc. Lett., 5, 201.