

# Synthesis and Characterization of ZnS Colloidal Quantum Dots

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**Abstract** — A way of colloidal ZnS QDs synthesis, different from knowing ways used for obtaining of these QDs (solvothermal and hydrothermal ways, solid state heating, ultrasonication) is proposed. It is similar to way for CdS synthesis, using oleates as metal precursor and trialkylphosphine sulfides as sulfur precursor. But instead of octadecene or diphenyl ether as solvents we used toluene. ZnS QDs with middle radius  $a = 1.77$  nm, what corresponds to intermediate confinement regime ( $a \approx a_B$ ,  $a_B = 2.5$  nm is the excitonic Bohr radius for bulk ZnS) were obtained.

**Key words** — zinc sulfide, quantum dots, synthesis, excitonic Bohr radius.

## I. INTRODUCTION

ZnS Quantum Dots (QDs) are interesting nano-materials with unique physical and chemical properties, the most striking of them is huge change in optical properties as a function of size and possibility to manipulate their chemical behavior by changing and combining of capping agents, used to stabilize them QDs in solutions. These QDs have great application possibilities as chemical sensors and biosensors [1], photoluminescence and electroluminescence devices [2,3], LEDs [4], biocompatible markers [16] and other possible interesting applications.

Currently several ways for ZnS QDs synthesis are known: solvothermal and hydrothermal methods with thiourea as sulfur source [5, 6, 7], solid state heating [8], microwave heating of aqueous solutions containing zinc and sulfur precursors with capping agent addition [9], precipitation from zinc precursor with capping agent solution by addition of inorganic sulfides [10, 11, 12] or thiourea [13] as sulfur sources, ultrasonication of thiosulfate complexes of zinc [14], thermolysis of non-elementoorganic zinc and sulfur precursors [15]. Interesting modification of sulfide sedimentation way is *in situ* generation of hydrogen sulfide by reducing sulfur with hydrazine hydrate [12].

In our work we tried to apply well-known and widely used way of cadmium sulfide and cadmium selenide synthesis for obtaining of ZnS QDs, using zinc oleate toluene solution as zinc precursor and mix of TOPS (trioctylphosphine sulfide) and TBPS (tributylphosphine sulfide) as sulfur precursor.

## II. EXPERIMENTAL DETAILS

Zinc precursor was prepared by heating of zinc acetate with an excess of oleic acid, followed by addition of toluene. It was done under the argon flux and constant stirring. Sulfur precursor was prepared by mixing elementary sulfur with mixture of TOP (trioctylphosphine) and TBP

(tributylphosphine) taken in excess and vigorous stirring of this mix until all the sulfur dissolves.

Sulfur precursor solution afterwards was added to the zinc precursor solution heated to the 100°C and this mix was maintained for an amount of time under constant mixing, heating and in the argon flux. Afterwards, argon flux, mixing and heating were stopped and reaction flask was placed into cooling bath. In the reaction mix was added cooled acetonitrile to precipitate formed ZnS QDs.

Precipitate was washed several times with acetonitrile and acetone and centrifuged at 8000 rpm to remove organic contaminants. Remains of acetonitrile and acetone were removed by heating. 55.2 mg of ZnS QDs were further suspended again in pure toluene.

UV-Vis absorption spectra were obtained using Perkin-Elmer Lambda 25 UV-Vis spectrophotometer.

## III. RESULTS AND DISCUSSION

Radius (in nanometers) of obtained ZnS QDs was calculated upon UV-Vis absorption spectra using following formula [16]:

$$a = \frac{\sqrt{\frac{13620}{\lambda_p} - 40.197} - 0.2963}{\frac{2481.6}{\lambda_p} - 7.34}, \quad (1)$$

where  $\lambda_p$  is wavelength of maximum absorption (nanometers).

UV-Vis spectra for ZnS QDs of different concentrations are presented in Fig. 1-3. Peaks are at 282.48, 283.64, 285.57, 285.17 and 289.28, what corresponds with radii of 1.76, 1.77, 1.80, 1.81 and 1.88 nm respectively.

In Figs. 1-3 one can see that with decreasing of QDs concentration in suspension the exciton absorption peak intensity also decreases almost linearly. It is experimental proof that observed characteristic peak of optical absorption belongs to ZnS QDs and good correlates with data from other works, where ZnS QDs were synthesized [13, 16, 17].

Obtained QDs radii are a little smaller than excitonic Bohr radius for bulk ZnS [16], that corresponds to intermediate exciton confinement regime. This regime is observable in semiconductor particles with intermediate sizes:  $a_e > a > a_h$ ,

where  $a_e = \frac{k\hbar^2}{m_e e^2}$  and  $a_h = \frac{k\hbar^2}{m_h e^2}$  are Bohr radii of electrons and holes respectively,  $m_e$  and  $m_h$  are masses of electron and hole respectively. In this case, the hole is localized in the center of quantum dot and moves in the average potential of the much faster electron. The region of hole motion around the QD center is much smaller than the QD radius and the size dependence of the exciton ground state can be described as localized at QD center donor behavior. The excitation spectrum of such donor-like exciton can be described as hole oscillation about the QD center [18].

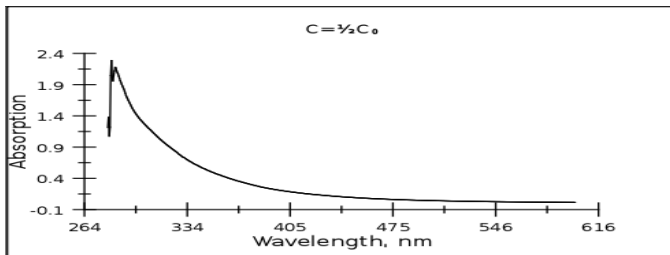


Fig. 1. Absorbance spectrum for initial concentration of ZnS QDs. Peaks are at 285.57 and 289.28 nm.

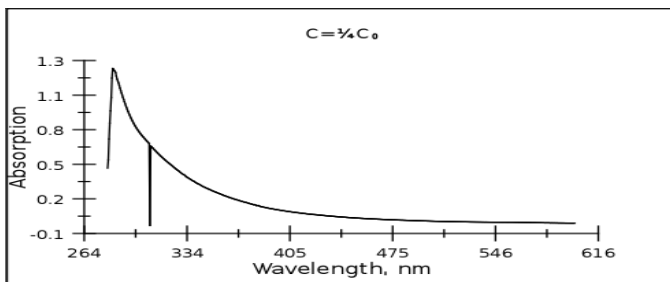


Fig. 2. Absorbance spectrum for  $\frac{1}{2}$  of ZnS QDs initial concentration. Peaks are at 282.48 and 285.17 nm.

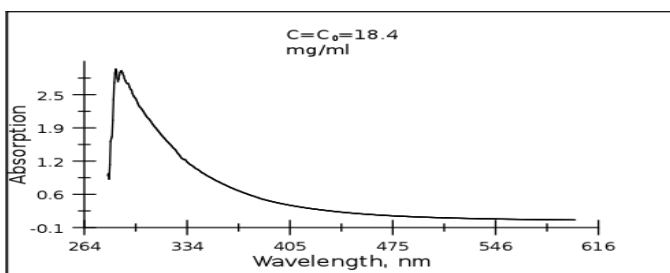


Fig. 3. Absorbance spectrum for  $\frac{1}{4}$  of ZnS QDs initial concentration. Absorption peak is situated at 283.64 nm.

On the optical absorption spectrum of the QDs suspension in toluene with concentration of  $\frac{1}{4}C_0$  a very narrow “failure” at  $\lambda = 310$  nm (Fig. 3) was found. The nature of “failure” is currently unclear. All the spectral curves on Fig. 1-3 have similar longwave “tails”, whose frequency behavior is caused by edges absorption. In case when on the continuous spectrum the discrete level is supposed, the known Fano antiresonance effect [19] takes place. This effect could be explained by the antiresonance phenomenon in optical absorption at  $\lambda = 310$

nm. However, firstly, it is unknown nature of the localized level in a continuous spectrum, and, secondly, it is unclear why the Fano antiresonance occurs at  $C = \frac{1}{4}C_0$  but not at  $C = C_0$  and  $C = \frac{1}{2}C_0$ .

#### IV. CONCLUSION

In conclusion we have successfully synthesized the ZnS QDs by a common way with CdS and CdSe using trialkylphosphine sulfides as precursor of sulfur, zinc oleate as precursor of zinc and oleic acid as capping agent. Obtained ZnS QDs have a middle radius 1.77 nm, which is slightly smaller than excitonic Bohr radius for bulk ZnS (2.5 nm).

#### REFERENCES

- [1] M.F. Frasco, N. Chaniotakis, “Semiconductor quantum dots in chemical sensors and biosensors”, *Sensors*, vol. 9, pp. 7266-7286, 2009.
- [2] P. Yang, M. Lu, D. Xu, D. Yuan, G. Zhou; *J. Lumin.*, vol. 93, p. 101, 2001.
- [3] J.H. Park, S.H. Lee, J.S. Kim, A.K. Kwon, H.L. Park, S.D. Han; *Journal of Luminescence*, vol. 126, p. 566, 2007.
- [4] J.M. Hwang, M.O. Oh, I. Kim, J.K. Lee, C.S. Ha, *Current Applied Physics*, vol. 5, p. 31, 2005.
- [5] Y. Li, Y. Ding, Y. Zhang, Y. Qian, *Journal of Physical Chemistry Solids*, vol. 60, p. 13, 1999.
- [6] M. Jayalakshmi, M.M. Rao, *J. Pow. Sourc.*, vol.157, p. 624, 2006.
- [7] Y. Zhao, Y. Zhang, H. Zhu, G.C. Hadjipanayis, J.Q. Xiao, *J. Am. Chem. Soc.*, vol. 126, p. 6874, 2004.
- [8] L.P. Wang, G.Y. Hong, *Mater. Res. Bull.*, vol. 35, p. 695, 2000.
- [9] J. Zhu, M. Zhou, J. Xu, X. Liao, *Mat. Lett.*, vol. 47, p. 25, 2001.
- [10] D. Denzler, M. Olschewski, K. Sattler, *Journal of Applied Physics*, vol. 84, p. 2841, 1998.
- [11] V.T. Liveri, M. Rossi, G.D. Arrigo, D. Manno, G. Micocci, *Applied Physics A*, vol. 69, p. 369, 1999.
- [12] R. Shahid, M.S. Toprak, H. M. A. Soliman, M. Muhammed, “Low temperature synthesis of cubic phase zinc sulfide quantum dots”, *Central European Journal of Chemistry*, vol. 10, Issue 1, pp 54-58, February 2012.
- [13] H. Kumar, P. B. Barman and R. R. Singh, “Development of CdS, ZnS quantum dots and their core/shell structures by wet chemical method,” *International Journal of Scientific & Engineering Research*, vol. 5, Issue 5, May 2014.
- [14] G.Z. Wang, B.Y. Geng, X.M. Huang, Y.W. Wang, G.H. Li, L.D. Zhang, *Appl. Phys. A*, vol. 77, p. 933, 2003.
- [15] J. Joo., H.B. Na, T. Yu, J.H. Yu, Y.W. Kim, F. Wu, J.Z. Zhang, T. Hyeon, *J. Am. Chem. Soc.*, vol. 125, p. 11100, 2003.
- [16] J.Q. Sun, X.P. Shen, K.M. Chen, Q. Liu, W. Liu; *Solid State Communications*, vol. 147, p. 501, 2008.
- [17] N. K. Abbas, K. T. Al-Rasoul, Z. J. Shanan, “New method of preparation ZnS nano size at low pH,” *International Journal of Electrochemical Science*, vol. 8, pp. 3049 — 3056, 2013.
- [18] V.L. Gayou, B. Salazar-Hernandez, R. Delgado Macuil, G. Zavala, P. Santiago, I. Oliva, “Structural studies of ZnS nanoparticles by high resolution transmission electron microscopy,” *Journal of Nano Research*, vol. 9, pp. 125-132, 2010.
- [19] Al. L. Efros, M. Rosen, “The electronic structure of semiconductor nanocrystals”, *Annual Review of Materials Science*, vol. 30, pp. 475-521, 2000.
- [20] U. Fano, “Effects of configuration interaction on intensities and phase shifts”, *Physical Review*, vol. 124, pp. 1866-1878, 1961.