Chapter 3

Synthesis of quantum dots

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In 1980s, the discovery of synthesis processes for nanostructured materials and the demonstration of the highly reactive properties of these materials have increased rapidly. The new synthesis processes have made available nanostructured materials in a wide variety of compositions, which have led to their exceptional changes in chemical, electronic and optoelectronic properties [1-24]. Synthesis of quantum dots is of great importance as the size, shape and hence their properties extremely depend on preparation technique. There are many popular methods to synthesize [1-4] semiconductor quantum dots. These are,

1. Molecular beam epitaxy (MBE)
2. Vapour phase epitaxy (VPE)
3. Metal organic chemical vapour deposition (MOCVD)
4. Radio frequency Sputtering
5. Electron beam lithography
6. Optical ablation
7. Chemical method
8. Quenching method.

In this chapter, we report synthesis of II- VI semiconductor quantum dots by and quenching method[8-9].

3.1 Overview of nanoparticles preparation techniques, adopted by other workers.

Kümmell et al. synthesize the CdSe quantum dots on ZnSe substrate by MBE growth technique [1]. Priscilla et al prepare [2] GaN nanoparticles on GaAs substrate by RF magneto sputtering. Morales et al synthesize Si nanoparticles by laser ablation[3] technique. Kouklin et al. fabricate [4] CdS nanoparticles on conducting matrix by MOCVD technique. Revaprasadu et al synthesize the ZnS quantum dots on tri-n-Octylphosphineoxide[5] (TOPO). Bandre et al prepare ZnO quantum dots on Poly vinyl pyrolidone[6]. Warad et al. synthesize[7] ZnS: Mn quantum dots on sodium tripolyphosphete. Biswas et al.[13] synthesize ZnS nanoparticle and nanorods by solvothermal process.. Lu et al. synthesize ZnO quantum dot on solid substrate [15] in volmer-weber growth mode.

3.2 Quantum dot synthesis technique adopted in the present Work

In this chapter, we report synthesis of II- VI semiconductor quantum dots by [8-9]. In case of quenching method, the particle size is controlled by matrix as well as sintering temperature of the specimen.

Quenching method remains an art in the sense that theory does not quantatively predict how to make new materials. Nevertheless, synthesis becomes extraordinary powerful, when optimized for specific reactions. In the present work, an attempt has been made to prepare II-VI semiconductor quantum dots[5-14] (ZnO, SnO_2 and Fe_2O_3) using quenching method which is simple, cheap and suitable for large scale production.

3.3 Quenching method

In quenching method, the bulk powder of the specimen is sintered in furnace at very high temperature for a long time and then it is immediately put into polymer matrix, kept at ice cold condition followed by its moderate stirring. Sudden cooling of very hot (about 1000^0C) semiconductor material, causes its fragmentation, and produce quantum dot nano particles. These nano particles enter into the gaps of matrix and produce stable quantum dots.

In quenching method, size of quantum dot can be controlled by varying

a. Sintering temperature.

b. Sintering period and

c. Temperature of matrix during quenching.

3.4 Physical properties of matrices used in the present work

We have selected two matrices as

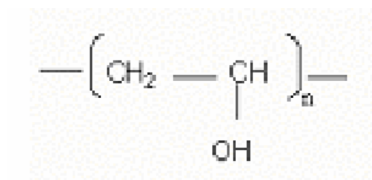
a. Polyvinyl Alcohol **(**PVA**)**

b. Polyvinyl Pyrrolidone (PVP)

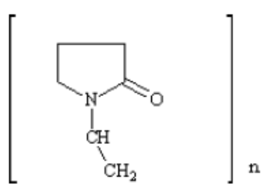
Table 3.1 lists the properties while figure 3.1 displays the polymeric structures of PVA and PVP respectively.

Physical Properties	PVA	PVP
Melting Temperature(^0C)	200	180
Specific gravity	1.30	2.3
Specific heat (J/gm-K)	1.66	0.7
Thermal conductivity (W/m-K)	2.0	1
Resistivity (Ohm.cm)	$(3.1\text{-}3.8) \times 10^7$	5×10^7
pH	Neutral or slightly acidic	3-8
Dielectric constant	2.0	7

Table 3.1 : Physical properties of PVA and PVP



a



b

Fig 3.1: Structures of polymers. a: PVA b: PVP

3.5 Synthesis of ZnO quantum dots on PVA matrix

ZnO quantum dots are prepared by quenching method on PVA matrix. The procedure [8-9] is as follows:

2 gms of bulk ZnO powder is kept in the furnace for sintering at 1000^0C for 5 hours. After sintering, the sample is taken out of the furnace very carefully and immediately put into 6wt% ice cold aqueous solution of PVA followed by its moderate stirring in room temperature for half an hour. After stabilizing the solution (by keeping it in dark chamber for 5 hours) it is cast over glass substrate and then dried in oven at 40^0 C to prepare film of ZnO quantum dots.

3.6 Synthesis of ZnO quantum dots on PVP matrix

To synthesize[22] ZnO quantum dots by quenching method,3 gms of ZnO powder (99.99% pure, E Merck) is calcined at ∼1200 ^{0}C for 10 hour and then quenched into 4 wt% aqueous solution of polyvinylpyrrolidone (PVP) matrix (99.9% pure, E Merck) kept at ice cold temperature followed by its moderate stirring (∼175 rpm). This solution contains ZnO quantum dots embedded in PVP. After stabilizing the solution (by keeping it in dark chamber for 6 hours) it is cast over glass substrate and then dried in oven at 40^0 C to prepare film of ZnO quantum dots.

3.7 Synthesis of SnO_2 quantum dots on PVP matrix

To synthesize[23] SnO_2 quantum dots by quenching method, 4 gms of SnO_2 powder (99.99% pure, E Merck) is calcined at ~ 1000°C for 12 hours and then quenched into 4 wt% aqueous solution of polyvinylpyrrolidone (PVP) matrix (99.9% pure, E

Merck) kept at ice cold temperature followed by its moderate stirring (~175 rpm). This solution contains SnO_2 quantum dots embedded in PVP. After stabilizing the solution (by keeping it in dark chamber for 7 hours) The film is developed on the laboratory glass slides by placing a few drops of SnO_2 quantum dot solution (embedded in PVP) on a clean slide and stretching over it by another clean slide.

3.8 Synthesis of Fe_2O_3 quantum dots on PVP matrix

To synthesize[24] Fe_2O_3 quantum dots by quenching method, 4 grams of Fe_2O_3 powder (99.99% pure, E Merck) is calcined at ~ 1400°C for 10 hours and then quenched into 4 wt% aqueous solution of polyvinylpyrrolidone (PVP) matrix (99.9% pure, E Merck) kept at ice cold temperature followed by its moderate stirring (~160 rpm). This solution contains Fe_2O_3 quantum dots embedded in PVP. After stabilizing the solution (by keeping it in dark chamber for 5 hours) The film is developed on the laboratory glass slides by placing a few drops of Fe_2O_3 quantum dot solution (embedded in PVP) on a clean slide and stretching over it by another clean slide.

3.9 Advantages and disadvantages of PVA matrix

a. Advantages of PVA matrix

I. PVA is easily soluble in water at room temperature.

II. It provides uniform gaps that are very close to each other and distributed in the form of array. So the quantum dots embedded in PVA matrix are of uniform size and arranged in the fashion of array.

III. It is not corrosive in nature. So the samples on the matrix can be easily used for electronic and optoelectronic studies.

IV. On PVA matrix, the particle size can be easily controlled by changing the reaction time or temperature.

V. The samples can be obtained in both liquid and solid form.

b. Disadvantages of PVA matrix

I. Quantum dot preparation on PVA matrix takes long time.

II. Quantum dots are very closely distributed in PVA matrix and so the property of individual sample is difficult to study.

3.10 Advantages and disadvantages of PVP matrix

a. Advantages of PVP matrix

I. It is stable for 2 years

II. Easily soluble in water at room temperature.

III. In this matrix particle size can be easily controlled by changing the temperature and reaction time.

IV. It is not corrosive in nature. So the samples on the matrix can be easily used for electronic and optoelectronic studies.

V. Matrix gapes are well organized, well arranged and circular in PVP. Therefore quantum dots embedded in PVP are circular in shape and well arranged on the matrix.

b. Disadvantages of PVP matrix.

I. PVP is slightly costly

3.11. Advantages and disadvantages of quenching methods

a. Advantages of quenching method

I. It is very simple method

II. The nano particles are obtained due to fragmentation of pure bulk powder. That is why, by quenching method, ultra pure quantum dots can be obtained, which is not possible in chemical route.

III. Like chemical method this route is also suitable for large scale production of samples

b. Disadvantages of quenching method

I. It is costlier than chemical method.

II. In ice cold condition, matrix solution becomes very condensed.

III. Care should be taken while taking out the sample from the furnace, because furnace temperature is very high (e.g. 1200^0C).

IV. Time required in quenching method is more than chemical route.

3.12 Conclusion:

The method adopted for semiconductor quantum dot fabrication [15-20] are simple, easy and do not need sophisticated instruments. By using two matrices quantum dots of different sizes and properties are obtained.

References:

[1] Kϋmmell,T.; Weigand, R.; Bacher, G. and Forchel, A., *Appl. Phys. Lett*., vol.73, p.3106, 1998.

[2] Preschilla, A. N.; Major, S.; Kumar, N.; Samajdar, I.and Srinivasa, R .S., *Appl. Phys. Lett,* vol.77, p.1861,2000.

[3] Morales, A M.and Lieber, C M., *Science*, vol.279, p.208, 1998.

[4] Kouklin, N.; Bandhyopdhayay,S.; Tereshin,S.; Varfolomeev, A. and Zarersky, D., *Appl Phys. Lett*., vol.76, p.460,2000.

[5] Revaprasadu, N.; Malik, Azad M.; O'Brien, P.and Wakefield,G., *J Mett. Res*., vol. 14, No. 8, p 3234,1999.

[6] Bandre ,B.S.and Mahamuni, S., *J Matt. Res*.,vol.19, No. 3, p. 737, 2004.

[7] Warad, H.C.; Ghosh, S. C.; Hemtanon, B.; Thanayanont, C.and Dutta, J., *Sci. and Tech. Adv. Materials,* vol. 6, p.296, 2005.

[8] Nath, S.S.; Chakdar, D.and Gope,G., *Nanotrends-A journal of nanotechnology and its application,* ,vol. 3,Issue 3, 2007.

[9] Nath, S.S.; Chakdar, D.; Gope,G., Talukdar, A. K.and Avasthi, D. K., *JDST*, vol.30, p.4, 2009 .

[10] Mugarza, A. ; Mascaraque, A. ; Pe'rez-Dieste, V.; Repain,V.; Rousset, S.; Garci'ade; Abajo, F. J. and Ortega, J .E., *Phys.Rev. Lett.* vol. 87, No.10, p.107, 2001.

[11] Nath, S.S.; Chakdar, D.; Gope, G.and Avasthi, D.K., *Journal of Nanoelectronics and optoelectronics,* vol. 3.No 2, p. 180,2008.

[12] Lee, Jun woo.; Cho, K.; Kim, Hyunsuk.; Kim, Jim Hyong.; Park, Byoungjun.; Noh, Taeyong.; Kim ,Sung Hyun.and Kim, Sungsig., *JJAP*, Vol. 44, No 10, p. 7694, 2005.

[13] Biswas,S.; Kar ,S.and Choudhary, S., *Synthesis and Reactivity in Inorganic, Metal Organic and Nano-Metal Chemistry,*vol. 36, Issue 1, 2006.

[14] Barik ,S.and Srivastava, A. K., *Solid State Comm.,* vol.127, p. 463, 2003.

[15] Lu ,J .G.; Ye, Z. Z.; Zhang, Y. Z.; Liang, Q. L.; Fulita, Sz.and Wang, Z. L., *APL*, vol.89, p.023122, 2006.

[16] Bendre, B.S. and Mahamuni, Shailaja., *J. Mater. Res.,* vol. 19, No. 3, p.737, 2004.

[17] Xu, J. and Cui,D., *IEEE Photonics Technology Lett*., vol. 17, No 10, 2005.

[18] Fan, Zhiyong; Chang, Pai-chun and Lu ,Jia G., *APL*, vol. 85, No. 25, p.6128, 2004.

[19] Alim, Khan A.; Fonoberov, Vladimir A. and Balandin, Alexander A., *Mater. Res. Soc. Symp. Proc.*, vol. 872, Materials Research Society, 2005.

[20] Nath, S. S.; Chakdar, D.; Gope, G.and Avasthi, D. K., *JAP*, 2008.

[21] Timp, G., *Nanotechnology, Springer-Verlag New York, Inc.,* p.257, 2005.

[22] Nath,S.S.; Chakdar,D.; Gope,G.and Avasthi,D.K., Novel effect of swift heavy ion on ZnO quantum dots prepared by quenching method, *Nanotrends J. Nanotechnology. Appl.,*vol.3, pp.1-10,2008.

[23] Choudhury,M.; Nath,S.S.and Bhattacharjee,R., Ethanol sensing property of SnO_2 quantum dots embedded on PVP, *Journal of Nanotech. Prog INT.,* vol. 5, Issue1, 2014.

[24] Choudhury,M.; Nath, S.S. and Bhattacharjee, R., Methanol sensing property of Fe_2O_3 quantum dots embedded on PVP, *International Journal of Nanoscience and Nanotechnology,* vol 5, Number 1, pp. 101-108, 2014.