

OPTICAL BEHAVIOUR OF SYNTHESIZED ZNO NANOTABLETS AND ITS TRANSFORMED NANORODS WITH THE ASSISTANCE OF A CATIONIC SURFACTANT CTAB

Pritam Saha¹ and Tapas Pal Majumder^{1,*} and Subhas Chandra Debnath²

¹Department of Physics, University of Kalyani, Kalyani-741235, West Bengal, India.

²Department of Chemistry, University of Kalyani, Kalyani-741235, West Bengal, India.

ABSTRACT

We are reporting the preparation of ZnO nanotablets at relatively low temperature (150°C) using zinc acetate [Zn(Ac)₂], NaOH, cetyltrimethylammonium bromide (CTAB) by solvothermal method. By adjusting the molar ratio of the reactants we obtained nanorods and we also obtained the variation of the dimension of the nanorods using hydrazine hydrate as capping reagent. The prepared samples were morphologically recognized as well crystallized. The average diameter of the ZnO nanotablets were ranging from 500 to 600 nm and the average thickness of the nanotablets were ranging from 85 to 90 nm. The length of ZnO nanorods were ranging from 300 to several micrometers and breadth of the ZnO nanorods were ranging from 80 to 160 nm. The optical properties of the prepared materials have also been studied with the exhibition of its interesting behavior.

Keywords

Nanostructures; Thin films; Sol-gel growth; X-ray diffraction; Optical properties

1. INTRODUCTION

In recent years one dimensional (1D) semiconductor nanostructures such as nanorods, nanowires, nanobelts and nanotubes have been attracted great attention due to their many unique properties. The possibility of such unique properties can be exploited for obtaining as building materials of the construction of future electronics and photonics devices [1-3]. 1D semiconductor nanostructures also has their applications in life sciences [4]. They also have potential uses as interconnectors, nanoscale electronics, optoelectronics and sensing devices [5]. It is generally accepted that 1D nanostructure are useful materials for investigating the dependence of electrical and thermal transport or mechanical properties based on dimensionality and size reduction or quantum confinement effects [6]. Zinc oxide having a wide direct band-gap (3.37 eV) with a large excitonic binding energy of 60 meV at room temperature, has been recently attracted due to their potential uses in ultra-violet (UV) luminescence devices, light emitting diodes (LEDs), gas sensors, solar cells and transparent thin film transistors [7]. ZnO is also a material that is biocompatible and biosafe. ZnO may be used as implantable biosensors and it also has biomedical applications.

In the past few years, much effort has been devoted to develop various 1D semiconductor nanostructures [8-10]. Several researchers have developed various kinds of ZnO nanostructures such as nanodots, nanorods, nanowires, nanobelts, nanotubes, nanobridges and nanonails, nanowalls, nanohelices, seamless nanorings, mesoporous single-crystal nanowires, and polyhedral cages [11-13]. Till date various synthetic methods have been reported such as vapour-liquid-solid (VLS) [14-16], vapour-solid (VS) [17] mechanism, laser ablation-catalytic growth [18-19], oxide-assisted growth [20], template-induced growth [21-22], solution-liquid-solid growth in organic solvents [23-24], metal-organic chemical vapour deposition (MOCVD) [25], hydrothermal synthesis, the micro-emulsion hydrothermal process, chemical vapour deposition (CVD) and a catalyst-free CVD method [26-29]. They have been largely reported on the synthesis of pure ZnO nanorods/ nanowires by solvothermal/ hydrothermal methods [30-34]. Among the 1D nanostructures ZnO nanorods and nanowires have been widely studied because of their easy nanomaterials formation and device applications.

In this paper, we have prepared ZnO nanotablets by the assistance of the cationic surfactant cetyltrimethylammonium bromide (CTAB). We extensively studied the variation of dimensions of ZnO nanorods by changing the reactant's molar ratio. We also studied that the diameter and length of the nanorods can be easily tuned by the introduction of the capping reagent hydrazine hydrate. The optical properties of the as prepared materials have been studied extensively for elaborating their comparable band gaps and photoluminescence behavior.

2. EXPERIMENTAL SECTION

All the reactants, purchased from E-Merck Germany, were of analytical grade and were used without any further purification.

a) Preparation of ZnO nanostructures

In a typical procedure to synthesize ZnO nanostructure, 6.00 gm of Zinc acetate ($Zn(Ac)_2$) was put into a glass beaker filled with 15 ml of double distilled water. The mixture was stirred for 10 minutes at room temperature to form a solution. Following the same procedure we make another solution putting 0.3 gm of CTAB into 10 ml of double distilled water. Then the solution of CTAB was added into the glass beaker containing the $Zn(Ac)_2$ solution and left for 15 minutes under vigorous stirring for proper mixing of the two solutions. Then we added dropwise the as prepared 15 ml of 4M NaOH solution into the glass beaker during vigorous stirring and left for another 15 minutes under that vigorous stirring. The colour of the solution was white. Then the solution was put into a Teflon lined stainless steel autoclave. The autoclave was maintained at average 120°C for 24 hours, and then allowed to naturally cool to room temperature. The resulting white precipitate was filtered, subsequently washed with double distilled water and absolute ethanol and dried in air at 65°C for 3 hours. We get nanotablets. This is the first experiment (i.e., ZnO 1) to obtain ZnO nanotablets. To change the shape of the nanostructure we repeated the same experiment with different molar ratio of the reactants and CTAB also and we got nanorods. Now to change the dimension of the nanorods we used hydrazine hydrate as a capping reagent in the same experiment keeping the other reactant's molar ratio constant and at the same reaction conditions. The detailed information about other experiments is given in Table no. 1.

Table 1 Summary of Experimental Conditions and the Morphology of Different ZnO Nanostructures.

Experiment No.	Nanostructures and energy band gap	Zn(Ac) ₂	NaOH Solution	CTAB	Capping Reagent (Hydrazine hydrate)	Temperature	Time Duration
1 (ZnO 1)	Nanotablets 2.6 eV	6 g m	15 ml 4M	0.3 gm	N i l	1 2 0 ⁰ C	24 hr.
2 (ZnO 2)	Nanorods 2.8 eV	7 g m	30 ml 5M	0.5 gm	N i l	1 2 5 ⁰ C	24 hr.
3 (ZnO 3)	Nanorods 2.6 eV	7 g m	40 ml 5M	0.5 gm	1 0 m l	1 2 5 ⁰ C	24 hr.
4 (ZnO 4)	Nanorods 2.2 eV	7 g m	50 ml 5M	0.5 gm	2 0 m l	1 2 5 ⁰ C	24 hr.

b) Characterization

Crystalline structure of the obtained products were characterised by X-ray diffraction studies (XRD) using a diffractometer (Bruker D8 Advance) with CuK α line. The morphology of these products was obtained by field emission scanning electron microscopy (FE-SEM) and the FE-SEM photos were taken with a S4800-JU at 5.0 kV. The FE-SEM measurements were done on the glass substrate coated with requisite samples using a programmable Spin Coater, Apex Instruments Co. with model No. SCU-2008C. UV-vis spectrophotometer (Model: TCC-240A, UV-2401 PC, Shimadzu, Japan) was used to record the electronic absorption spectra of the obtained products at room temperature. Photoluminescence spectra were carried out on a LS55, Fluorescence spectrometer, PerkinElmer using excitation source of the 300 nm and 500 nm line of a He-Cd laser.

3. RESULTS AND DISCUSSION

a) Crystalline structure and Morphology

The structure and size of the ZnO nanostructures can easily be seen by the low and high magnification of FESEM images shown in Fig. 1 (a – h). The average thickness of the nanotablets is about 90 nm and the thickness is ranging on average from 85 to 95 nm. The average diameter of the nanotablets is ranging from 500 to 600 nm. The nanotablets are almost uniform in shape and size. The shape of the nanorods is straight. The length of the nanorods is ranging from 300 nm to several micrometers and the diameter of the nanorods is ranging from 80 to 160 nm.

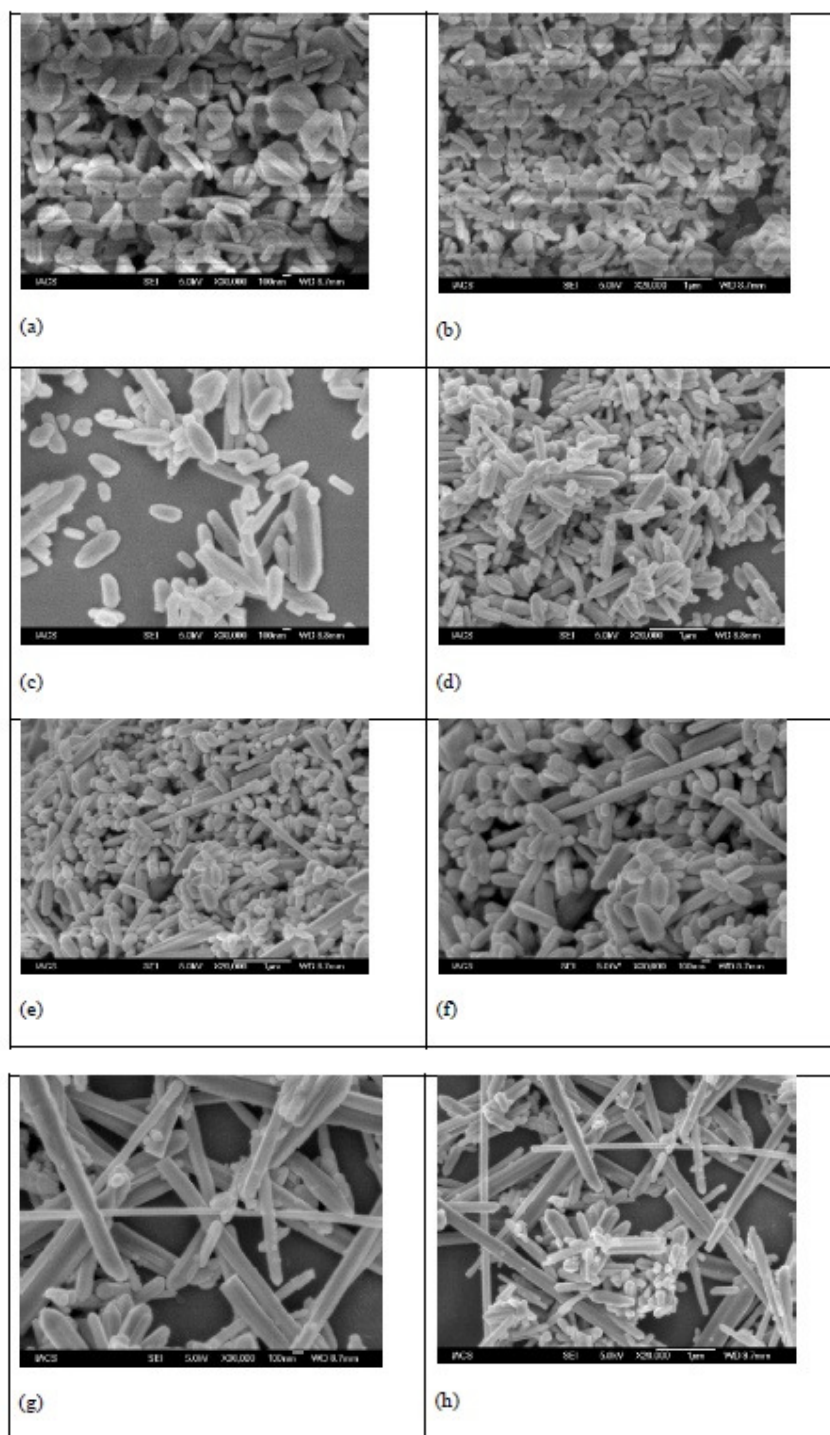


Fig. 1 FESEM micrograph of different types of ZnO nanostructures. a nanotablets (ZnO 1) with 100 nm resolution, b nanotablets (ZnO 1) with 1 μm resolution, c nanorods (ZnO 2) with 100 nm resolution, d nanorods (ZnO 2) with 1 μm resolution, e nanorods (ZnO 3) with 100 nm resolution, f nanorods (ZnO 3) with 1 μm resolution, g nanorods (ZnO 4) with 100 nm resolution and h nanorods (ZnO 4) with 1 μm resolution.

The crystal structure and crystallinity of the as prepared products were investigated by XRD. Fig 2(a - d) shows a typical XRD pattern of ZnO precursors, in which all the diffraction peaks can be well indexed to the hexagonal wurtzite ZnO crystal with lattice constant $a = 3.249 \text{ \AA}$ and $c = 5.208 \text{ \AA}$, in good agreement with the standard PDF data (JCPDS file 36-1451). No additional reflections are observed which indicates that there are no additional crystalline structures present in the samples. The strong and sharp diffraction peaks demonstrate that the products are well crystalline. The XRD patterns of ZnO samples show the characteristic hexagonal wurtzite planes at (100), (101), (002), (102), (110), (103), (200), (112), (201), and (202) and those are located at 31.73° , 34.35° , 36.22° , 47.52° , 56.61° , 62.86° , 66.35° , 67.89° , 69.09° , and 76.87° in the 2θ range graph from 20° to 80° (Fig. 2(a-d)). In addition, the intense and sharp diffraction peaks are observed at (100), (002), (101) etc (hkl) planes. Fig 2(a - c) suggest that the obtained products are well crystallized. By using the XRD analysis, the d-spacing of the ZnO nanotablets and nanorods have been calculated for the hexagonal wurtzite structures and compared with the standard JCPDS data (Table 2). In our experiment for XRD analysis, $\text{CuK}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation is used whereas in case of JCPDS (36 - 1451), $\text{CuK}\alpha 1$ ($\lambda = 1.5405981 \text{ \AA}$) radiation was used. Moreover, the Debye-Scherrer Equation is given below as:

$$d = 0.9 \cdot \lambda / \beta \cos \theta \dots\dots\dots(1)$$

where 'd' is the breadth of the nanorods, λ = wavelength of the $\text{CuK}\alpha$ radiation (i.e. $\lambda = 1.5418 \text{ \AA}$), β = FWHM (Full Width Half Maxima) of the XRD peaks, θ = the angle at which the corresponding peaks occur. By using Debye-Scherrer equation (Eqn(1)) we calculated the average thickness of the nanotablets and average breadth of the nanorods. The average thickness of the ZnO nanotablets (ZnO1) is 92 nm and we get the following values of breadths of the as prepared ZnO nanorod products, those are 90 nm for ZnO2, 93 nm for ZnO3, and 110 nm for ZnO 4.

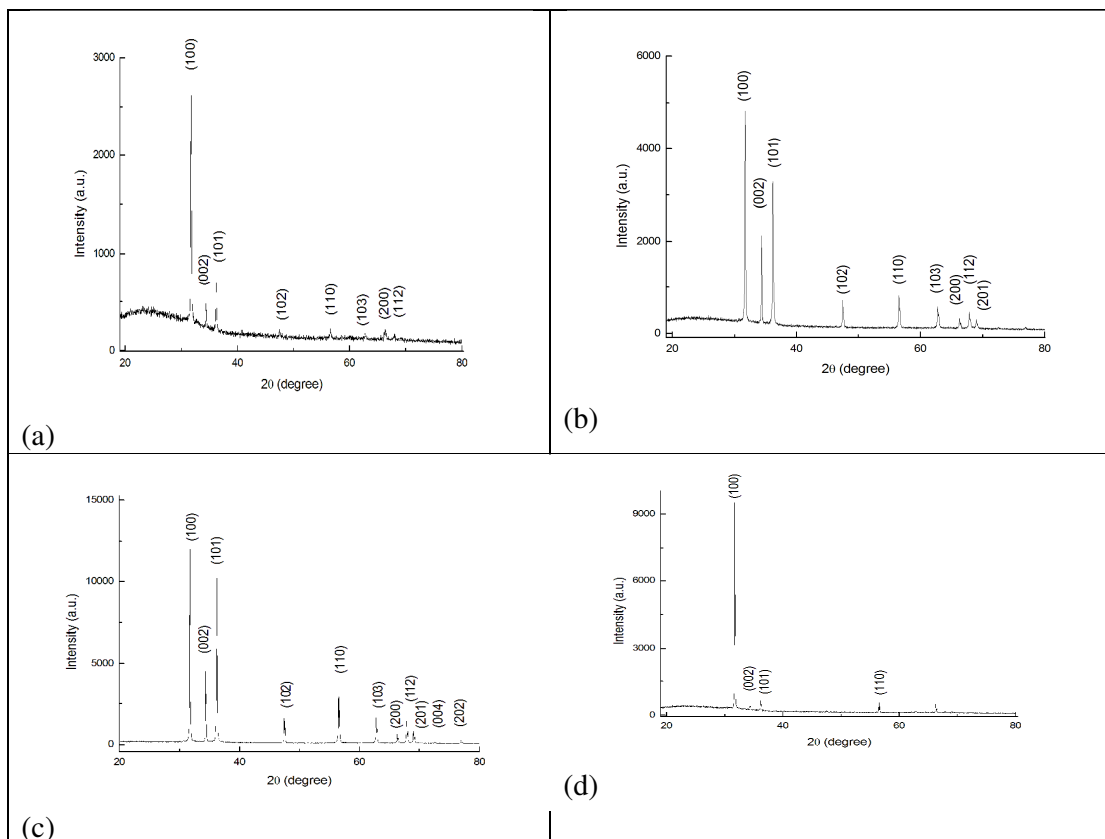


Fig. 2 XRD diffraction pattern of different types of ZnO nanostructures. **a** nanotablets (ZnO 1), **b** nanorods (ZnO 2), **c** nanorods (ZnO 3) and **d** nanorods (ZnO 4).

Table 2 The comparison of d-values, obtained from XRD and JCPDS, and illustration of the corresponding (h k l) values.

Peak	2θ	d-XRD(Å)	d-JCPDS(Å)	(hkl)
1	31.73	2.8199	2.8143	100
2	34.35	2.6106	2.6033	002
3	36.22	2.4800	2.4759	101
4	47.52	1.9133	1.9111	102
5	56.61	1.6258	1.6247	110
6	62.86	1.4783	1.4771	103
7	66.35	1.4088	1.4071	200
8	67.89	1.3805	1.3781	112
9	69.09	1.3594	1.3582	201
10	76.87	1.2401	1.2380	202

b) Optical Properties

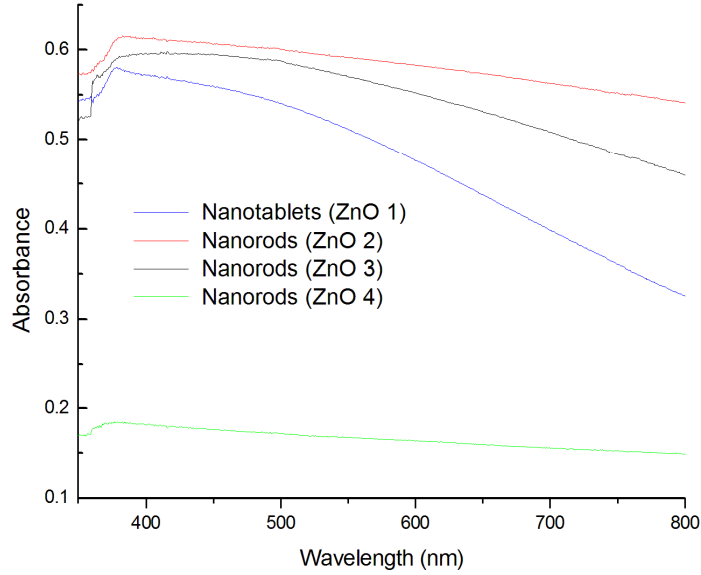


Fig. 3 UV-vis absorption spectra of different types of ZnO nanostructures.

The optical properties of semiconductor nanomaterials depend on the size and shape of the particles. The UV-Vis spectra, recorded at room temperature of the as prepared ZnO products are shown in Fig. 3. The absorption edge of ZnO products is about 500 nm and the corresponding energy is approximately 2.48 eV. The weak absorption peak is observed at 400 nm and the corresponding energy is approximately 3.1 eV. The excitonic absorption features are not very sharp. The optical bandgap (E_g) for semiconductors can be evaluated with the following relation as given below [35-36].

$$\alpha h\nu = A (h\nu - E_g)^n / h\nu \quad (2)$$

Where, A is a constant related to the effective masses associated with the bands, n is a constant and $n = 1/2$ for a direct band gap material, 2 for an indirect band gap material and 3/2 for a forbidden direct energy gap, the estimated E_g values are in the range from 1.70 to 2.30 eV as reported earlier [19]. α is calculated with the following relation as given below [20]:

$$\alpha = 1/t \ln(1/(1-A)) \quad (3)$$

We obtained the bandgap of all ZnO products by extrapolating the linear portion of the plot $(\alpha h\nu)^2$ versus $(h\nu)$ as shown in Fig.4. Bandgap is changing from 2.2 to 2.85 eV depending on different geometric configurations of ZnO products. The ZnO nanomaterials band gap value differs from bulk (3.37 eV) material due to quantum confinement effect.

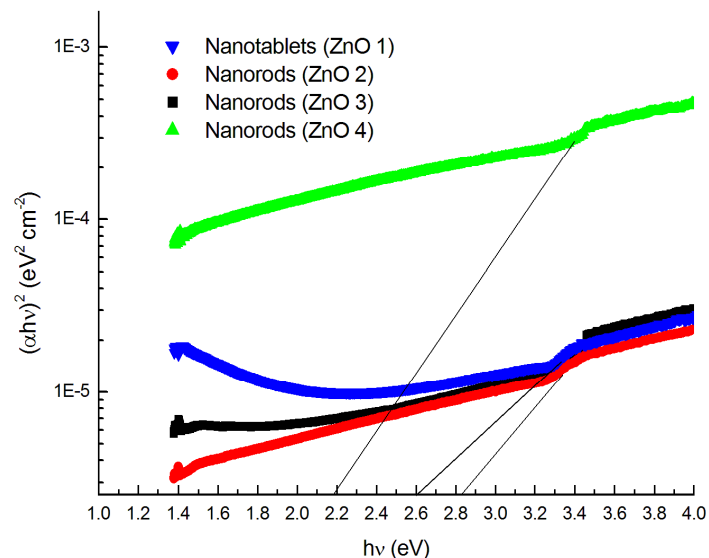


Fig. 4 Bandgap energy of different types of ZnO nanostructures.

The photoluminescence spectra of the as prepared ZnO nanotables and nanorods, recorded at room temperature for the excitation wavelength 325 nm, is shown in fig. 5. In the present work the emission property of the as prepared ZnO products was studied from photoluminescence spectrum in the spectral region from 300 to 800 nm. We observed a broad peak at around 425nm and a very strong peak at around 650nm. Their corresponding energies are 2.92 and 1.91eV, respectively. Therefore the energy loss for the first peak is 0.90eV, and for the second weak peak is 1.91eV. It is clearly indicative that the difference between band gap energy and energy loss corresponding to second photoluminescence peak is ranging from 0.29 to 0.94. So that the previous difference of energy may be associated with non radiative transition. That implies that different types of excitonic energy level are formed for different types of ZnO nanostructures which is definitely associated with quantum confinement effect.

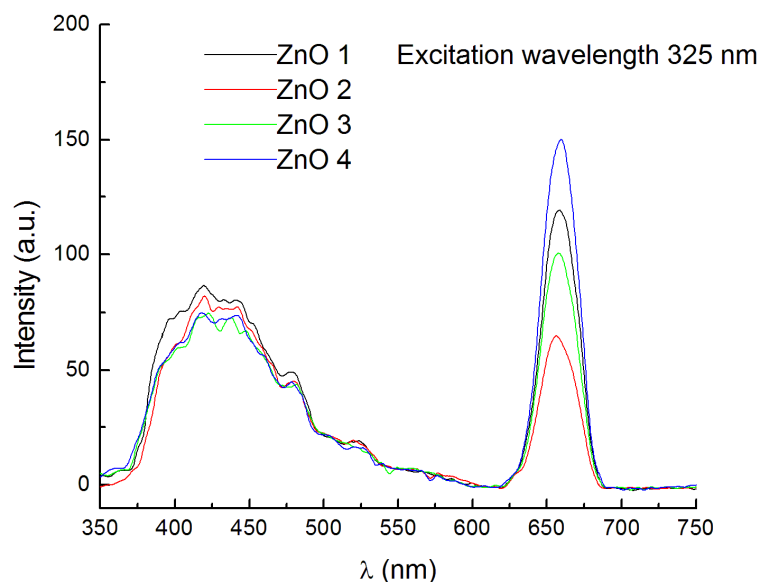


Fig. 5 Photoluminescence spectra of different types of ZnO nanostructures with 325 nm excitation wavelength.

4. CONCLUSIONS

In summary, we are reporting the synthesis of ZnO nanotablets by the assistance of CTAB, a cationic surfactant. The shape of the nanotablets can be changed to nanorods by simply changing the reactant's molar ratio. Again we have shown that the dimension of the nanorods can be changed by varying the capping reagent's (Hydrazine hydrate) amount. The particle size and morphology was verified by powder XRD and FESEM. The optical properties are changed with the change of the size, shape and dimension of the ZnO nanoproducts. We can tune the band gap energy by simply changing the shape and size of the as prepared ZnO nanoproducts.

5. ACKNOWLEDGEMENTS

The work was supported by the funding agency DST, Government of India for providing the financial assistance with the completed project number SR/S2/CMP-0020/2009 and greatly thankful to IACS, Jadavpur for XRD and FE-SEM measurement.

REFERENCES

- [1] D. Appell, *Nature* 419 (2002) 553.
- [2] L. Samuelson, *Materials Today* 6 (2003) 22.
- [3] X. F. Duan, Y. Huang, Y. Cui, J. F. Wang, C. M. Lieber, *Nature* 409 (2001) 66.
- [4] Y. Cui, Q. Wei, H. Park, C. M. Lieber, *Science* 293 (2001) 1289.
- [5] Y. N. Xia, P. D. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, H. Yan, *Advanced Materials* 15 (2003) 353.
- [6] K. Pal, T. Pal Majumder, S. Ghosh, S. K. Roy, *Journal of Molecular Structure* 1041 (2013) 16.

- [7] Ü Özgür, Y. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. DÖgan, V. Avrutin, S. J. Cho, H. Morkoc, *Journal of Applied Physics* 98 (2005) 041301.
- [8] P. D. Yang, C. M. Lieber, *Science* 273 (1996) 1836.
- [9] A. M. Morales, C. M. Lieber, *Science* 279 (1998) 208.
- [10] X. G. Peng, J. Wickham, A. P. Alivisatos, *Journal of American Chemical Society* 120 (1998) 5343.
- [11] Z. L. Wang, *Materials Today* 7 (2004) 26.
- [12] J. H. Park, H. J. Choi, Y. J. Choi, S. H. Sohn, J. G. Park, *Journal of Materials Chemistry* 14 (2004) 35.
- [13] J. H. Park, H. J. Choi, J. G. Park, *Journal of Crystal Growth* 263 (2004) 237.
- [14] R. S. Wagner, W. C. Ellis, *Applied Physics Letters* 4 (1964) 89.
- [15] A. I. Klimovskaya, I. P. Ostrovskii, A. S. Ostrovskaya, *Physica Status Solidi A* 153 (1996) 465.
- [16] O. Toshio, N. Masayuki, *Journal of Crystal Growth* 46 (1979) 504.
- [17] Y. Iwao, S. J. Hajime, *Journal of Crystal Growth* 45 (1978) 511.
- [18] D. P. Yu, X. S. Sun, C. S. Lee, I. Bello, S. T. Lee, H. D. Gu, K. M. Leung, G. W. Zhou, Z. F. Dong, Z. Zhang, *Applied Physics Letters* 72 (1998) 1966.
- [19] X. F. Duan, C. M. Lieber, *Journal of American Chemical Society* 122 (2000) 188.
- [20] R. Q. Zhang, Y. Lifshitz, S. T. Lee, *Advance Materials* 15 (2003) 635.
- [21] W. Q. Han, S. S. Fan, Q. Q. Li, Y. D. Hu, *Science* 277 (1997) 1287.
- [22] C. R. Wang, K. B. Tang, Q. Yang, B. Hai, G. Z. Shen, C. H. An, W. C. Yu, Y. T. Qian, *Inorganic Chemical Communication* 4 (2001) 339.
- [23] Y. Jiang, Y. Wu, X. Mo, W. C. Yu, Y. Xie, Y. T. Qian, *Inorganic Chemistry* 39 (2000) 2964.
- [24] C. R. Wang, K. B. Tang, Q. Yang, Y. T. Qian, *Journal of Electrochemical Society* 150 (2003) G163.
- [25] M. Yazawa, M. Koguchi, A. Muto, M. Ozawa, K. Hiruma, *Applied Physics Letters* 61 (1992) 2051.
- [26] C. L. Jiang, W. Q. Zhang, G. F. Zou, W. C. Yu, Y. T. Qian, *Journal of Physical Chemistry B* 109 (2005) 1361.
- [27] X. M. Sun, X. Chen, Z. X. Deng, Y. D. Li, *Materials Chemistry and Physics A* 78 (2003) 99.
- [28] J. J. Wu, S. C. Liu, *Advance Materials* 14 (2002) 215.
- [29] J. J. Wu, S. C. Liu, *Journal of Physical Chemistry B* 106 (2002) 9546.
- [30] J. Q. Xu, Y. P. Chen, J. N. Shen, *Journal of Nanoscience Nanotechnology* 6 (2006) 248.
- [31] Y. Zhang, J. Q. Xu, Q. Xiang, H. Li, Q. Y. Pan, P. C. Xu, *Journal of Physical Chemistry C* 113 (2009) 3430.
- [32] L. Vayssieres, *Advance Materials* 15 (2003) 464.
- [33] J. X. Wang, X. W. Sun, Y. Yang, H. Huang, Y. C. Lee, O. K. Tan, L. Vayssieres, *Nanotechnology* 17 (2006) 4995.
- [34] L. E. Greene, M. Law, J. Goldberger, F. Kim, J. C. Johnson, Y. F. Zhang, R. J. Saykally, P. D. Yang, *Angew Chemistry International* 115 (2003) 3031.
- [35] R. B. Kale, C. D. Lokhande, *Semiconductor Science and Technology* 20 (2005) 1.
- [36] K. Pal, U. N. Maiti, T. Pal Majumder, P. Dash, N. C. Mishra, N. Bennis, J. M. Otón, *Journal of Molecular Liquids* 164 (2011) 233.