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ON THE POSSIBILITY OF ENHANCED EFFICIENCY IN (ZN, CD)S DYE SENSITIZED SOLAR CELL

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Nanoparticles of zinc sulphide and cadmium sulphide are synthesized by aqueous chemical method. XRD data show cubic phase for both the systems. UV-Vis absorption spectra of nano ZnS and nano CdS are blue shifted from the respective bulk. The PL spectra of the above dye sensitized nanomaterials show two broad emission at 402 nm and 510 nm (absent in nano ZnS) which are compared with earlier investigations and discussed. The efficiency of dye sensitized nanocrystalline ZnS solar cell was found to be 0.09 % (Eosin Yellowish Dye) and 0.016 % (Methyl Blue dye). The efficiency of dye sensitized CdS was found to be 0.06 % and this makes it possible for improved efficiency.

Keywords: NANO ZINC SULPHIDE, NANO CADMIUM SULPHIDE, PHOTO-LUMINESCENCE, DYES, SOLAR CELL, EFFICIENCY.

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1. INTRODUCTION

Zinc Sulphide (ZnS), an important II-VI semiconductor with E_g of 3.6 eV is widely used as phosphor material and now in the nano form this material can exhibit enhanced optical properties and so has attracted considerable attention in flat-panel displays, electroluminescence devices, quantum devices, multilayer dielectric filters, and solar cells [1-3].

Cadmium Sulphide (CdS), a direct band gap II-VI semiconductor has 2.42 eV (515 nm) a promising candidate among II-VI compounds for detecting visible radiation. Also it is used as window material for hetero junction solar cells to avoid the recombination of photogenerated carriers which improves the solar cell efficiency [5]. It has also application in light emitting diodes [5], photo detectors [6], sensors [7], address decoders [8], and electrically driven lasers [9].

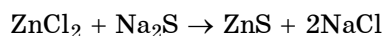
Dye sensitized solar cells have been attracting considerable attention because of their high efficiency, simple fabrication process and low production cost [10]. When this cell is irradiated by sunlight, the electrons of the dye are excited from the ground state to excited state by absorbing photons. The excited electrons are injected to the conduction band of anode and then transfer to the substrate. In the dye sensitized nano crystalline cell, recombination occurs only at the interface where the injected electrons can recombine with oxidized dye molecules or with oxidized species in the electrolyte.

For the application of dye sensitized solar cell some of the major adopted criteria are porous, conducting, stable and of large surface area working electrode. The synthesis as well as physical and chemical understanding of these wide band gap materials is still in preliminary stage.

TiO₂ or ZnO are proved to be electron collection layer as well as hole blocking layer in the solar cells. Since these sulphides are good phosphor and LED materials, ZnS and CdS are attempted here as collecting layers separately for solar cell applications.

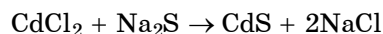
2. SYNTHESIS

Synthesis of zinc sulphide nanoparticles is done by chemical method. To start with 0.02 M ZnCl₂ solution and mercaptoethanol solution are added with constant stirring for one hour. To this solution sodium sulphide was drop wise added. Zinc sulphide nanoparticles capped with mercaptoethanol chains begin to precipitate.



The precipitate is washed several times in water to remove unreacted sodium and zinc. By centrifuging and drying, powder of zinc sulphide is obtained. The powders are highly stable and do not show any coalescence or agglomeration. The same procedure is followed with 0.015 M solution of ZnCl₂, Na₂S.xH₂O and mercaptoethanol. By changing the concentrations of zinc chloride, sodium sulphide and mercaptoethanol nanoparticles with different sizes are obtained.

CdS nanoparticles are prepared by wet chemical route method. For synthesis 0.015 M aqueous solution of CdCl₂.2H₂O, thioglycerol (C₃H₈O₂S) and Na₂S.xH₂O were prepared. Firstly, thioglycerol solution was added drop wise to CdCl₂ solution at the rate of 1 ml per minute, while stirring it continuously, Na₂S solution was added in a similar manner.



The precipitate of CdS is insoluble in water and was thoroughly washed in double distilled water, centrifuged and then air dried. Two different samples were prepared with different concentrations (0.02 M, 0.015 M).

3. RESULTS AND DISCUSSION

3.1 XRD Analysis

The powders obtained from synthesis are structurally characterized by X-ray diffraction (PANalytical X'pert PRO X-Ray Diffractometer) with CuK_α ($\lambda = 1.54060 \text{ \AA}$) as the source of incident radiation and shown in Fig. 1 for 0.02 M and 0.015 M concentrations of ZnS and CdS nanoparticles. The three Bragg peaks at (111), (220) and (311) reveal sphalerite cubic phase with lattice parameter 5.404 Å for both 0.02 M (A) and 0.015 M (B) for the ZnS nanoparticles. CdS nanoparticles shows cubic phase with lattice parameter 5.832 Å. The Bragg peaks and lattice parameter of ZnS and CdS systems are confirmed by JCPDS card No. 04-007-1615 and JCPDS card No. 65-2887 respectively. The average particle size of the synthesized ZnS and CdS nanoparticles are determined using Debye-Scherrer formula and tabulated in Table 1. They are identified as sample A and B here. Since the size is very

small, local strain and dislocation density will be appreciable and so they are also calculated and given in Table 1. But it is known that the accuracy of Scherrer formula for particle size below 5 nm is questionable as instrumental broadening of the diffractometer will mask. So, here these sizes are taken as only guideline values.

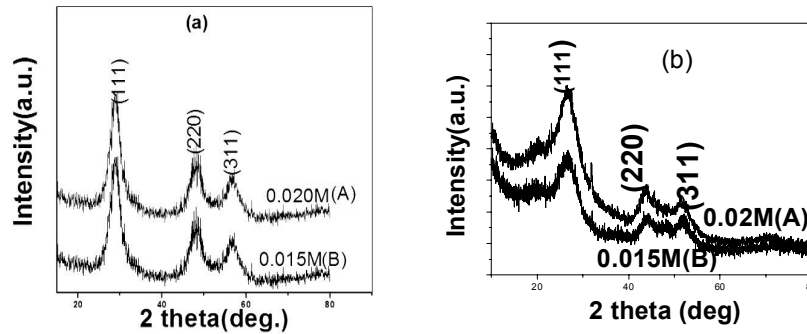


Fig. 1 – (a) XRD pattern of ZnS nanoparticles (b) XRD pattern of CdS nanoparticles

Table 1 – Particle size Strain Dislocation density of the ZnS and CdS nanoparticles

S.No.	Nanoparticles	Molar Concentration	Particle size(nm)	Strain	Dislocation density(lines/m ³)
1.	ZnS	0.02 M (A)	3	0.0190	1.097×10^{17}
		0.015 M (B)	2.2	0.0205	1.002×10^{17}
2.	CdS	0.02 M (A)	3.9	0.0131	6.36×10^{16}
		0.015 M(B)	4.5	0.0116	4.92×10^{16}

3.2 SEM Analysis

Scanning Electron Microscopy (SEM) picture of these particles were taken using JEOL, JSM-840 microscope and shown in Fig. 2. The particles are fairly spherical and monodispersive and the particle size of nano ZnS was found to be 15 nm and nano CdS was found to be 33 nm. Such result was reported also by Jin Song et al. [3].

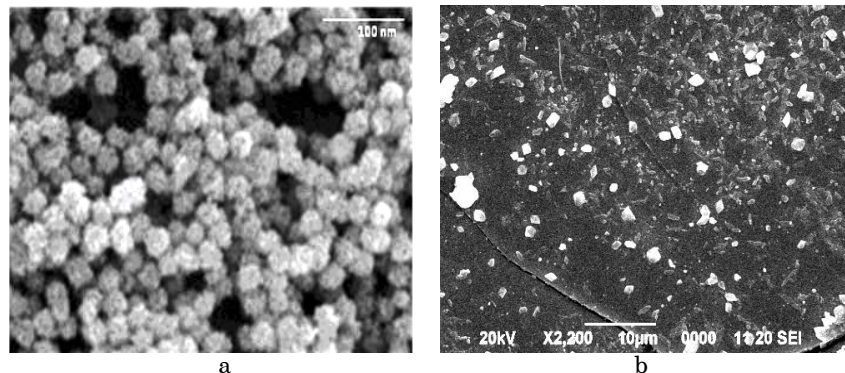


Fig. 2 – (a) SEM image of 0.015 M nano ZnS (b) SEM image of 0.015 M nano CdS

3.3 UV-Vis Analysis

The optoelectronics properties were investigated by ultraviolet-visible absorption spectra using the Shimadzu UV Spectrophotometer in the spectral range 200-900 nm at room temperature in the absorption mode where the onset of absorption is at 295 nm (4.2 eV) for the case (A) and 297 nm (4.185 nm) for the case (B) which are blue shifted when compared with the bulk value of 346 nm (3.6 eV) of ZnS (Fig. 3a). This is due to quantum confinement resulting in a more discrete energy spectrum of the individual nanoparticles. The similar trend was observed by Yun Chen et al. [11] and Borse et al. [12]. Fig.3b shows the UV-VIS spectra of CdS nanoparticles which are blue shifted from the bulk 2.42 eV. The similar trend was observed by Suhail et al. [13].

From the optical band gap of nano ZnS and the theoretical model [14], the size of the nanoparticles is estimated from Eqn. 1.

$$E_{gn} = \left[E_{gb}^2 + \left\{ \frac{2h^2 E_{gb} \left(\frac{\pi}{R} \right)^2}{m^*} \right\} \right]^{\frac{1}{2}} \quad (1)$$

where R is the radius of the quantum size particles (i.e.) nanoparticles. E_{gn} and E_{gb} are the band gap of nano and bulk system respectively and m^* is the effective mass ($m^* = 0.34 m_e$, for cubic ZnS) and the average particle size of the sample found using this Brus model is tabulated in Table 2. These results compared with the SEM observations, where as there is a considerable difference between these values and the size observed from XRD, as expected.

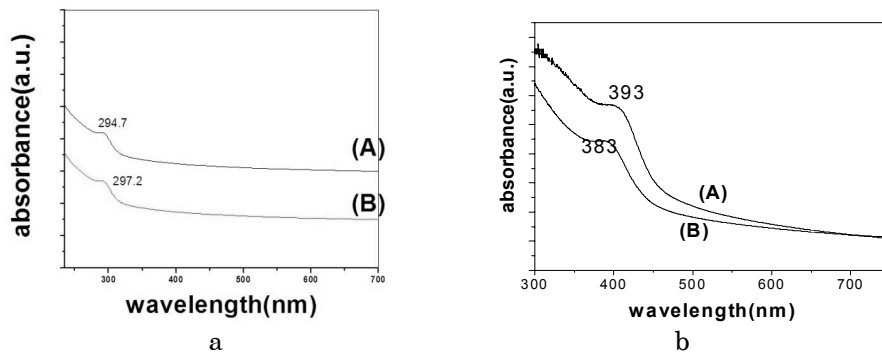


Fig. 3 – (a) UV-Vis spectra of nano ZnS, (b) UV-Vis spectra of nano CdS

Table 2 – UV-Vis absorption of ZnS and CdS nanoparticles

S.No.	Nanoparticle	UV-Vis absorption of nanoparticles	Particle Size(nm)
1.	ZnS	294.7 nm(4.2 eV)	15
		297.2 nm(4.18eV)	15
2.	CdS	383 nm(3.24eV)	12
		393 nm(3.16eV)	13

3.4 UV-VIS Analysis for dye sensitized nanoparticles

It is known that a dye acts as a photo sensitizer in a solvent and the solvents used may be alcohols, ketons, ethers and nitrogen compounds such as acetonitrile where interfacial electron transfer occurs as a result of selective light absorption.

Methyl Blue is a titanometric dried, with an absorption maxima 595-605 nm in distilled water. UV-Vis absorption (Fig. 5a) for methyl blue shows two broad peaks at 310 nm in UV region and at 599 nm in visible region. Here we present the optical properties of methyl blue sensitized ZnS nanoparticles using UV-Vis spectra and such work is not reported in literature. ZnS nanoparticles were dipped in the dye solution (1.2 mM in 20 ml of ethanol) for 24 hours in refrigeration for the adsorption of dye on ZnS nanoparticles. Fig. 4 shows the UV-Vis absorption spectra of dye sensitized ZnS particles (A) & (B). When Fig. 3a and Fig. 4a are compared absorption at 600 nm is due to the dye and such visible range absorption is not there for nano ZnS. Only when the dye molecules are adsorbed in the nanostructures, UV-Vis spectrum can show such a peak and this reveals that methyl blue dye can be used as a sensitizer when the material is prepared for solar cell.

The UV-Vis absorption spectra of dye sensitized CdS particles are shown in the Fig. 4b. Absorption at 530 nm is attributed to the adsorption of dye molecules which is not found in Fig. 3b.

This absorption in the visible region produces electricity due to the formation of free electrons.

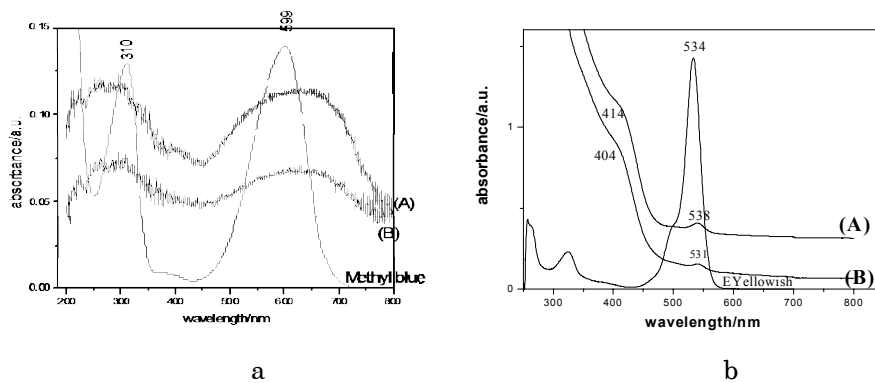


Fig. 4 – (a) UV-VIS spectra of methyl blue sensitized nano ZnS (b) UV-Vis spectra of Eosin Yellowish sensitized nano CdS

3.5.1 PL Analysis for nanoparticles

The room temperature PL spectra of nano ZnS particles are recorded using Perkin-Elmer LS-55 fluorescence spectrophotometer. PL spectra recorded with an excitation wavelength 324 nm is given in Fig. 5a where a peak at $\lambda = 402$ nm for 0.02 M (A) and $\lambda = 400$ nm for 0.015 M (B) when excited at 324 nm which are blue shifted from the bulk ZnS ($\lambda = 443$ nm) are observed. This can be attributed to the donor-acceptor (D-A) band transition and shows that these materials can be used as purple light emitting nanodevices because the emission peak is in the visible region. The same result was

reported by Yun Chen et al. [11] and Borse et al. [12]. The emission at 402 nm for (A) and 400 nm for (B) is attributed to sulphur vacancies, which agrees well with peak value (428 nm) reported by Wageh et al. [18].

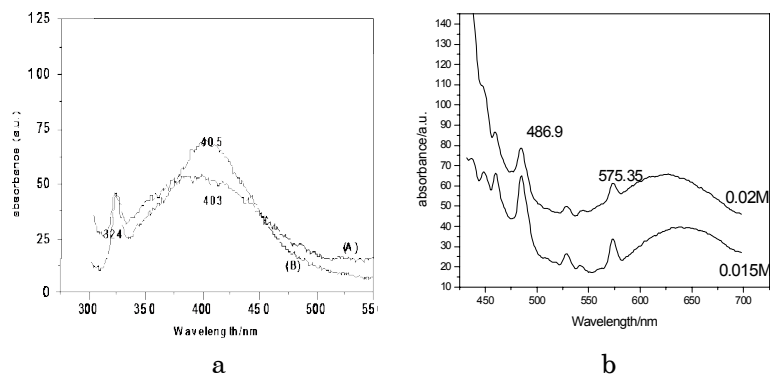


Fig. 5 – (a) PL spectra of nano ZnS, (b) PL spectra of nano CdS

Fig. 5b shows the PL spectra for CdS nanoparticles where two peaks at 487 nm and 576 nm are recorded with an excitation wavelength of 386 nm. Emission in the visible region is attributed to (D-A) band transition [16] and these materials can be used as red light emitting nano devices.

3.5.2 PL Analysis for dye sensitized nanoparticles

PL spectra for dye sensitized ZnS are measured for excitation wavelength of 362 nm and are shown in Fig. 6a. When Fig. 5a and Fig. 6a are compared, a new emission at 510 nm which is not in nano ZnS is found. Similarly a new emission occurs at 560 nm as in Fig. 6b for dye sensitized CdS nanoparticles which is not found in nano CdS. This implies visible absorption due to dye. The sensitizer adsorbed on the surface of the nanocrystalline semiconductor is used to absorb the incoming photon flux. Since the solar spectrum is centered on the visible light wavelength (400-800 nm) it can absorb optimally the light in the visible region. This plays a vital role in solar cell application. ZnS core shell quantum dots of 4 nm diameter have a maximum emission around 550 nm which would be ideally suited for amorphous silicon solar cells as reported by van Sark et al. [18].

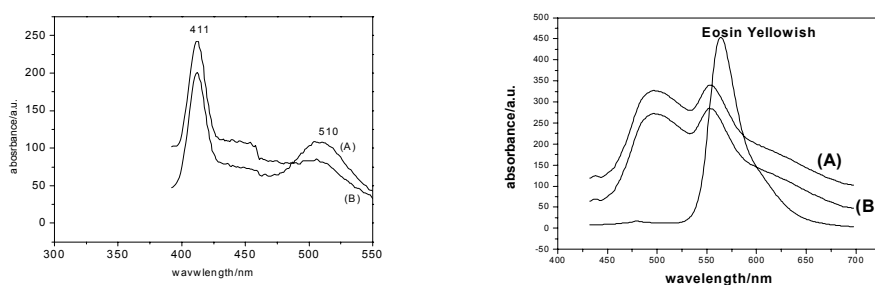


Fig. 6 – (a) PL spectra of methyl blue sensitized nano ZnS (b) PL spectra of Eosin Yellowish sensitized nano CdS

3.6 Solar Cell

ZnS electrodes and CdS electrodes were prepared as follows for the solar cell. 0.5 g of synthesized ZnS nanopowder was mixed with 0.3 mL acetic acid and ground by using mortar pestle for 30 minutes. An ITO coated glass plate was cut into smaller pieces on one side of the glass in order to avoid disturbance to the conductive layer. Scotch tape was placed along three edges of the conductive side of the glass such that the effective area of the solar cell was restricted to 1.0 cm². The paste was spread along the tape using a glass rod, without rolling the rod because rolling causes lumps in the paste. The tape was removed after the paste was dried for about a minute. The ZnS coated glass plate was annealed on a hot plate for about 40 minutes in air at temperature of 60 °C. The annealing allowed sintering of ZnS particles together to better transport of electrons, since disconnected particles cause electron trapping. Sintered ZnS electrodes were soaked in dye solution (0.25 g of dye in 20 ml of ethanol) for 24 hours. It is then taken out in air and is kept at room temperature for 2 hours and is sandwiched with the carbon coated counter electrode. The electrolyte was composed of 0.3 M lithium chloride and 0.05 M Iodide.

3.7 Current Voltage Characteristics

Photocurrent-voltage curve was measured with Oriel Class-A Simulator (M-91900 A, Newport) with Xenon lamp as a light source with the intensity 100 mW/Cm⁻². A computer controlled Auto lab PGSTAT302N electrochemical work station was used for current-voltage measurements. The light intensity of the illumination source was checked using calibrated light intensity meter (OPHIR laser measurement group, NOVA Oriel). Fig. 7 shows photocurrent voltage characteristics of the cell using ZnS electrode and CdS electrodes.

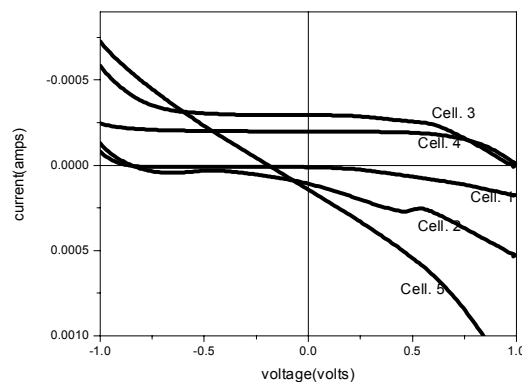


Fig. 7 – *I-V Curve of dye sensitized electrodes*

The list of various cell configurations and their performances are tabulated in Table 3. The Cell 1 is composed of ZnS electrode sensitized by Methyl Blue dye(MB) in KI+I₂ electrolyte in Ethylene Glycol with candle soot on the other ITO as counter electrode. The maximum solar cell conversion efficiency (η) of the DSSC containing KI+I₂ as electrolyte

increased to 0.016 % with Methyl blue (MB) dye and 0.090 % with Methyl Blue dye (MB) in 0.3 M of LiCl_2 and 0.05 M of I_2 as electrolyte (Cell 2). Eosin Yellowish (EY) dye sensitized ZnS electrode with 0.3 M of LiCl_2 and 0.05 M of I_2 as electrolyte results in 0.099 % efficiency (Cell 4) whereas Basic Blue 3 dye (Cell 3) sensitized ZnS electrode results in 0.088 % efficiency. ZnS/ZnO composite with ruthenium dye was reported with the efficiency of 0.08 % by Liao Jung-Yu et al. [10]. Cell 5 is composed of CdS electrode sensitized by Eosin Yellowish (EY) in $\text{KI}+\text{I}_2$ electrolyte in Ethylene Glycol with candle soot on the other ITO as counter electrode results in 0.066 % efficiency. Generally ruthenium dyes are very good sensitizers and so effective for DSSC.

Table 3 – Cell configurations and their performances

Cell	Configuration	V_{oc}	I_{sc}	η (%)	F.F.
Cell 1.	ITO/ZnS/MB dye/ $\text{KI}+\text{I}_2$ electrolyte/carbon/ITO	- 0.79	7.96×10^{-6}	0.016	1.63
Cell 2.	ITO/ZnS/MB dye/ LiCl_2+I_2 electrolyte/carbon/ITO	- 0.82	1.09×10^{-4}	0.090	1.00
Cell 3.	ITO/ZnS/BB3 dye/ $\text{LiCl}_2 +\text{I}_2$ electrolyte/carbon/ITO	0.90	3.053×10^{-5}	0.088	0.32
Cell 4.	ITO/ZnS/EY dye/ LiCl_2+I_2 electrolyte/carbon/ITO	0.90	$- 1.95 \times 10^{-5}$	0.099	0.56
Cell 5.	ITO/CdS/EY dye/ LiCl_2+I_2 electrolyte/carbon/ITO	0.16	1.984×10^{-4}	0.066	1.99

No other reports are available on this methyl blue dye sensitized nano ZnS DSSC and nano CdS DSSC and so, the present work will be a guideline value for the design of solar cell with this nano material.

4. CONCLUSION

ZnS and CdS nanoparticles were synthesized by simple chemical route. Structural characterizations were done by XRD where results revealed the cubic phase. The optical properties of nanomaterials and dye sensitized nanomaterials show a strong visible absorption at 600 nm in UV-Vis analysis. Current-voltage characteristics was studied for various types of solar cells and the overall efficiency of Eosin Yellowish (EY) sensitized ZnS solar cell was found to be 0.09 % and 0.016 % for Methyl Blue (MB) dye. Eosin Yellowish sensitized CdS solar cell was found to be 0.06 %. Even though ZnS and CdS is a very good light sensing material, the conversion efficiency with dyes for solar cells be improved further and this is possible from the present investigations.

REFERENCES

1. Zh. Wang, L. L. Daemen, Yu. Zhao, C.S. Zha, R.T. Downs, X. Wang, Zh. L. Wang, R. J. Hemley, *Nat. Mater.* **4**, 922 (2005).
2. I.A. Banerjee, L. Yu, H. Matsui, *J. Am. Chem. Soc.* **127**, 16002 (2005).
3. Jin-Song Hu, Ling-Ling Ren, Yu-Guo Guo, Han-Pu Liang, An-Min Cao, Li-Jun Wan, Chun-Li Bai, *Angew. Chem.* **117**, 1295 (2005).
4. Arturo Morales-Acevedo, *Sol. Energ. Mat. Sol. C* **90**, 2213 (2006).
5. H. Murai, T. Abe, J. Matsuda, H. Sato, S. Chiba, Y. Kashiwaba, *Appl. Surf. Sci.* **244**, 351 (2005).

6. Y. Wang, S. Ramanathan, Q. Fan, F. Yun, H. Morkoe, S. Bandyopadhyay, *J. Nanosci. Nanotechnol.* **6**, 2077 (2006).
7. A. Ponzoni, E. Comini, G. Sberveglieri, J. Zhou, S.Z. Deng, N.S. Xu, Y. Ding, Z.L. Wang, *Appl. Phys. Lett.* **88**, 203101 (2006).
8. Z. H. Zhong, D.L. Wang, Y. Cui, M.W. Bockrath, M.C. Lieber, *Science* **302**, 1377 (2003).
9. X. Duan, Y. Huang, R. Agarwal, C.M. Lieber, *Nature* **421**, 241 (2003).
10. Jung-Yu Liao, Kuo-Chuan Ho, *Sol. Energ. Mat. Sol. C.* **86**, 229 (2005).
11. Yun Chen, Qing-Sheng Wu, Ya-Ping Ding, *J. Braz. Chem. Soc.* **18**, 924 (2007).
12. P.H. Borse, N. Deshmukh, R. F. Shinde, S. K. Date, S. K. Kulkarni, *J. Mat. Sci.* **34**, 6087 (1999).
13. A.M. Suhail, M.J. Khalifa, N.M. Saeed, O.A. Ibrahim, *Eur. Phys. J. Appl. Phys.* **49**, 30601 (2010).
14. L. Brus, *J. Phys. Chem.* **90**, 2555 (1986).
15. William G. Becker, Allen J. Bard, *J. Phys. Chem.* **87**, 4888 (1983).
16. N. Chestnoy, T.D. Harris, R. Hull, L.E. Brus, *J. Phys. Chem.* **90**, 3393 (1986).
17. S. Wageh, Zhao Su Ling, Xu Xu-Rong, *J. Cryst. Growth* **255**, 332 (2003).
18. W.G.J.H.M. van Sark, A. Meijerink, R.E.I. Schropp, J.A.M.van Roosemalen, E.H. Lysen, *Semiconductors* **38**, 962 (2004).