

Study of Structural and Optical Properties of Undoped and Cu Doped ZnO Nanostructures (NSs) in PVP Matrix by Wet Chemical Route

M.K. Debanath¹, S.M. Borah² and S. Karmakar³

^{1,3}Department of Instrumentation & USIC, Gauhati University, Guwahati 781014, Assam, India

²Department of Applied Sciences, Gauhati University, Guwahati 781014, Assam, India

E-mail: ¹mrinaldebanath@rediffmail.com, ²sankarmoni@gmail.com, ³sanjibkab@rediffmail.com

Abstract—Syntheses of nanostructures (NSs) are becoming the subject of major interest as they involve simple and inexpensive processes. In this report, the synthesis of polyvinylpyrrolidone (PVP) capped undoped zinc oxide (ZnO) and copper (Cu) doped zinc oxide (ZnO) NSs by simple wet chemical method at temperature 60 °C and the effect of doping on structural and optical properties on the as-synthesized NSs has been studied. The obtained NSs are characterized by X-ray diffraction (XRD), energy dispersive analysis of X-rays (EDAX), high resolution transmission electron microscopy (HRTEM), UV-vis absorption spectroscopy and photoluminescence (PL) spectroscopy for their structural and optical properties. The studies of XRD and HRTEM confirm nanoformation of the as-synthesized NSs. The EDAX spectra revealed the presence of Zn and O elements for undoped ZnO (SZO), whereas Zn, Cu and O elements in Cu doped ZnO (SZOCu) as expected for the as-prepared samples. UV-vis absorption spectra of the synthesized samples indicate the presence of blueshift. It was observed that the room temperature PL spectra of the samples exhibit UV emission peaks along with defects related emission peaks

Keywords: ZnO nanostructures, XRD, EDAX, HRTEM, UV-vis, PL.

1. INTRODUCTION

Nanostructure materials have attracted immense attention worldwide due to their exotic properties as compared to their bulk counterparts [1, 2]. ZnO is an important II-VI wide-band-gap (3.3 eV, at 300K) semiconductor material exhibits interesting properties including high exciton binding energy of 60 meV, strong adsorption ability and low growth temperature, which makes it a wide variety of interesting applications in photocatalysts, chemical sensors, piezoelectric transducers, transparent electrodes [3,4], electroluminescent devices, ultraviolet laser diodes [5,6], photonic crystals [7], photodetectors [8], varistors [9] and solar cells [10]. Properties of ZnO can be tuned by doped with various metal atoms to suit specific needs and applications. Doping of Cu in ZnO is important because of its physical and chemical properties that are similar to those of Zn and can be changed the microstructure and the optical properties of the ZnO system

[11]. Various processes have been applied to the synthesis of ZnO NSs, wet chemical method shows many advantages over other techniques such as its simplicity and low equipment cost.

The present study report the effect of Cu doped ZnO NSs on structural and optical properties of ZnO NSs with PVP as capping agent by simple wet chemical method.

2. EXPERIMENTAL

2.1. Synthesis of undoped ZnO NSs

All materials were purchased from the commercial market and used without further purification. To synthesize undoped ZnO (SZO) NSs, 100 ml of 0.1 M solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was stirred constantly for 30 min at 60 °C (solution A). 3 wt% of PVP was stirred constantly at 60 °C for 30 min (solution B). Now NH_4OH was slowly added drop by drop into solution A and stirred at room temperature for 15 min and the pH of the solution was continuously measured. When the pH of the solution is 7.5 and a white solution (solution C) of ZnO is formed and the addition of NH_4OH is stopped. The final mixture (solution B and solution C) is stirred constantly for 1 h at 60 °C and allowed to cool down at room temperature till the white precipitate of ZnO is formed. The whole solution is allowed to settle overnight in a dark chamber. Finally, the precipitate is filtrated which is washed with distilled water to dissolve the impurities and dried at 60 °C in an oven for 12 h to obtain ZnO nanocrystalline powder [12].

2.2. Synthesis of Cu doped ZnO NSs

For the preparation of Cu doped ZnO NSs, above wet chemical method has been followed (sample named as SZO), while 100 ml of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ of 0.0075 M solution was added in the prepared sample and stirred constantly at 60 °C for 3 hrs for preparing 7.5 M % Cu doped ZnO NSs at pH = 7.5. The as-prepared sample named as SZOCu.

2.3. Characterization methods

Powder X-ray diffraction (XRD) pattern of as-prepared NSs are recorded by Philips X-ray Diffractometer (X'Pert Pro) with $\text{Cu } K_{\alpha 1}$ radiation ($\lambda = 1.5406 \text{ \AA}$). Scanning electron microscope (SEM with EDX, JEOL JSM Model 6390 LV) has been used for compositional analysis of the as-prepared samples. Transmission Electron Microscopy (TEM) observations are carried out on a JEM 2100 electron microscope. The optical absorption spectra are recorded by a UV-vis spectrometer (HITACHI U-3210) and PL spectra were measured on Fluorescence Spectrometer (HITACHI-2500) at room temperature.

3. RESULTS AND DISCUSSION

3.1. Structural and compositional studies

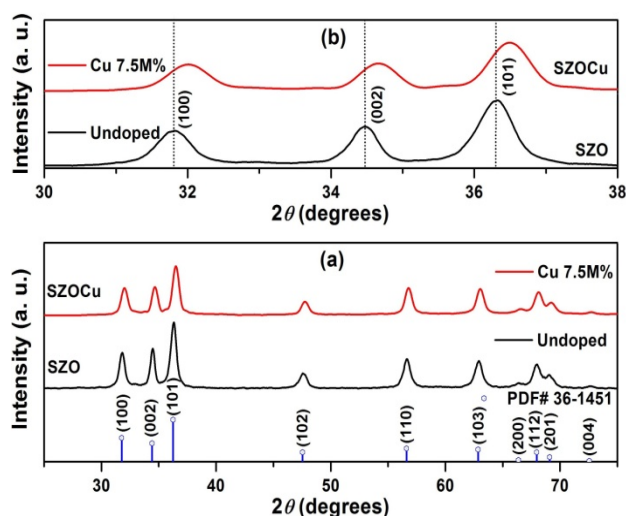


Fig. 1: XRD pattern of undoped and Cu doped ZnO NSs (a) undoped (SZO) and 7.5M % (SZOCu) and (b) comparison of (100), (002), and (101) peaks.

The XRD pattern of undoped ZnO (SZO) and 7.5M % Cu doped ZnO (SZOCu) are recorded in the range of 25° – 75° (2θ) at a scanning rate of $0.02^{\circ}/\text{s}$ and 0.5 sec/step are shown in Fig. 1. All the peaks corresponds to (100), (002), (101), (102), (110), (103), (200), (112), (201) and (004) planes are well indexed with the *Powder Diffraction File* (PDF No. 36-1451), indicating hexagonal wurtzite phase of ZnO with space group $P6_3mc$ (186) and no other diffraction peaks corresponding to Cu related secondary and impurity phases except ZnO has been detected, which revealed that the Cu^{2+} ions have substituted into the Zn lattice sites without affecting the crystal structure of ZnO. This may be due to the fact that ionic radius of Cu^{2+} (0.73 \AA) is very close to that of Zn^{2+} (0.74 \AA), so Cu can easily penetrate into ZnO lattice [13]. The crystallite sizes of SZO and SZOCu are calculated by using the peak broadening of the peaks in the XRD pattern. This can be done according to the method of Scherrer [14]. The average

crystallite sizes of the NSs for undoped and Cu doped ZnO are found to be $\sim 16.50 \text{ nm}$ and $\sim 13.64 \text{ nm}$ respectively from the (100), (002) and (101) index planes. The results are shown in Table 1, it is seen that with Cu doping in ZnO, the peaks are broadened and shifted to higher diffraction angle (2θ), indicating decreasing value of crystallite size.

Table 1: hkl , 2θ , d -value, FWHM and crystallite sizes.

Sample	hkl	2θ (degree)	d (\AA)	FWHM (degree)	Crystallite size (nm)	Average size (nm)
SZO (undoped)	100	31.78	2.8134	0.5448	15.24	16.50
	002	34.44	2.6019	0.4251	19.53	
	101	36.30	2.4728	0.5675	14.75	
SZOCu (doped)	100	31.98	2.8377	0.6293	13.07	13.64
	002	34.66	2.6204	0.5666	14.75	
	101	36.49	2.4603	0.6414	13.08	

The lattice parameters such as the d values (distance between adjacent planes) are calculated from the Bragg equation ($\lambda = 2d\sin\theta$), lattice constants (a and c) and unit cell volume V is calculated from the *Lattice Geometry* equation [6] given below

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

$$V = \frac{\sqrt{3}}{2} a^2 c = 0.866 a^2 c$$

Table 2: Lattice constants (a , c) and unit cell volume (V).

Sample	Lattice constants (\AA)		Unit cell volume (V) (\AA^3)
	a	c	
SZO (undoped)	3.2496	5.2039	47.59
SZOCu (doped)	3.2378	5.1718	46.95

It is evident from the Table 2 that there is a variation of lattice constants as compared with PDF No. 36-1451 [$a = 3.24982(9)$, $c = 5.20661(15)$] and also Table 1 shows that there is a slight shifting or splitting of diffraction peaks for undoped and Cu doped ZnO NSs. This may be attributed to incorporation of Cu^{2+} ion into the ZnO lattice and also indicating that there is no major change by Cu doping in the ZnO crystal lattice. The slight shifting of XRD pattern and the change in the d -value and lattice parameters with Cu doped in ZnO nanostructures revealed that Cu has really doped into ZnO lattice [13].

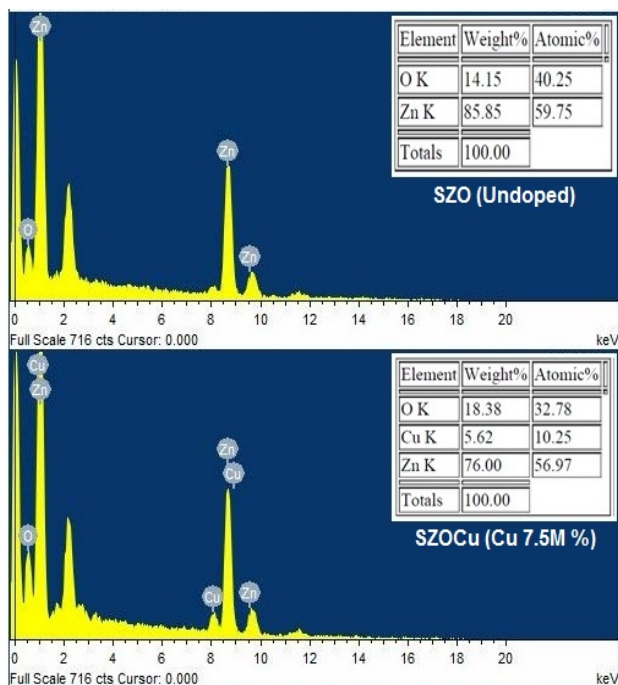


Fig. 2: EDAX spectra of undoped ZnO (SZO) and 7.5M % Cu doped ZnO (SZOCu).

The EDAX analysis depicted in Fig. 2 show presence of only Zn and O as expected for undoped ZnO, whereas Zn, Cu and O are found in Cu doped ZnO NSs. No other impurity elements were present in the samples. It is observed that the as-prepared undoped ZnO and Cu doped ZnO NSs are non-stoichiometric. The Cu/Zn weight percentage ratio is found to be 7.39 % in 7.5 % molar Cu source doped in ZnO, which revealed that the presence of Cu in the ZnO system and wt % is nearly equal to their nominal stoichiometry within the experimental error. Therefore, the EDAX spectrum shows well agreement with experimental concentration used for Cu doped ZnO system.

Fig. 3 shows HRTEM images of as-prepared samples SZO and SZOCu. HRTEM images show aggregation of smaller ZnO and Cu doped ZnO NSs which are shown in Fig. 3 (a) and (c). The particle size calculated from HRTEM image shown in Fig. 3 (b) is found to be ~19.53 nm for SZO, whereas it is found to be ~18.1 nm for SZOCu shown in Fig. 3 (d).

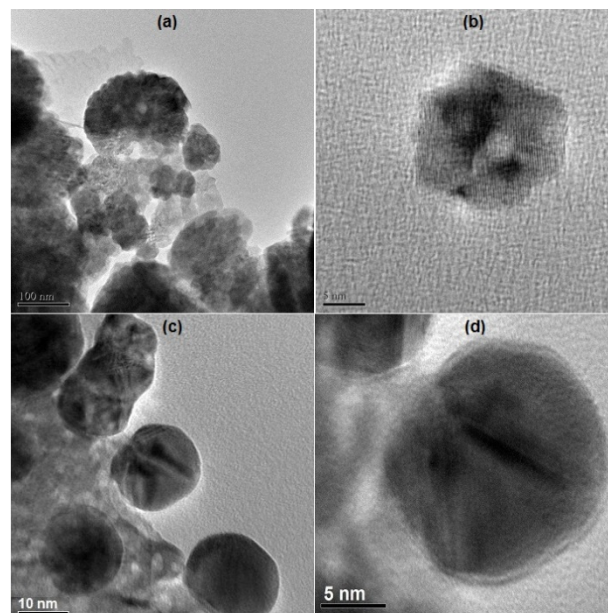


Fig. 3: HRTEM images of undoped ZnO (SZO) and Cu doped ZnO (SZOCu) (a) aggregation of smaller SZO NSs, (b) a single hexagonal SZO nanoparticle, (c) aggregation of smaller SZOCu NSs and (d) a single quasi-spherical SZOCu nanoparticle.

3.2. Optical studies

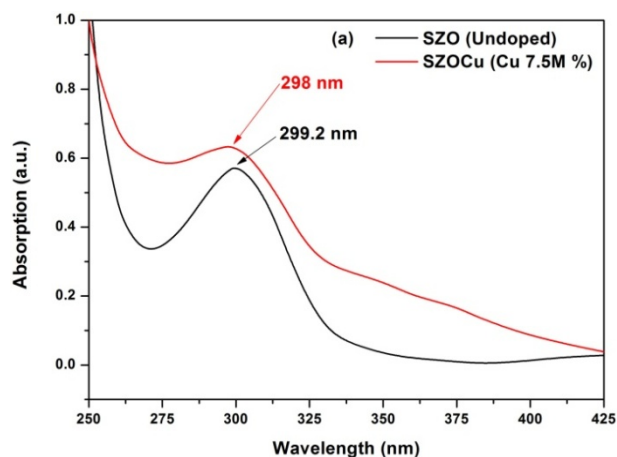


Fig. 4: Absorption spectra of undoped ZnO (SZO) and 7.5M % Cu doped ZnO (SZOCu).

The UV-vis absorption spectra of SZO and SZOCu are shown in Fig. 4. It is seen that strong peak absorbance wavelengths at ~299.2 nm and ~298 nm for undoped and Cu doped ZnO NSs respectively, which indicate the presence of blueshifts with decrease in particle sizes with respect to bulk ZnO (wavelength ~376 nm; 3.3eV) and this could be attributed to the confinement effects [15].

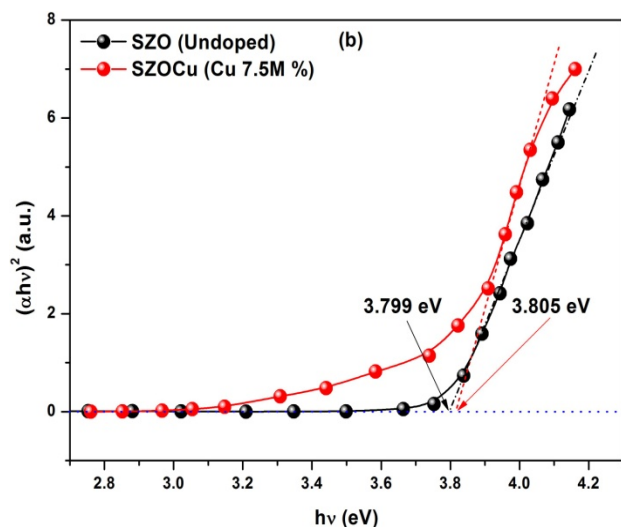


Fig. 5: Plot to determine direct band gap of undoped ZnO (SZO) and 7.5M % Cu doped ZnO (SZOCu).

The direct band gap of as-prepared samples are estimated from the graph of $h\nu$ versus $(\alpha h\nu)^2$ for the absorption coefficient α which is related to the band gap E_g as $(\alpha h\nu)^2 = k(h\nu - E_g)$, where $h\nu$ is the incident light energy and k is a constant. The extrapolation of the straight line in Fig. 5 to $(\alpha h\nu)^2 = 0$ gives the value of band gap energy E_g . The optical band gap (E_g) is found to be size dependent and there is an increase in the band gap of the semiconductor with a decrease in particle size. The optical band gap values obtained for SZO and SZOCu NSs are ~ 3.799 eV and ~ 3.805 eV respectively. Such an increase in the band gap energies are in good agreement with the corresponding blueshifts seen in the absorption spectra mentioned above.

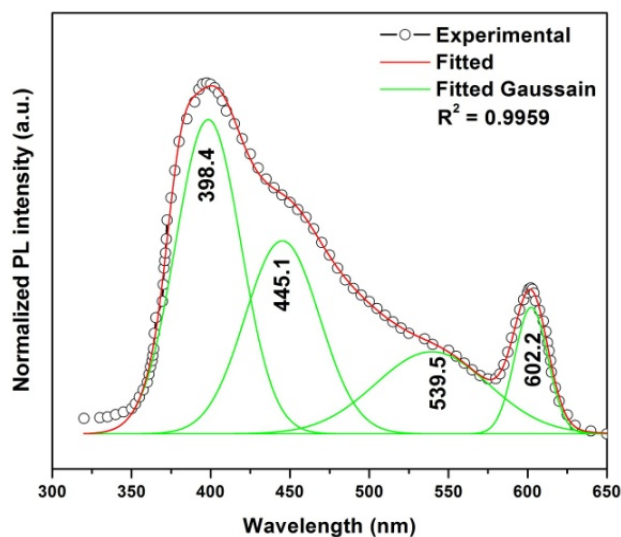


Fig. 6 (a): Room temperature PL spectra of undoped ZnO (SZO) (The Gaussian peaks marked as green colour at the bottom of the fitted curve marked with red colour).

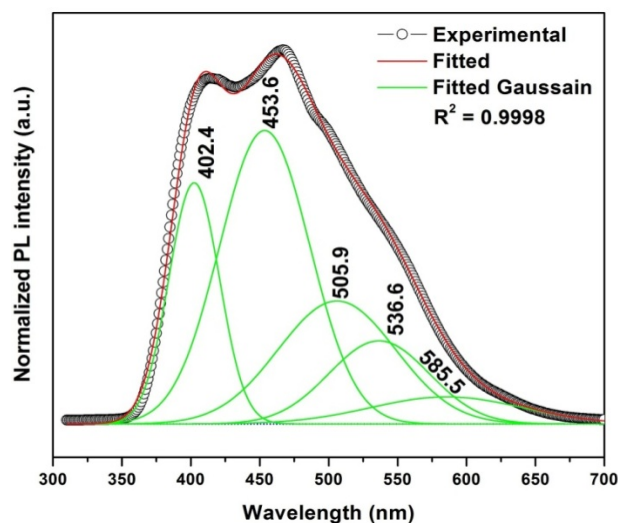


Fig. 6 (b): Room temperature PL spectra of doped ZnO (SZOCu) (The Gaussian peaks marked as green colour at the bottom of the fitted curve marked with red colour).

Fig. 6 (a) and (b) show the room temperature PL spectra under excitation wavelength of 300 nm for samples SZO and SZOCu which can be fitted by Gaussian peaks. Interestingly, a small redshift of UV emission peak from ~ 398.4 nm (3.11 eV) to ~ 402.4 nm (3.08 eV) as compared to undoped sample SZO and defect related green peak centered at ~ 536.6 nm (2.31 eV) which has been shifted from ~ 539.5 nm (2.30 eV) as observed in SZO. The UV emission peak corresponds to the near-band-edge (NBE) emission [16]. The shift in NBE emission and a shift in green band (GB) emission confirmed the substitution of Cu into Zn-O lattice. The green peak can be attributed to the oxygen vacancies and intrinsic defects and also due to the impurity levels correspond to the singly ionized oxygen vacancy in ZnO [17, 18]. The yellow emission peak at ~ 602.2 nm (2.06 eV) is due to oxygen interstitials [19].

4. CONCLUSIONS

The structural and optical properties of undoped and Cu doped ZnO NSs prepared by wet chemical route has been studied. The variation of crystallite/particle sizes are determined from the method of Scherrer and by HRTEM which are all in good agreement. Decrease in lattice parameters and crystallite size has been observed for Cu doped sample. The incorporation of Cu (7.5M % solution of Cu source) into ZnO, the nearly hexagonal structures of as-prepared NSs have been changed to quasi-spherical structure and decrease in particle size which is confirmed by both XRD and TEM analyses. The as-prepared NSs indicate the presence of blueshift with respect to bulk ZnO. It is evident from the UV-vis absorption analyses that smaller particle has larger band gap energy and vice-versa. The as-prepared samples exhibit UV emissions as well as defect related emissions. Therefore, the NSs may have wide applications in different optoelectronic devices.

5. ACKNOWLEDGEMENTS

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REFERENCES

- [1] Alvisatos, A. P., "Semiconductor Clusters, Nanocrystals, and Quantum Dots", *Science*, 271, 5251, 1996, pp. 933-937.
- [2] Nasr, C., Hotchandani, S., Kim, W. Y., Schmehl, R. H., and Kamat, P. V., "Photoelectrochemistry of composite semiconductor thin films. Photosensitization of SnO_2/CdS coupled nanocrystallites with a Ruthenium complex", *Journal of Physical Chemistry B*, 101, 1997, pp. 7480-7487.
- [3] Duran, P., Capel, F., Tartaj, J., and Moure, C., "A Strategic Two-Stage Low-Temperature Thermal Processing Leading to Fully Dense and Fine-Grained Doped-ZnO Varistors", *Advanced Materials*, 14, 2, January 2002, pp. 137-141.
- [4] Bauer, C., Boschloo, G., Mukhtar, E., and Hagfeldt, A., "Electron injection and recombination in $\text{Ru}(\text{dcbpy})(2)(\text{NCS})(2)$ sensitized nanostructured ZnO", *Journal of Physical Chemistry B*, 105, 2001, pp. 5585-5588.
- [5] Yuen, C., Yu, S. F., Lau, S. P., and Chen, G. C. K., "Design and fabrication of ZnO light-emitting devices using filtered cathodic vacuum arc technique", *Journal of Crystal Growth*, 287, 1, 2006, pp. 204-212.
- [6] Liang, S., Sheng, H., Liu, Y., Hio, Z., Lu, Y., and Shen, H., "ZnO Schottky ultraviolet photodetectors", *Journal of Crystal Growth*, 225, 2001, pp. 110-113.
- [7] Koch, M. H., Timbrell, P. Y., and Lamb, R. N., "The influence of film crystallinity on the coupling efficiency of ZnO optical modular waveguides", *Semiconductor Science and Technology*, 10, 1995, pp. 1523-1527.
- [8] Gorla, C. R., Emanetoglu, N. W., Liang, S., Mayo, W. E., Lu, Y., Wraback, M., and Shen, H., "Structural, optical, and surface acoustic wave properties of epitaxial ZnO films grown on (0112) sapphire by metalorganic chemical vapor deposition", *Journal of Applied Physics*, 85, 5, March 1999, pp. 2595-2602.
- [9] Dong, L., Jiao, J., Tuggle, D. W., Petty, J. M., Elliff, S. A., and Coulter, M., "ZnO nanowires formed on tungsten substrates and their electron field emission properties", *Applied Physics Letters*, 82, 7, February 2003, pp. 1096-1098.
- [10] Jo, S. H., Lao, J. Y., Ren, Z. F., Farrer, R. A., Baldacchini, T., and Fourkas, J. T., "Field-emission studies on thin films of zinc oxide nanowires", *Applied Physics Letters*, 83, 23, December 2003, pp. 4821-4823.
- [11] Zhang, Z., Yi, J. B., Ding, J., Wong, L. M., Seng, H. L., Wang, S. J., Tao, J. G., Li, G. P., Xing, G. Z., Sum, T. C., Huan, C. H. A., and Wu, T., "Cu-doped ZnO nanoneedles and nanonails: morphological evolution and physical properties", *The Journal of Physical Chemistry C*, 112, 26, June 2008, pp. 9579-9585.
- [12] Debanath, M. K., and Karmakar, S., "Study of blueshift of optical band gap in zinc oxide (ZnO) nanoparticles prepared by low-temperature wet chemical method", *Materials Letters*, 111, August 2013, pp.116-119.
- [13] Muthukumaran, S., and Gopalakrishnan, R., "Structural, FTIR and photoluminescence studies of Cu doped ZnO nanopowders by co-precipitation method" *Optical Materials*, 34, June 2012, pp. 1946-1953.
- [14] Klug, H. P., and Alexander, L. E., "X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials". 2nd ed., John Wiley and Sons, New York, p. 491, 1954.
- [15] Gu, Y., Kuskovsky, I. L., Yin, M., O'Brien, S., and Neumark, G. F., "Quantum confinement in ZnO nanorods", *Applied Physics Letters*, 85, 17, August 2004, pp. 3834-3835.
- [16] Karunakaran, C., Gomathisankar, P., and Manikandan, G., "Preparation and characterization of antimicrobial Ce-doped ZnO nanoparticles for photocatalytic detoxification of cyanide", *Materials Chemistry and Physics*, 123, 2-3, October 2010, pp. 585-594.
- [17] Monticone, S., R. Tufeu, R., and Kanaev, A. V., "Complex Nature of the UV and Visible Fluorescence of Colloidal ZnO Nanoparticles", *Journal of Physical Chemistry B*, 102, 16, March 1998, pp. 2854-2862.
- [18] Ahsanulhaq, Q., Umar, A., and Hahn, Y. B., "Growth of aligned ZnO nanorods and nanopencils on ZnO/Si in aqueous solution: growth mechanism and structural and optical properties" *Nanotechnology*, 18, 11, February 2007, pp. 115603-115607.
- Ahn, C. H., Kim, Y. Y., Kim, D. C., Mohanta, S. K., and Cho, H. K., "A comparative analysis of deep level emission in ZnO layers deposited by various methods," *Journal of Applied Physics*, 105, 1, 2009, pp. 013502-013506.