

Project Completion Report

“Development of ZnO nanorods for luminescent device application”

UFUP-44314

(2008-2011)



Principal Investigator

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Comprehensive Report

2008-2009 (FUC and report submitted before)

The approval letter for the aforesaid project was received in August 2008. After following general procedures, the project fellow was selected and the fellow (Mr. S. Bayan) joined in the department on 20-11-2008. Apart from the relevant literature survey, a few experimental works related to microemulsion based synthesis of ZnO nanostructures have been carried out. The structural and optical studies have been performed.

2009-2010 (FUC and report submitted before)

Terbium (Tb^{3+}) doped ZnO nanorods were fabricated using a cost-effective, one-step solid state fabrication and their structural and luminescence responses after 80-MeV Nitrogen ion irradiation have been studied. Various defect related emission of ZnO were observed, along with $^5D_4 - ^7F_6$ and $^5D_4 - ^7F_5$ transitions of Tb^{3+} in the photoluminescence under 325 nm excitation. On 80 MeV N^{4+} ion irradiation, the nanorods show improved emission at a particular fluence of (5×10^{11} ions/cm²). The improved emission of the ZnO system was because of the formation of more zinc vacancy defect states under irradiation.

2010-2011 (FUC is attached separately with unspent balance. This is final report)

A) 80 MeV Nitrogen (N^{4+}) ion irradiation on ZnO nanorods

Synthesis of ZnO nanorods: The ZnO nanorods were synthesized using a simple microemulsion method. Hexane, M N-cetyl-N,N,N, trimethyl ammonium bromide, and n-butanol were stirred together for about 15 min to form a homogeneous mixture. The mixture was then partitioned into two equal parts and aqueous zinc chloride ($ZnCl_2$) and sodium hydroxide (NaOH) were added into the two separate mixtures to give two different microemulsions. Lastly, the two precursors were mixed and stirred for 8 hrs. The elongated ZnO nanostructures were obtained after centrifugation, ultrasonication and heating ($\sim 80^\circ C$ for 2 hrs) in air.

Irradiation of nanorods: The ZnO nanorod-dispersed in Polyvinyl alcohol (PVA) films were casted on laboratory glass slides ($1 \times 1 \text{ cm}^2$) for the irradiation experiment. The samples were irradiated in the Material Science chamber under a high vacuum (pressure of $\sim 10^{-6}$ mbar) condition and using 80 MeV N^{4+} ion beams (with a beam current of ~ 1 pA, particle-nanoampere), available at the 15UD tandem pelletron accelerator of Inter University Accelerator Centre, New Delhi. Ion fluence was varied in the range of 1.25×10^{11} to 8×10^{12} ions/ cm^2 .

Results and discussion: The Transmission Electron Microscopy (TEM) image of the as-synthesized ZnO nanosticks/rods are shown in Figure 1(a). The diameter and the length of the nanorods were within 25-30 nm, and 700-750 nm range. The X-Ray Diffraction (XRD) pattern of the nanorods (Figure 1b) corresponds to the formation of hexagonal wurtzite phase of ZnO having preferred orientation along (101) plane. The room temperature photoluminescence (PL) spectra of the nanorods were recorded at an excitation of 325 nm (Figure 1c). The PL spectra depicts the emission due to the presence of various defect states of ZnO. The major peak located at ~ 403 nm corresponds to the zinc vacancy (V_{Zn}) related defect of ZnO. The signature of oxygen vacancy (V_{O}^+) related defect was also found at ~ 490 nm. Whereas the emission at the higher wavelength side is dominated by defects like oxygen interstitial (O_i), double ionized oxygen vacancy (V_{O}^{++}) etc.

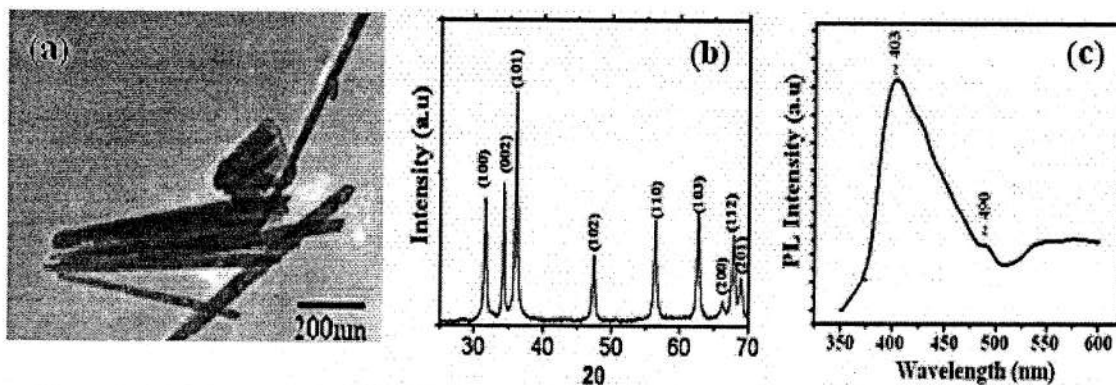


Figure 1: (a) TEM image, (b) XRD pattern and (c) PL spectra of the nanorods before irradiation.

On the other hand, the PL response of the irradiated nanorods depict the evolution of other defects also (Figure 2). Upon irradiation at 1.25×10^{11} ions/cm² the zinc interstitial (Zn_i) gets improved along with the V_O⁺ and O_i related emission. As the fluence increases from 5×10^{11} to 2×10^{12} ions/cm², a competition between V_{Zn} and Zn_i defects is observed. At a fluence of 2×10^{12} ions/cm², the Zn_i related emission is found to dominate. While at the highest fluence 8×10^{12} ions/cm², emission due to both V_{Zn} and Zn_i defects gets suppressed and the Zn_i⁺ related emission dominates the spectra. The V_O⁺ and O_i related emissions also get enhanced at the highest fluence. As the Zn_i atoms are mobile at room temperature even, it is expected that due to irradiation led deposition of energy, there is a possibility of annihilation of V_{Zn} defects by Zn_i atoms.

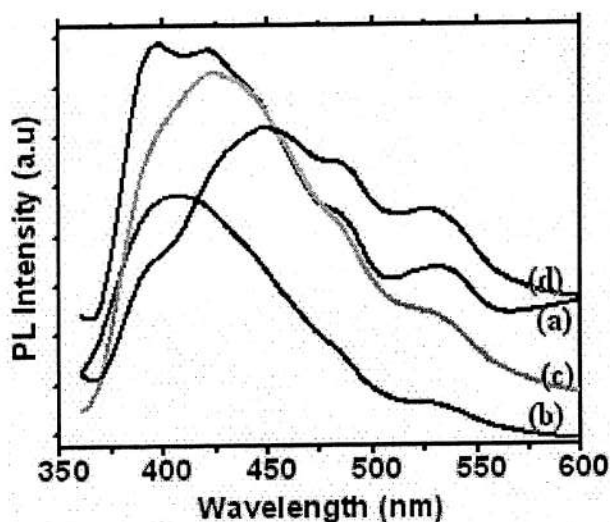


Figure 2: PL spectra of the ZnO nanorods after irradiation at (a) 1.25×10^{11} , (b) 5×10^{11} , (c) 2×10^{12} and (d) 8×10^{12} ions/cm².

Therefore, the competition between the V_{Zn} and Zn_i defects is due to the creation/annihilation of Zn related defects. Though various defect related emission of ZnO gets evolved at the highest fluence, the structural order was lost at that fluence (Figure 3). The agglomeration of the nanorods took place due to the enormous energy deposition at the highest fluence, leading to the amorphization of the matrix and coalescence of the nanorods.



Figure 3: Agglomeration of the nanorods at the highest fluence

B) 120 MeV Silver (Ag²⁺) ion irradiation on ZnO nanorods

Synthesis of ZnO nanorods: A mixture of zinc acetate dehydrate (ZAD), cetyl trimethyl ammonium bromide (CTAB), and sodium hydroxide (NaOH) with a molar ratio of

1:0.4:3 were ground together in an agate mortar for ~ 45 min at room temperature. The unidirectional grinding was accompanied by the release of heat while the reaction was in progress. After ultrasonication, the product was washed repeatedly with double distilled water and ethanol and finally dried in air ($\sim 80^\circ\text{C}$) for 2 hrs.

Irradiation of the nanorods: The PVA dispersed ZnO nanorods films on 1 cm x 1cm glass plates, were irradiated in the Material Science chamber under a high vacuum (pressure of $\sim 10^{-6}$ mbar) condition and using 120 MeV Ag^{9+} ion beams (with a very low beam current of ~ 0.3 pA, particle-nanoampere), available at the 15UD tandem pelletron accelerator of Inter University Accelerator Centre, New Delhi. In order to prevent from agglomeration the ion fluence was varied in the range of 3×10^{10} to 9×10^{10} ions/cm².

Results and discussion: The formation of nanorods having length 50-60 nm and diameter of 10-15 nm is evident from the TEM image (Figure 4a). The XRD pattern reveals the hexagonal wurtzite phase of ZnO (Figure 4b).

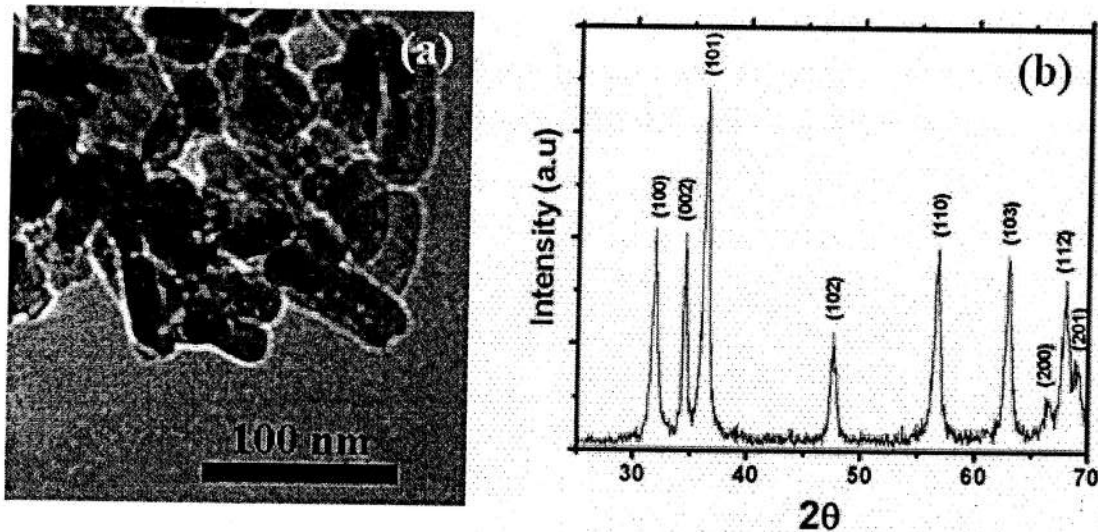


Figure 4: (i) TEM image and (ii) XRD pattern of the as synthesized ZnO nanorods.

The room temperature PL spectra of the nanorods (excitation at 325 nm) as shown in Figure 5, demonstrate the dominance of Zn_i related defects along both neutral and ionized zinc vacancy defects. Upon irradiation at 3×10^{10} ions/cm², the V_{Zn}^- related peak gets

enhanced and becomes maximum at highest fluence (Figure 5). At the highest fluence the spectra becomes broad owing to the prominence of the various defects. The detailed analysis of these defect related emission subjected to 120 MeV Ag^{9+} ion irradiation is still under investigation.

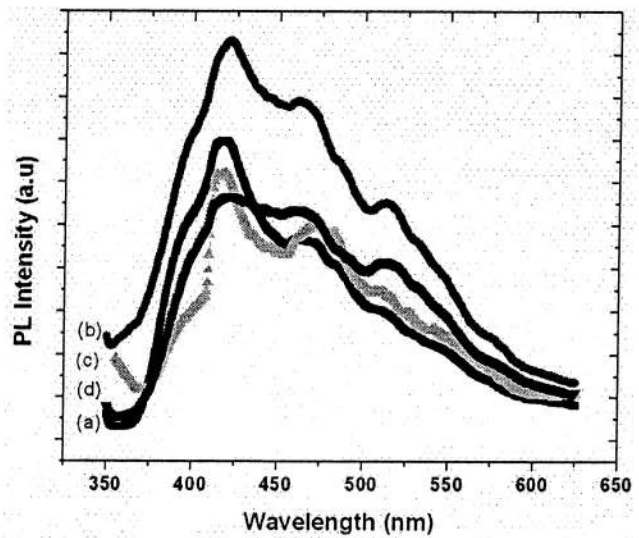


Figure 5: PL spectra of the ZnO nanorods (a) before irradiation and after irradiation at (b) 3×10^{10} , (c) 6×10^{10} and (d) 9×10^{11} ions/cm².

Apart from irradiation related features, through this project we have been able to find a route to obtain randomly oriented ZnO nanorods and urchins on $\text{Al}/\text{Al}_2\text{O}_3$ substrates (Figure 6). In addition, a natural template of processed peacock feather was used to grow self assembled ZnO nanostructures (Figure 7) and the hybrid system was studied for tuning photonic properties.

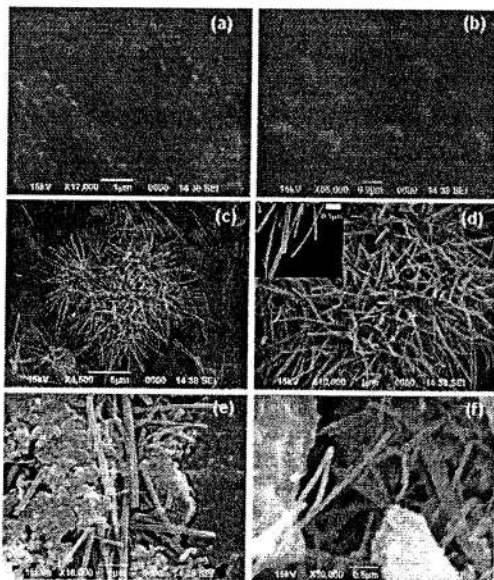


Figure 6: SEM images at different magnifications, of Eu-doped ZnO systems: (a) and (b) annealed at 80°C, (c) and (d) annealed at 300°C with inset at higher magnification, and (e) and (f) annealed at 650 °C.

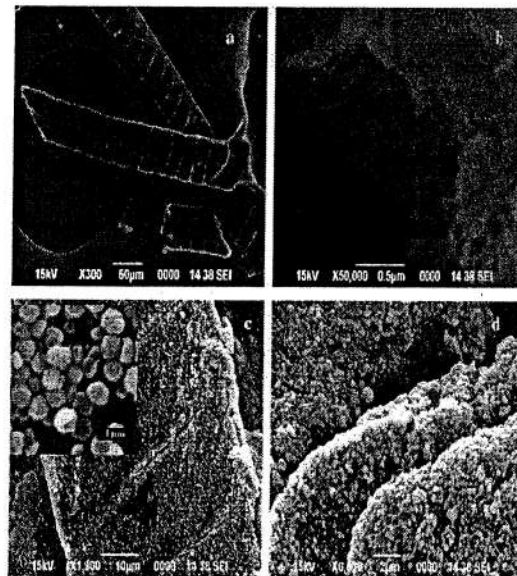


Figure 7: SEM micrograph of blue barbules (a, b) before and (c, d) after developing ZnO nanospheres (inset in (c) depicts the hexagonal nanostructures at higher magnification).

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References

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- [3] Z.-B. Fang, Y.-S. Tan, X.-Q. Liu, Y.-H. Yang, Y.-Y. Wang, *Chin. Phys.* **13**, 1330 (2004).
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- [6] K. E. McBean, M. R. Phillips, E. M. Goldys, *Microsc. Microanal.* **12**, 327 (2006).

Outputs:

- *J. Mater. Res.* **25**, 814 (2010). DOI: 10.1557/JMR.2010.0119
- *J. Appl. Phys.* **108**, 023512 -1-6 (2010) DOI:10.1063/1.3462396
- *Phys. Status Solidi A*, **207**, 1859 (2010). DOI 10.1002/pssa.200925525
- *Nucl. Instrum. Meth. B.* **269**(3), 374-379 (2011). DOI:10.1016/j.nimb.2010.11.044
- *Euro. Phys. J. D*, **61** (2), 463-468 (2011). DOI: 10.1140/epjd/e2010-10457-7

FUND UTILIZATION CERTIFICATE

(PROJECTS/SCHEMES)

Name of the Nodal Institution/
Department of Organisation : TEZPUR UNIVERSITY

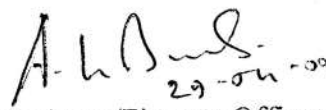
Name of the Project/Scheme : **“Development of ZnO nanorods for luminescent device applications ”**

Certified that out of Rs. 15,000/- of grant-in-aid sanctioned during the financial year 2008-09 in favour of Tezpur University on the subject UFUP-44314 project IUAC (NSC), New Delhi as per sanction order no. IUAC/IC.16.1/Vr.no.597-2974 dated 08.10.2008 and Rs. NIL unspent balance of the previous year, a sum of Rs. 15,172/- has been utilized during the current financial year 2008-09 on the project/ scheme and the committed amount of Rs.172/- remaining unadjusted upto 31.03.2009 due to shortage of fund and will be paid for the grant-in-aid payable for the next year 2009-10.


Project Investigator

Principal Investigator

Department of Physics
TEZPUR UNIVERSITY


Registrar/Finance Officer
Registrar
Tezpur University

**Expenditure statement of IUAC UFUP-44314 project titled:
"Development of ZnO nanorods for luminescent device applications "**

Sl. No.	Heads of account	Received grant (Rs.)	Expenditure during 2008-09 (Rs.)	Total expenses (Rs.)
1.	Contingency	15,000.00	15,172.00*	15,172.00
2.	Fellowships	0.00	0.00	0.00
			15,172.00	15,172.00

* An amount Rs. 15,172 /- is spent for advertisement for the position of a JRF / project fellow. The committed amount (Rs. 172 /-) will be adjusted after receiving the next installment under the head contingency.

Deputy Registrar (Finance) *[Signature]*
Tezpur University Assit. Finance Officer
TEZPUR UNIVERSITY

[Signature] 27/11/09
Registrar / Finance Officer
Tezpur University
Finance Officer
Tezpur University

FUND UTILIZATION CERTIFICATE

(PROJECTS/SCHEMES)

Name of the Nodal Institution/
Department of Organisation : TEZPUR UNIVERSITY

Name of the Project/Scheme : **“Development of ZnO nanorods for luminescent device applications”**

Certified that out of Rs. 1,45,926/- of grant-in-aid sanctioned during the financial year 2009-10 in favour of Tezpur University on the subject UFUP-44314 project IUAC (NSC), New Delhi as per sanction order no. IUAC/XIII.7/UFUP-44314/64 dated 31.03.2009 and IUAC/XIII.7/UFUP-44314/302 dated 14.05.2009 and IUAC/XIII.7/UFUP-44314/2389 dated 30.10.2009, a sum of Rs. 1,45,715/- has been utilized during the current financial year 2009-10 upto 31.03.2009 and the unspent balance of Rs.211/- will be utilized for the year 2010-11.


Project Investigator

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Registrar/Finance Officer
Registrar

Tezpur University

**Expenditure statement of IUAC UFUP-44314 project titled:
"Development of ZnO nanorods for luminescent device applications "**

Sl. No.	Heads of account	Received grant (Rs.)	Expenditure during 2009-10 (Rs.)	Total expenses (Rs.)
1.	Contingency	15,000	14,789	14,789
2.	Fellowships	1,30,926*	1,30,926*	1,30,926
TOTAL		1,45,926	1,45,715	1,45,715

* Note that the amount for Rs. 34,926/- against fellowship vide sanction letter IUAC/XIII.7/UFUP-44314/64 dated 31.03.2009 was actually sanctioned for the year 2008-09 and the corresponding Utilization Certificate was also sent.

Deputy Registrar (Finance)
Tezpur University

Co. Registrar (Finance)
Tezpur University


Registrar / Finance Officer
Tezpur University
Finance Officer
TEZPUR UNIVERSITY

FUND UTILIZATION CERTIFICATE
(PROJECTS/SCHEMES)

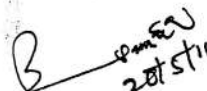
Name of the Nodal Institution/
Department of Organisation : TEZPUR UNIVERSITY

Name of the Project/Scheme : "Development of ZnO nanorods for luminescent
device applications "

Certified that out of Rs. 1,10,789/- of grant-in-aid sanctioned during the financial year 2010-11 in favour of Tezpur University on the subject UFUP-44314 project IUAC (NSC), New Delhi as per sanction order no. IUAC/XIII.7/UFR-44314/666 dated 25th June 2010 and Rs. 211/- unspent balance of the previous year, a sum of Rs. 1,03,333/- has been utilized during the current financial year 2010-11 on the project/scheme and the unspent balance of Rs.7,667/- till 31.03.2011 is being returned owing to completion of the project.


Project Investigator

Development of ZnO


Registrar

Expenditure statement of IUAC UFUP-44314 project

Title: "Development of ZnO nanorods for luminescent device applications "

Sl. No.	Heads of account	Received grant (Rs.)	Expenditure during 2010-11 (Rs.)	Unspent Balance (Rs.)
1.	Contingency	14,789.00 (with a balance of Rs. 211.00 of previous year)	13,733.00	1,267.00
2.	Fellowships	96,000.00	89,600.00	6,400.00
			1,03,333.00	7,667.00

Unspent balance amount: Rupees Seven thousand six hundred and sixty seven only


Registrar
Tezpur University


Finance Officer
Tezpur University