

# Photoluminescence and ultraviolet photoresponse in ZnO nanophosphors prepared by thermal decomposition of zinc acetate

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## ABSTRACT

In the present work, simple, low-cost, and direct route is used for the UV- photodetection and photoluminescent zinc-oxide nanoparticles (NPs) by decomposing zinc acetate in air at 400 °C for 12 hrs. The X-ray diffraction (XRD) result indicates that the synthesized ZnO NPs is pure and single crystalline structure with wurtzite type. The crystallite size of the ZnO nanoparticles is in the range of 20–50 nm and average crystallite size of synthesized nanoparticles is found to be ~33 nm. The synthesized ZnO NPs exhibits several photoluminescence peaks centered at 396 nm, 418 nm, 441 nm, 481 nm and 522 nm. The time-resolved rise and decay of photocurrent spectrum shows initial significant increase in photocurrent and, subsequently falls gradually under UV-illumination. The photocurrent abruptly falls when illumination is turned off. The variation of photo and dark-current with applied field is found to follow power law i.e  $I \propto V$ . At low voltage the behavior is sub-linear which becomes super-linear at high voltages. The ZnO NPs is found to have double traps of 0.59 eV and 0.67 eV. Copyright © 2011 VBRI press.

**Keywords:** Photoconductivity, XRD, ZnO, nanophosphors.



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## Introduction

Recently, zinc oxide (ZnO) has attracted tremendous interest for scientific community because of their wide band gap (~ 3.37eV) and high exciton binding energy (~ 60 meV) at room temperature. It has been reported to display good photoconductivity and high transparency in the visible region and used as transparent electrodes for solar cells [1]. Number of synthesis methods has been used to synthesize ZnO nanoparticles (NPs) such as chemical vapor deposition [2], sol-gel method [3], spray pyrolysis [4], co-precipitation method [5] and hydrothermal method [6]. Thermal decomposition of Zn(AC)<sub>2</sub>·2H<sub>2</sub>O have been studied [7-8] previously for their emission and optical properties. In the present work, ZnO NPs have been prepared by thermal decomposition method. This is a simple, low-cost and direct mass-scale production method.

In this work, photoluminescence and photoconductivity properties of ZnO NPs have been investigated. Generally, ZnO NPs are usually n-type semiconductor due to oxygen vacancies and other native defects such as interstitial Zn ions which act as donors in ZnO lattice. These native defects are believed to be responsible for visible photoluminescence. Photoconductivity in NPs is also governed by surface related processes such as adsorption and desorption of chemisorbed oxygen at the surface of materials because of large surface to volume ratio. Bulk related process of photogeneration of carriers governing photoconductivity is however considered to be faster than surface related process.

## Experimental

### Sample preparation

The zinc acetate dihydrate (Zn (CH<sub>3</sub>COOH)<sub>2</sub> · 2H<sub>2</sub>O) (99%, purity) from E. Merk Ltd. Mumbai, 400018, India was used as a precursor to prepare ZnO NPs. In this process, 1 gm of Zn (CH<sub>3</sub>COOH)<sub>2</sub> · 2H<sub>2</sub>O was put into the crucible and calcined at 400 °C for 12 hr in muffle furnace in air. Finally, ZnO NPs powder was obtained.

### Instrumentation

The crystal structure of ZnO nanoparticles were characterized by X-ray diffraction (XRD), Rigaku D/MAX-2200H/PC, Cu K $\alpha$  radiation. Photoluminescence spectrum was studied with Perkin Elmer LS-55 fluorescence spectrometer. The photo and dark conductivity of ZnO NPs have been measured using thick film of powder without any binder. In photoconductivity measurements, a cell type device is used which was formed by putting a thick layer of powdered samples in between two Cu electrodes etched on a Cu plate, printed circuit board (PCB), having a spacing of 1 mm. In this cell type device, the direction of illumination is normal to field across the electrodes. The cell was mounted in a dark chamber with a slit. The dark chamber consists of a hole on its upper surface and cell was kept below the hole. The upper surface of the cell was illuminated using 300 W mercury lamp of 365 nm light. A stabilized dc field (50 V/cm to 500 V/cm) was applied across the cell to which a dc nano-ammeter for the measurement of current and RISH Multi 15S with adapter RISH Multi SI 232 were connected in series. Before measuring photoconductivity of the sample, the cell is first kept in dark till it attains equilibrium.

## Results and discussion

### Structural study

**Fig. 1** shows the X-ray diffraction (XRD) pattern of ZnO NPs synthesized by thermal decomposition method. X-ray diffraction pattern of ZnO nanoparticles exhibit that ZnO has hexagonal wurtzite structure and the peaks could be indexed according to standard JCPDS data [card No. 75-0576] with  $a = 0.325$  nm and  $c = 0.521$  nm [8]. Furthermore, it can be seen that the diffraction peaks have broadening which implies that the ZnO nanoparticles have nanocrystalline nature. The crystallite size has been estimated using the Scherer's formula as shown in equation (1):

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad \text{----- (1)}$$

where  $D$  is the grain size,  $\beta$  is full width at half maximum [FWHM] in radians of XRD pattern,  $\lambda$  is the X-ray wavelength and  $\theta$  is the Bragg diffraction angle of the XRD peak. The calculated grain size of synthesized nanoparticles is found to be 20-50 nm range and their average size is ~33 nm. No other peak of impurities such as Zn(OH)<sub>2</sub> is observed.

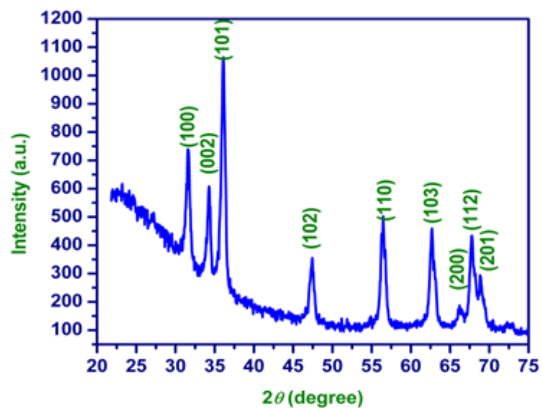


Fig. 1. XRD pattern of ZnO NPs synthesized by thermal decomposition method.

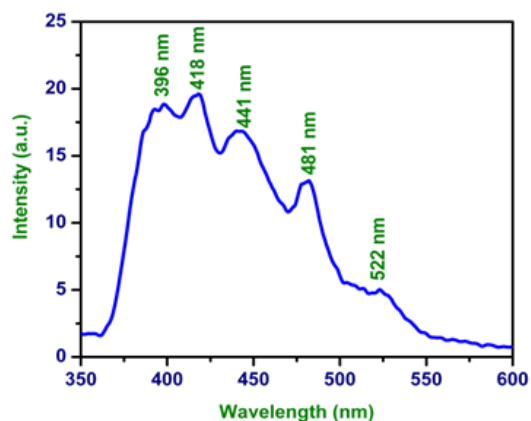


Fig. 2. Photoluminescence spectrum of ZnO NPs synthesized by thermal decomposition method.

#### Photoluminescence study

Fig. 2 shows photoluminescence spectrum of ZnO NPs synthesized by thermal decomposition method at excitation wavelength of 325 nm. Generally, visible emission in ZnO is due to different intrinsic defects such as oxygen vacancies ( $V_o$ ), zinc vacancies ( $V_{Zn}$ ), oxygen interstitials ( $O_i$ ), zinc interstitials ( $Zn_i$ ) and oxygen antisites ( $O_{Zn}$ ). In PL spectrum, several emission bands, including band edge emission at 396 nm ( $\sim 3.12$  eV) and violet emission at 418 nm ( $\sim 2.96$  eV), blue emission at 441 nm ( $\sim 2.81$  eV), blue-green emission 481 nm ( $\sim 2.56$  eV) and green emission 522 nm ( $\sim 2.37$  eV) were observed. Band edge emission centered at around  $\sim 396$  nm should be attributed to the recombination of excitons [9]. The origin of violet emission centered at 2.96 eV ( $\sim 418$  nm) is ascribed to an electron transition from a shallow donor level of neutral  $Zn_i$  to the top level of the valence band [10]. A blue emission centered at  $\sim 2.56$  eV (481 nm) is due to a radiative transition of an electron from the shallow donor level of  $Zn_i$  to an acceptor level of neutral  $V_{Zn}$  [11]. Another blue emission was reported to appear at around 2.81 eV (441 nm) [12]. This emission may be related to surface defects of ZnO nanostructure or may be due to singly ionized  $V_{Zn}^-$ ,

although the detailed mechanism for blue emission at 441 nm has been not clarified. The green emission 522 nm ( $\sim 2.37$  eV) are attributed to radiative transition from conduction band to the edge of the acceptor levels of  $O_{Zn}$  caused by oxygen antisites ( $O_{Zn}$ ) [13].

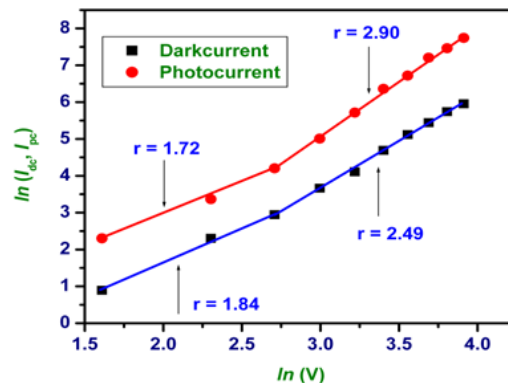


Fig. 3. Voltage dependence of photocurrent and dark-current on logarithmic scale as a function of applied voltage for ZnO NPs.

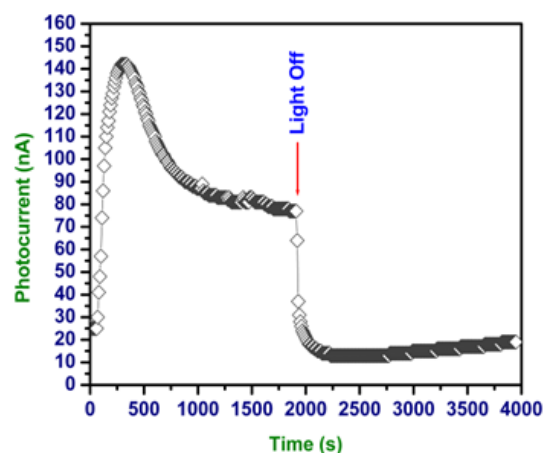


Fig. 4. Time-resolved growth and decay photocurrent spectrum for ZnO NPs under UV (365 nm) light illumination.

#### Photoconductivity study

Effect of field: Fig. 3 shows current-voltage characteristics of ZnO NPs under intensity of illumination and in dark on a logarithmic ( $\ln$ - $\ln$ ) scale. The  $\ln(I)$  vs  $\ln(V)$  curves are straight line having different slopes with respect to varying voltage according to power law,  $I \propto V^r$ , where ' $r$ ' represents slope of different straight line segments and different for lower and higher voltages of the curves, increases with increasing voltage. The dark current ( $I_{dc}$ ) as well as photocurrent ( $I_{pc}$ ) varies super-linearly at lower and upper voltage range. The super-linear ( $r > 2$ ) variation may be attributed to flow of trap limited as well as space charge limited current inside the material [6]. The current at higher voltages arise from a space charge of excess carriers injected from one of electrodes. This mechanism is known

as space charge limited current. If the materials has traps, then dark current will also be determined by traps referred to as trap limited space charge limited current [14, 15].

Time-resolved growth and decay photocurrent: **Fig. 4** shows growth and decay of photocurrent spectrum of ZnO NPs under UV illumination with fixed photo-flux and bias voltage (2500 lux, 20V). ZnO NPs exhibit fast rise in photocurrent under UV illumination and rapid decay in photocurrent when the light is turned off. In this process, oxygen molecules in the grain boundaries contribute to the photoconduction. The fast rise and decay in photocurrent suggesting that photo-response under UV illumination is mainly due to the generation of photocarriers and their radiative and non-radiative recombination through local recombination centers present inside the materials [16, 17]. In growth and decay photocurrent spectrum, the trap depths are calculated from decay portion of spectrum into the possible number of exponentials that governed by exponential law of the current amplitude which can be represented by the equation  $I = I_0 \exp(-pt)$ , according to Bube model [15] where  $I_0$  is the current at the time when light is switched off,  $I$  is photocurrent at any instant of time for growth and decay function and the  $p = S \exp(-E/kT)$ , probability of escape of an electron from trap per second. The trap depth ( $E$ ) for different exponentials can be calculated by using following equation (2):

$$E = kT \left[ \log_e S - \log_e \frac{I_0}{I} \right] \dots\dots\dots (2)$$

where  $E$  denotes trap depth,  $k$  is Boltzman constant ( $1.381 \times 10^{-23}$  J/K),  $T$  is absolute temperature and  $S$  is the frequency factor [7, 15] of the order of  $10^9$  at room temperature. The ZnO NPs is found to have double traps of 0.59 eV and 0.67 eV.

## Conclusion

Present investigation demonstrates photoluminescence and photoconductivity of ZnO NPs. ZnO NPs with particle size 20-50 nm and hexagonal wurtzite structure are synthesized by thermal decomposition method. The photoluminescence spectrum exhibits broad visible emission whereas photoconductivity shows fast growth and decay of photocurrent under UV illumination which is due to the fast generation and recombination of photocarriers. Voltage dependence photocurrent and dark-current follows power law. The trap depth is found to be 0.59 eV and 0.67 eV. The present work suggests promising applications in optoelectronics devices, such as switches, solar cells, photoconductor and sensors.

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