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**Der Pharma Chemica, 2013, 5(3):265-270**
*(http://derpharmachemica.com/archive.html)*

**ISSN 0975-413X**
**CODEN (USA): PCHHAX**

# Facile synthesis of nano-sized ZnO by direct precipitation method

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## ABSTRACT

*In this contribution we are presenting a simple precipitation method to synthesize zinc oxide (ZnO) nanoparticles using zinc nitrate and urea in aqueous solution. The obtained precipitated compound was calcined and structurally characterized by Powder X-ray diffraction (XRD), Thermogravimetric analysis (TGA), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR) and UV-Vis spectroscopic techniques. The powder X-ray data indicates that the calcined compound exhibits hexagonal (Wurtzite) structure with space group of P63mc (No. 186). The thermal behavior of as-prepared compound was examined and it indicates that there is no further mass loss above 450 °C. Scanning electron micrographs show uniform spherical like morphology of ZnO. The TEM results reveal that the particle sizes were in the order of 30–50 nm and the average particle size is around 35 nm. The FT-IR result shows the existence of $OH^-$, $NO_2^-$, CO, $CO_2$ groups in uncalcined sample. The band gap was higher for synthesized ZnO particles than their bulk counterparts. The results indicate that urea is an attractive material that can be used as precipitation agent for preparing ZnO.*

**Key words**: Zinc oxide, XRD, Nanostructure, Precipitation, Urea

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## INTRODUCTION

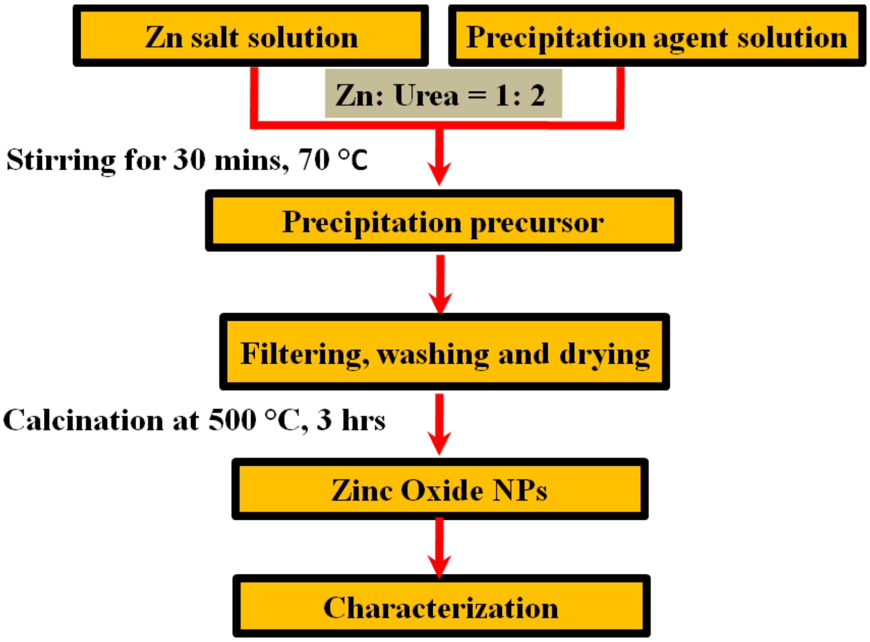
ZnO is a unique and key inorganic material that has been attracted an extensive research due to its characteristic features and novel applications in wide areas of science and technology. It has multiple properties like semiconducting, piezoelectric, pyroelectric, catalysis, optoelectronics and powder metallurgy [1]. In addition, the optical properties of ZnO nanoparticles play a very important role in optoelectronic, catalytic and photochemical properties [2]. Recently, the material scientists all over the world have used different methods such as chemical vapor deposition (CVD), electro deposition (ED), hydrothermal, electrochemical, solution combustion, sol–gel, vapor–liquid–solid process, pulsed laser deposition and precipitation method for the preparation of ZnO powder and thin films with varied morphology and controlled growth which was stimulated because of strong dependency of its properties on size, shape and ratio of orientation [3-11].

ZnO is an intrinsic n-type semiconductor material that has been hexagonal structure with lattice parameters of a=b=0.3250 nm and c=0.5207 nm [12, 13]. Also, it has wide band gap of 3.37 eV gives this material an upper hand compared to others [14, 15]. Due to this special criteria, the ZnO has an edge for applications of semiconductor including transparent electronics, ultraviolet (UV) light emitters, piezoelectric device, chemical gas sensor, transistors, solar cells, catalysts and spin electronics [16-19]. Among all methods, precipitation and sol-gel technique provides suitable control of nucleation, ageing and growth of particles in solution. The direct precipitation is also one of the simple and cost effective method for bulk production of materials [20]. In this method, particle growth owes to interact between different aqueous solutions and therefore very small particles are formed. Tiny size particles with lower solubility product dissolve and re-precipitate on the surface of larger particles in solution; consequently agglomeration takes place in solution as the particles clog together to minimize surface energy [21]. In this paper, a simple and cost effective direct precipitation method was used to synthesize ZnO nanoparticles using urea as a precipitating agent. The precipitating agent will help to control particle size and dispersion in the solution and also expansion during calcinations.

## MATERIALS AND METHODS

### Starting Materials and Synthesis of Zinc Oxide Nanoparticles

Zinc nitrate ($Zn(NO_3)_2.6H_2O$) and urea ($CO(NH_2)_2$) were purchased from Fisher scientific, Germany and used without further purification. Double distilled water was used to prepare precursor solution. ZnO nanoparticles were synthesized by direct precipitation method using zinc nitrate and urea as precursors. In a typical synthesis, 0.5 M (4.735 gm) zinc nitrate ($Zn(NO_3)_2.6H_2O$) was dissolved in 50 ml of distilled water and it was kept under constant stirring for 30 min to complete dissolution in the same way 1M (3.002 gm) urea was also prepared in 50 ml of distilled water with constant stirring for 30 min [22]. Urea solution was acted as precipitating agent and added drop-wise into zinc nitrate solution with vigorous stirring at 70 °C for 2 hr to allow complete growth of nanoparticles. The final precipitating solution was turned to whitish cloudy. The white precursor product was centrifuged at 8000 rpm for 10 min and washed with distilled water to remove any impurities or possible absorbed ions. The obtained product was calcined at 500 °C in air atmosphere for 3 hr using muffle furnace. The chemical reactions occurred in this process is shown in Scheme 1.



**Scheme 1: Chemical reactions to synthesize zinc oxide nanostructure**

### Structural Characterization

The as-synthesized ZnO was subjected to thermogravimetric analysis (TGA) and it was performed in the temperature range 30–800 °C at a heating rate of 5 °C/min under nitrogen atmosphere using a SDTA-85 1e from Mettler Toledo. To determine the crystal phase identification and estimate the crystallite size, powder X-ray diffraction (XRD) patterns were recorded for synthesized samples using Bruker - D8 Advance Powder X-ray diffractometer with Cu $K_\alpha$ radiation, ($\lambda_{Cu}$ = 1.5418 Å) working at 30 mA and 40 kV. To measure the particle size and morphology of ZnO nanoparticles, transmission electron microscopy (TEM), LEO-Libra 120 and scanning electron microscopy (SEM), Zeiss Supra 35VP were used. Fourier transform infrared spectra (FT-IR) were obtained on KBr pellets at ambient temperature using a Bruker FT-IR spectrometer (TENSOR 27). FT-IR spectroscopy in the transmission mode gives qualitative information about the way in which the adsorbed molecules are bonded to the surfaces as well as the structural information of solids. The UV–Vis absorption spectra were recorded by Mettler Toledo spectrophotometer. The nanoparticles were dispersed in ethanol and were sonicated prior to UV–Vis measurement for uniform dispersion.

## RESULTS AND DISCUSSION

### Powder X-ray diffraction (XRD) studies

The powder XRD patterns for the synthesized compound (calcined at 500 °C for 3 hr) obtained from direct precipitation of 0.5 M $Zn(NO_3)_2.6H_2O$ and 1 M $CO(NH_2)_2$ were shown in Fig. 1. The XRD peaks in the wide angle range of 2θ from 10° to 90° with $CuK_\alpha$ radiation. It can be seen from Fig. 1, the powder XRD patterns were indexed to pure hexagonal structure with lattice parameter of $a$ = 3.25 Å and $c$ = 5.2 Å and its space group: $P6_3mc$. The peaks appeared at 2θ range of 31.76°, 34.42°, 36.25°, 47.53°, 56.59°, 62.86°, 66.37°, 67.94°, 69.08°, 72.56°, 76.95°, 81.38° and 89.61° values corresponds to pure ZnO. They are matching with the standard JCPDS card no. 01-79-0206, indicating that the ZnO particles are crystalline structure. The average crystallite sizes were calculated by using the Debye - Scherrer equation:

$$D = \frac{K\lambda}{\beta\cos\theta} \qquad (1)$$

where D is the diameter of the crystallite size, K is the shape factor (the typical value is 0.9) λ is the wavelength of incident beam, β is the broadening of the diffraction line measured in radians at half of its maximum intensity (FWHM) and θ is the Bragg's angle [23]. From the XRD data, the average crystallite sizes were found to be 35 nm. No other peaks were observed in calcined compound, which indicates the formation of a pure hexagonal structure of ZnO.

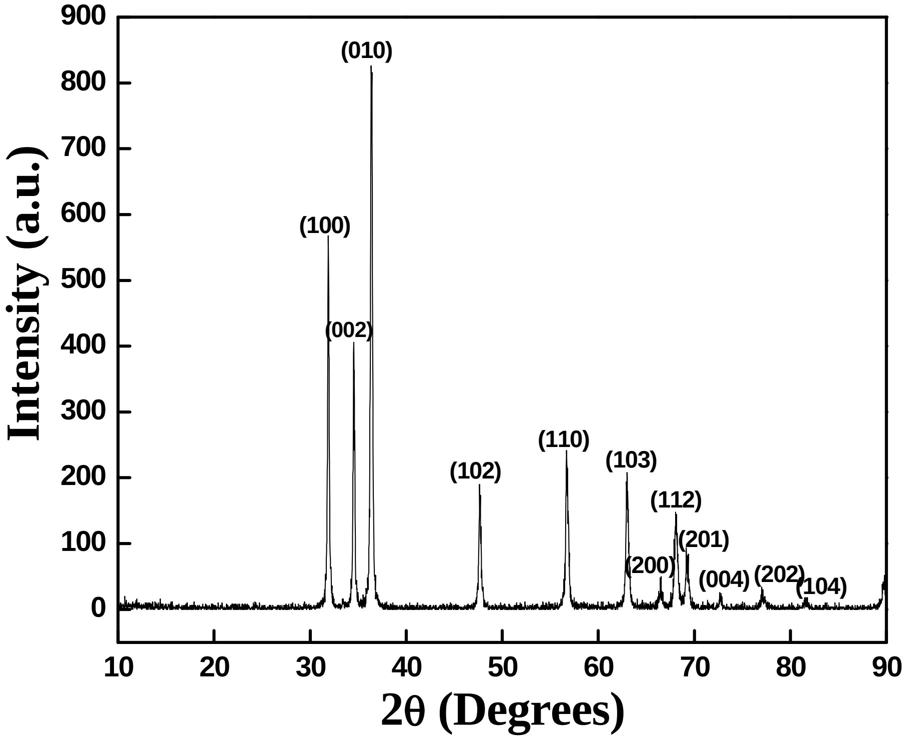


**Fig 1. X-ray diffraction patterns of zinc oxide nanoparticles**

### Thermogravimetric (TGA) analysis

To know the decomposition and phase formation that occurs during heat treatment of the as-prepared compound, the thermal analysis was carried out in the temperature range of 30°C–800°C. TGA of an as-prepared compound was performed by heating it in an alumina crucible in air at 5°C/min. Figure 2 shows the thermal behavior (TGA) of as-prepared compound obtained from direct precipitation of 0.5 M $Zn(NO_3)_2.6H_2O$ and 1 M $CO(NH_2)_2$. It can be seen that there are two pronounced mass loss steps in the temperature ranges 30°C–150°C and 160°C–450°C, respectively, in TG curve. The first weight loss is mainly attributed to the evaporation of surface adsorbed water, whereas the second one might be ascribed to the volatilization and combustion of organic species in sample. The first mass loss step was gradual and in the range of 30°C–150°C. The mass loss was 18.9%, and this loss of mass is attributed to the removal of surface adsorbed water from aqueous urea and nitrate solution. The second step was main mass loss occurred at 160°C –450°C, and the weight loss was 32.6% which is due to the volatilization and combustible organic species present in the sample. There is no associated signal with these latter thermal events in the TGA curve confirming the crystallization and phase transition events of ZnO nanoparticles.

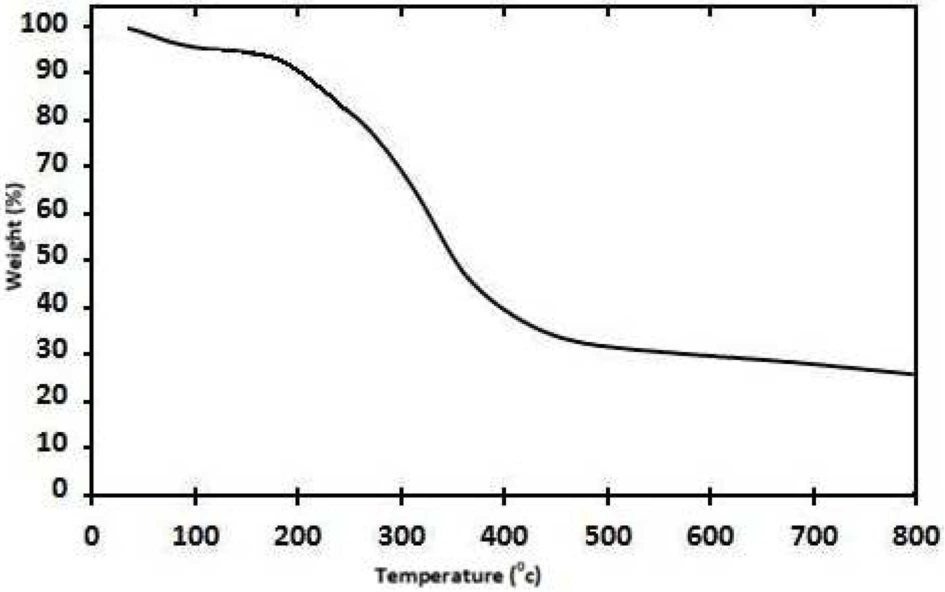


**Fig 2. TGA curve of precipitation precursor**

## SEM and TEM analysis

Electron photomicrographs of ZnO nanoparticles obtained from direct precipitation of 0.5 M $Zn(NO_3)_2.6H_2O$ and 1 M $CO(NH_2)_2$ calcined at 500 °C for 3 hr are shown in Fig. 3. Figure 3(a) reveals the SEM images of ZnO nanoparticles and we observed the particles were well defined and small spherical shaped with agglomerated particles. The TEM images of ZnO nanoparticles obtained from direct precipitation of 0.5 M $Zn(NO_3)_2.6H_2O$ and 1 M $CO(NH_2)_2$ calcined at 500 °C for 3 hr are shown in Fig. 3(b). After the heat treatment at 500 °C for 3 hr, the ZnO particles were found in the range of 30–50 nm. It can be observed that ZnO nanoparticles mainly present granules with small spherical shape and are well crystallized.

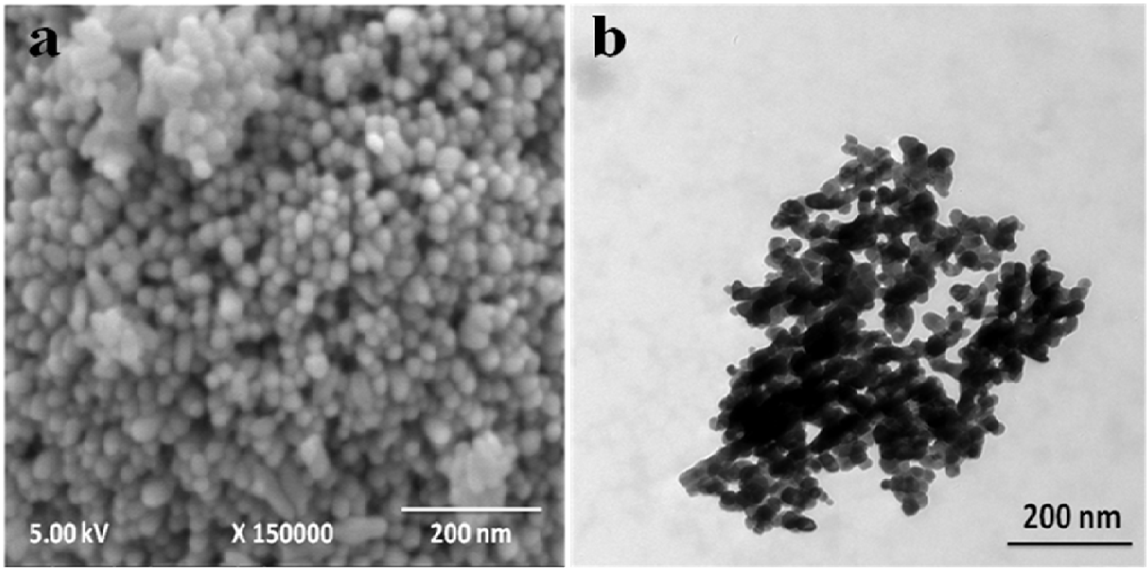


**Fig 3. Electron photomicrographs of ZnO nanoparticles (a) SEM image and (b) TEM image**

## FT-IR Spectroscopy

Infrared spectroscopy was used to detect the presence of functional groups adsorbed on the surface of synthesized nanoparticles during precipitation process. Figure 4 represents the FT-IR spectra of ZnO powder obtained 0.5 M $Zn(NO_3)_2.6H_2O$ and 1 M $CO(NH_2)_2$ calcined at 500 °C for 3 hr. Figure 4 indicates that the absorption peak in the range of 3200–3600 $cm^{-1}$ was observed. This was centered at 3438 $cm^{-1}$ corresponds to the stretching vibration of intermolecular hydrogen bond (O–H) existing between the adsorbed water molecules and indicates the higher amount of hydroxyl group. The results were well matched with the observation done by Xianxi et al. [24]. The peaks at 1389 and 1633 $cm^{-1}$ are attached to $ZnCO_3$ and bending vibrations of $Zn(OH)_2$, and the absorption band in 600–

1100 cm$^{-1}$ is due to the lattice vibration of $CO_3^{2-}$. It is interesting to note the two weak bands at 2930 and 2856 cm$^{-1}$ in calcined compound corresponding to the C–H stretching modes of urea carbon chain, which indicates that its molecules were present on the surface of ZnO nanoparticles. The band near at 2346 cm$^{-1}$ confirms the presence of bending vibrations of the intercalated O=C=O species produced by the urea decomposition in the initial process of preparation. The weak band at 692 and 887 cm$^{-1}$ appearing in IR spectrum of calcined (500 °C) compound indicates the presence of stretching and bending vibrations of the intercalated C–O species. The characteristic peak around 532 cm$^{-1}$ becomes stronger, indicating the formation of stretching mode of ZnO. This indicates the presence of ZnO nanoparticles in calcined compounds.

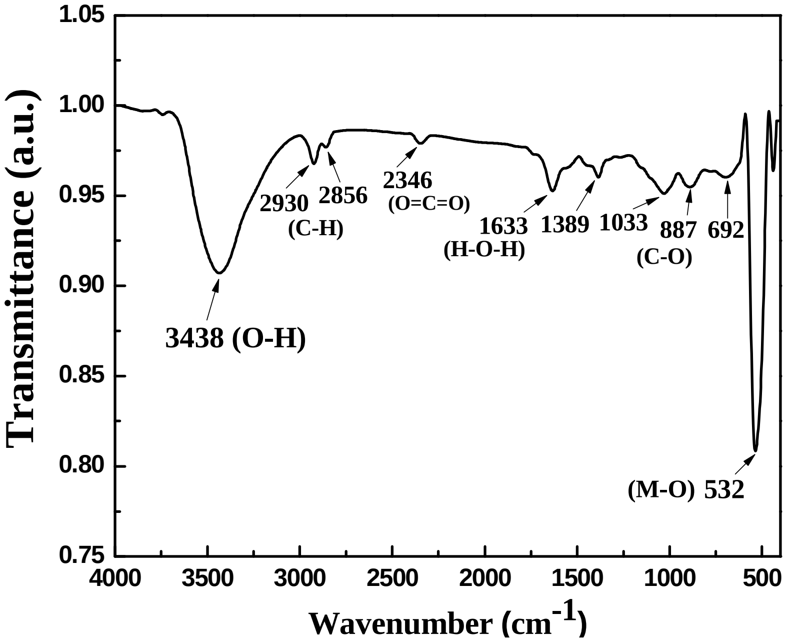


**Fig 4. FT-IR spectra of ZnO obtained from 0.5 M $Zn(NO_3)_2.6H_2O$ and 1 M $CO(NH_2)_2$ calcined at 500 °C for 3 hr**

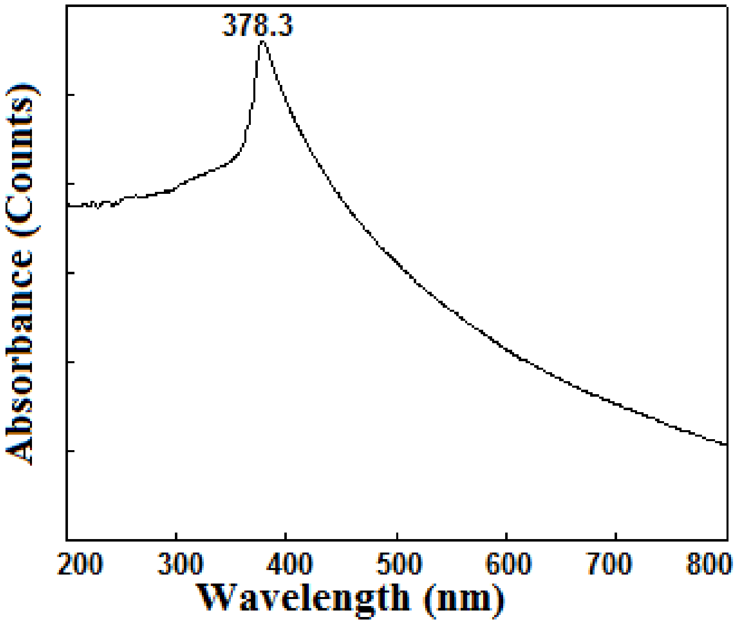


**Fig 5. UV–Vis spectra of ZnO obtained from 0.5 M $Zn(NO_3)_2.6H_2O$ and 1 M $CO(NH_2)_2$ calcined at 500 °C for 3 hr**

### UV–Vis spectroscopy

The UV–Vis spectra of ZnO nanoparticles obtained from 0.5 M $Zn(NO_3)_2.6H_2O$ and 1 M $CO(NH_2)_2$ and calcined at 500 °C for 3 hr were shown in Fig. 5. For recording UV–Vis spectra, the sample of ZnO solution was prepared by ultrasonically dispersing them in absolute ethanol. The absorption peak in Fig. 5 correspond to ZnO sample calcined at a temperature of 500 °C showing the strong absorption in the wavelength of 378.3 nm. This can be assigned to the intrinsic band gap absorption of ZnO due to the electron transitions from the valence band to the conduction band

[6]. The band gap (*Eg*) of ZnO nanoparticles was calculated by using the formula $Eg=hc/\lambda$ [25], where $h$ = Planck's constant, $c$ = velocity of light and $\lambda$ = wavelength. The corresponding band gap was found to be 3.27 eV. Further, the XRD and TEM results suggest that the ZnO particles are in the range of 30–50 nm. The present precipitation method for generating ZnO nanoparticles is in the blue region compared to the bulk ZnO (3.37 eV).

## CONCLUSION

In the present work, the nanosized ZnO particles were successfully generated by direct precipitation method using zinc nitrate as zinc source and urea as precipitating agent in aqueous solution. In XRD analysis, the size range of the generated ZnO powder was approximately 30–50 nm. TGA revealed that the sample contains $NO^-_2$, CO, $CO_2$, and $H_2O$. The SEM analysis shows that the particles morphology was spherical structure. The TEM images confirmed the small spherical shape of ZnO nanoparticles and that they are well crystallized in the nanosize of 30–50 on nanometer scale. The FT-IR spectrum shows the existence of $OH^-$, $CO_2$, $NO^-_2$ and CO groups in uncalcined sample. The band gap was lower for synthesized ZnO nanoparticles than their bulk counterparts. Thus, the synthesis of ZnO nanoparticles by direct precipitation method is simple, fast and eco-friendly in nature.

**Acknowledgment**
The authors thank to Nanotechnology and Catalysis research center, University of Malaya, Malaysia for providing lab facilities and this work was supported by the University of Malaya through post doctoral fellowship (HIR grant) and also project grant no. PV-128/2012A.

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