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RESEARCH ARTICLE

Estimation of Particle Size and Band Gap of Zinc Oxide Nanoparticle Synthesized by Chemical Precipitation Method

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Abstract

Zinc oxide (ZnO) nanoparticles were synthesized by chemical precipitation method using 0.1M and 0.3M [$Zn(NO_3)_2.6H_2O$] and Na_2CO_3 solutions. The particle size and band gap of ZnO nanoparticles were estimated and effect of concentration on it was investigated. The synthesized nanoparticles were characterized by X-ray diffraction (XRD), Transmission electron microscopy (TEM), Energy dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FTIR) and UV-visible spectroscopy. The XRD result revealed that synthesized ZnO nanoparticles have pure hexagonal wurtzite structure and the particle size varies from 27.0 nm to 29.9 nm estimated by using Debye-Scherrer's equation. The TEM image also projected the average particle size in the range of 20-30 nm and selected area electron diffraction (SAED) further verified the formation of hexagonal wurtzite structure. The FTIR result showed a broad absorption band related to Zn-O vibration band. The UV-visible absorption showed a red shift in the absorption edge with increasing concentration of $Zn(NO_3)_2.6H_2O$ solution. The sizes and band gaps of ZnO nanoparticles increased and decreased, respectively with increasing concentration of $Zn(NO_3)_2.6H_2O$ solution from 0.1M to 0.3M.

Keywords: ZnO nanoparticles, chemical precipitation, UV-visible spectroscopy, XRD, EDX

Introduction

Zinc oxide is one of the most important binary (Group II-IV) semiconductor compounds with natural n-type electrical conductivity, a direct energy wide band gap of 3.37 eV at the room temperature, and a large exciton binding energy [1,2]. It has been considered as a significant semiconducting material for a variety of applications due to its good transparency, wide band gap, strong room temperature luminescence, high optoelectronic efficiencies, high exciton binding energy and dielectric constant [3,4]. ZnO is considered as a promising material for electronic and optoelectronic device applications [5]. ZnO with controlled n-type conductivity has many important applications as transparent contacts and high electron mobility transistors (HEMTS) [6].

The ZnO nanoparticles can be used as gas sensors, photocatalysts for the removal of waste water pollutants, semiconductors, UV-photodiodes, rubber, medical and dental materials, pigments and coatings, ceramics, concrete, antibacterial and bactericide, and composites [7]. ZnO usually exists in two forms of structures as hexagonal wurtzite and cubic zinc blende among which wurtzite is the most stable and common [8,9]. This crystal structure can only be observed under electron microscopic examination. The bonding in ZnO is largely ionic as in most of Group II-VI materials which explains its strong piezoelectricity [10]. All those properties of ZnO are dependent to its average size and band gaps. Here, we report the estimation of average particle size and band gaps of ZnO nanoparticles and show their variation on changing the concentration of source compound [$Zn(NO_3)_2.6H_2O$].

Materials and Methods

Synthesis of ZnO nanoparticles

ZnO nanoparticles can be synthesized through different methods like sol-gel method, hydrothermal method, mechanochemical method, solvothermal method, wet chemical method [11]. Simple chemical precipitation method is a widely used method for synthesis of zinc oxide which makes it possible to obtain a product with repeatable properties. This method is fast, spontaneous and limits the growth of the particles in the specified dimension [12].

ZnO nanoparticles were synthesized by chemical precipitation method using 0.1M and 0.3M $[Zn(NO_3)_2.6H_2O]$ and Na_2CO_3 solutions. For this, solutions of $[Zn(NO_3)_2.6H_2O]$ was taken in 1000 mL beaker and stirred it using magnetic stirrer for few minutes. The corresponding concentration of Na_2CO_3 solution was added to it drop-wise with vigorous stirring. The reaction between $Zn(NO_3)_2$ and Na_2CO_3 yields white precipitate of $ZnCO_3$.

$$Zn(NO_3)_2 + Na_2CO_3 \rightarrow ZnCO_3 + 2NaNO_3$$

The white precipitate of $ZnCO_3$ formed in the solution was collected by the filtration process by using Whatman no. 42 filter paper. Thus, obtained precipitate was washed with ethanol and dried at 100 ^oC for 6 hours, then was annealed in air at 600 ˚C for 2 hours to obtain ZnO nanoparticles.

$$ZnCO_3 \rightarrow ZnO + CO_2$$

Characterization

The crystallite size and structure of ZnO nanoparticles were determined by XRD (Rigaku ultima IV model) employing CuKα radiation (λ = 0.15406 nm). The average crystalline size of the ZnO nanoparticles was estimated from the most intense XRD diffraction peak using Debye Scherrer's relation.

$$\text{Average crystalline size} \quad (D) = \frac{0.9\,\lambda}{\beta \cos\theta}$$

Where, λ is the wave length of X-ray, β is full width at half maximum (FWHM) of the most intense XRD peak expressed in radians and θ is Bragg's diffraction angle [13]. The crystalline structure of ZnO nanoparticles was confirmed from XRD peaks.

The average particle size and crystalline structure of ZnO nanoparticle were also determined from TEM images (Technai G^2 20 electron Microscope) and SAED pattern. The assay of elemental compositions was estimated using EDX (Technai G^2 20 electron Microscope). The formation of ZnO nanoparticles was confirmed with the help of FTIR (IRTracer-100, SHIMADZU) analysis and band gaps were determined from UV-Visible spectra (ELICO SL 177 spectrophotometer).

Results and Discussion

XRD pattern

Figures 1(a) and 1(b) are the XRD patterns of ZnO nanoparticle synthesized from 0.1M and 0.3M $[Zn(NO_3)_2.6H_2O]$ solutions, respectively.

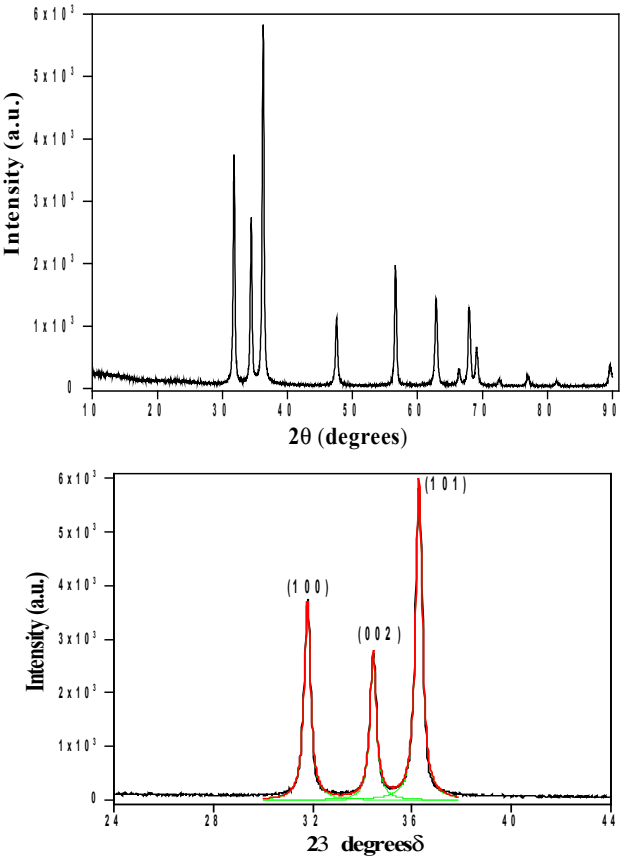

Figure 1(a): *XRD pattern of the ZnO nanoparticle synthesized using 0.1M $[Zn(NO_3)_2.6H_2O]$ and Na_2CO_3 and corresponding Lorentzian fitting*

Lorentzian profile was fitted to each sample to obtain FWHM value and the average particle size was calculated from Debye-Scherrer's equation as 27.0 nm and 29.9 nm synthesized from 0.1M and 0.3M precursors, respectively. The diffraction peaks at 2θ values of around 32^0, 34.5^0 and 36.5^0 correspond to (100), (002) and (101) crystalline planes of hexagonal structure (JCPDS card 36-1451) [5].

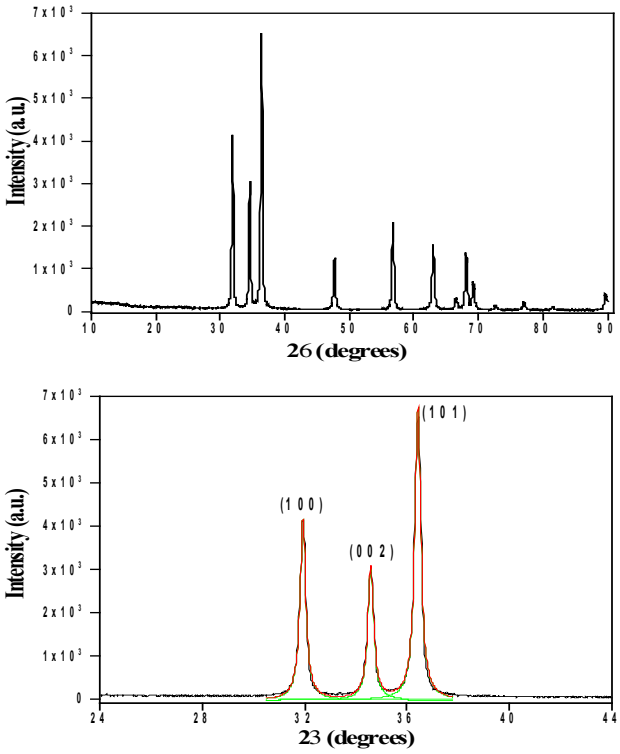

Figure 1(b): *XRD pattern of the zinc oxide nanoparticle synthesized using 0.3M [$Zn(NO_3)_2.6H_2O$] and Na_2CO_3 and corresponding Lorentzian fitting.*

TEM analysis

Figure 2 displays TEM micrographs of ZnO nanoparticles obtained from 0.1M solution of [$Zn(NO_3)_2.6H_2O$] and Na_2CO_3 showing spherical shape [8,14]. The average diameter was found to be in the range of (20-30) nm supported by the histogram and the Gaussian fitting spectra obtained from ImageJ software as shown in figures 3 (a) and 3(b), respectively.

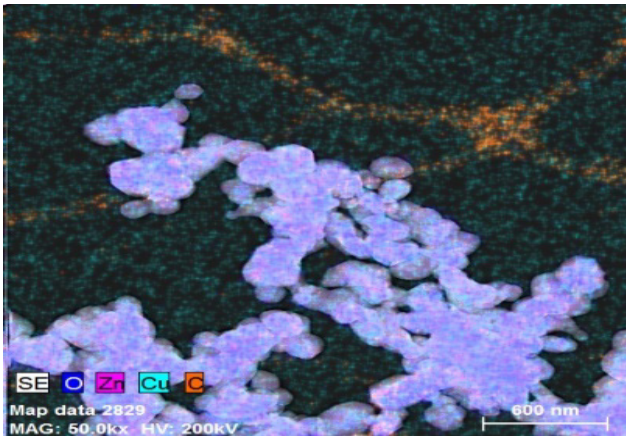

Figure 2: *TEM image of ZnO nanoparticles prepared from 0.1M solution of [$Zn(NO_3)_2.6H_2O$] and Na_2CO_3*

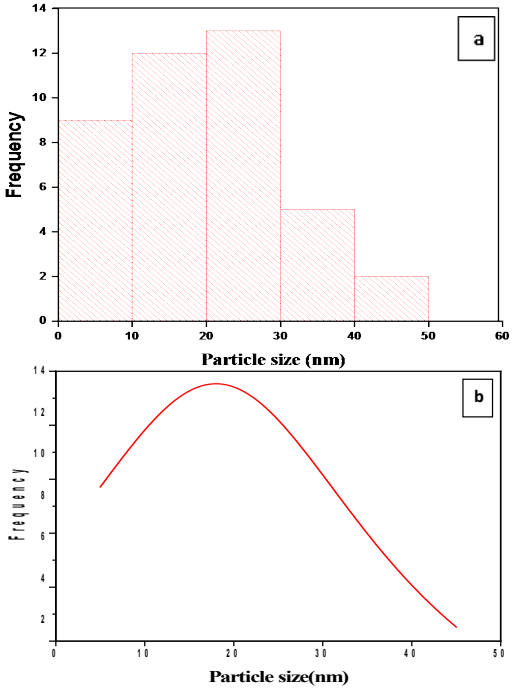

Figure 3: *(a) Histogram and (b) Gaussian fitting corresponding curve obtained from ImageJ software*

Elemental analysis

The TEM-EDX pattern is shown in figure 4 which confirms the synthesis of pure ZnO nanoparticles due to presence of only corresponding zinc and oxygen peaks.

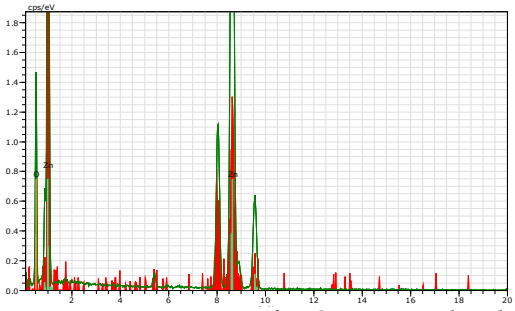

Figure 4: *TEM-EDX spectra of ZnO nanoparticles obtained from 0.1M solution of [$Zn(NO_3)_2.6H_2O$] and Na_2CO_3*

The average atomic percentage ratio of Zn:O atoms was found to be 63.3:36.7 as revealed in Table 1.

Table 1: *TEM-EDX result showing the composition of ZnO nanoparticle*

Elements	Atomic Weight %
Zinc	63.30
Oxygen	36.70
Total	100.00

SAED analysis

The selected area electron diffraction (SAED) pattern of the ZnO nanoparticles is illustrated in the figure 5.

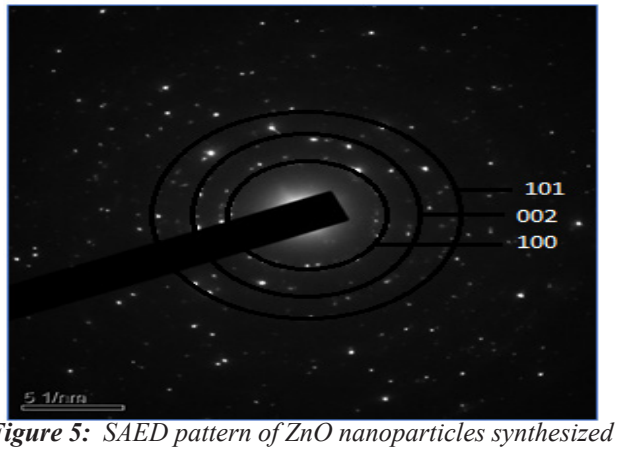

Figure 5: *SAED pattern of ZnO nanoparticles synthesized from 0.1M solutions of [$Zn(NO_3)_2.6H_2O$] solution and Na_2CO_3*

This pattern confirms the characteristic diffraction rings corresponding to (100), (002) and (101) indices of hexagonal wurtzite crystal structure of ZnO nanoparticles [3].

FTIR analysis

The FTIR spectra of ZnO nanoparticle synthesized using 0.1M [$Zn(NO_3)_2.6H_2O$] and Na_2CO_3 solutions is shown in figure 6. The spectrum showed the peak at 668 cm^{-1} is the infra-red band related to Zn-O vibration [5].

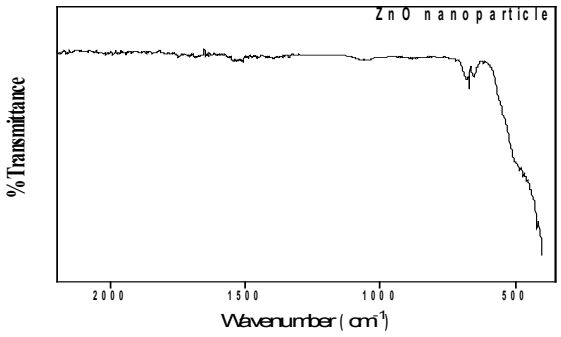

Figure 6: *FTIR spectra of ZnO nanoparticle prepared using 0.1M [$Zn(NO_3)_2.6H_2O$]*

UV-Visible analysis

Figure 7 (a) shows the UV-vis absorption spectra of the ZnO nanoparticles prepared using 0.1M and 0.3M solutions of [$Zn(NO_3)_2.6H_2O$]. A broad absorption peak was observed in each spectrum at (360-380) nm, which is the characteristic absorption band for the pure ZnO [15]. The spectra show the slight red shift from 371 nm to 379 nm as the concentration increased from 0.1M to 0.3M. The band gap was calculated by extrapolating the curve drawn between $(\alpha h\nu)^2$ vs $(h\nu)$ to the x-axis as shown in figure 7 (b)

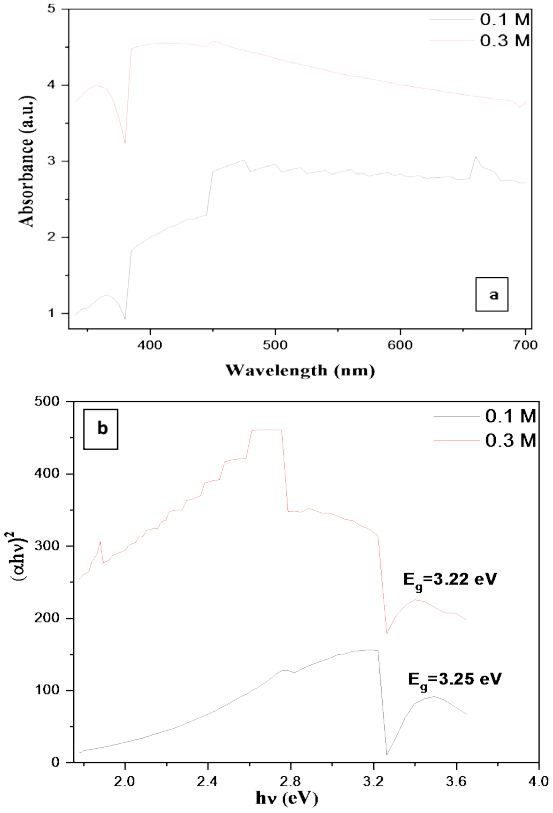

Figure 7: *(a) UV-visible absorption spectra of ZnO nanoparticles synthesized using 0.1M and 0.3M solution of [$Zn(NO_3)_2.6H_2O$], (b) Corresponding plot of (hν) vs $(\alpha h\mu)^2$*

and are found to be 3.25 eV and 3.22 eV for samples synthesized from 0.3M and 0.1M [$Zn(NO_3)_2.6H_2O$] solutions, respectively. These band gaps fall under the reported value of ZnO nanoparticles [16,17].

Conclusion

ZnO nanoparticles have been successfully synthesized using 0.1M and 0.3M solutions of [$Zn(NO_3)_2.6H_2O$] and Na_2CO_3 by chemical precipitation method. The average particle size of ZnO nanoparticle increases and the band gap decreases with increase in the concentration [$Zn(NO_3)_2.6H_2O$] solution. The average particle size, purity of the synthesized ZnO nanoparticles obtained from XRD, EDX, TEM, SAED, FTIR and UV-VIS spectroscopy are quite supportive with each other. XRD pattern confirmed the pure hexagonal wurtzite structure which is further verified from SAED pattern. The average particle size obtained were 27.0 nm and 29.9 nm determined from XRD pattern using Debye-Scherrer's equation whereas band gap calculated as 3.25 eV and 3.22 eV as precursor concentration increased from 0.1M to 0.3M, respectively. TEM image demonstrated the formation of spherical shaped ZnO nanoparticles

while EDX, FTIR and UV-VIS spectra confirmed the formation of pure ZnO nanoparticles.

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