Physics AUC, vol. 29, 61-67 (2019) PHYSICS AUC

# Green Synthesis of Ultrafine Zinc Oxide Nanoparticles and Determination of its Band-gap in view of Effective Mass Model

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## Abstract

Synthesis of non-toxic nanoparticles for use especially in various biomedical applications is a big challenge to the researchers. Green synthesis is a simple method to get rid of this problem A simple green approach has been followed and reported here to synthesize ultrafine ZnO nanoparticles. The synthesized nanoparticles exhibit high transparency in the visible region. The size of the nanoparticles was estimated from the UV-visible absorption spectrum and was calculated to be 4.7 nm. The band gap was also calculated to be 3.53 eV. This band gap enhancement compared to bulk ZnO occurred due to strong quantum confinement effect. The value of this band gap was found to be in agreement that obtained from the effective mass model for nanosystem.

**Keywords:** Nanoparticles; Green-synthesis; Absorption; Bandgap; Quantum-confinement

## Introduction

Compound semiconductor nanostructures are in the forefront of materials research because of their multifunctional properties leading to wide applications starting from nanoelectronics to biomedical devices and drug delivery. The band gap of these compound semiconductors can be tuned very easily. Most widely studied compound semiconductors are $TiO_2$, CuO, ZnO, ZnS, CdS, and CdSe [1-13]. The fundamental requirement for nanomaterials to be used in biological applications like antimicrobial activity, drug delivery is that the materials must not create any toxic effect within the body. $TiO_2$ has been found to be very effective in this context for use in biological applications [2, 3]. Besides, there are also reports of the biomedical applications of CdS, ZnS, CdSe nanoparticles [5-12]. Again, to control the targeted drug delivery optical and magnetic properties are very much essential. In this context ZnO is very promising than other compound semiconductors. ZnO is a direct band gap semiconductor of band gap energy of 3.4 eV. Thus, it exhibits UV photoluminescence under suitable excitation [14]. But due to presence of various crystal defects ($Zn^{2+}$, $V_O$, $Zn_i$, $O_{Zn}$) shallow levels are created leading to lower energy state transitions. This results in visible photoluminescence from ZnO nanostructures [15]. Thus, ZnO can be used not only in optoelectronics but also fluorescence based biomedical applications like targeted drug-delivery, cell imaging, MRI contrast imaging and many more. There are several reports on the synthesis of ZnO nanoparticles using various leaf extract. There is a report of synthesis of

ZnO nanoparticles using Laurus nobilis L. leaves aqueous extract [16]. Researchers have also used Solanum torvum (L), Azadirachta indica, insulin plant, *Hibiscus rosa-sinensis* for synthesis of nanoparticles to reduce the toxic effect of the nanoparticles [17-19]. However, there are not much report on the synthesis of ZnO nanoparticles using fruit extract. Here, in this paper, we report the synthesis of ZnO nanoparticles using apple extract followed by typical optical characterization towards biological applications.

## Experimental

### *Preparation of apple extract*

Fresh apple was purchased from the local market of Contai, East Midnapore. The apple was peeled and cut into small pieces. 20 g of the apple crush was taken in a beaker with 100 mL methanol and heated at 60°C for 30 min. The brown extract was then cooled down to room temperature and filtered. The filtered solution was then refrigerated for 24 hr for further use.

### *Preparation of ZnO nanoparticles*

We have followed a simple wet chemical method for the synthesis of ultrafine ZnO nanoparticles. The chemicals used here were of analytical grade (Merck, 99.99% pure) and used without further purification. To prepare 13 mM solution, Zinc acetate dihydrate of 2.95 g of was dissolved in 125 ml of the above extract at room temperature and stirred magnetically till all the precursor was dissolved. The temperature of the solution was then slowly raised to 60°C. In the next step, 0.03 M of NaOH was prepared by dissolving appropriate amount of sodium hydroxide in 65 ml of apple extract. Now, so prepared NaOH solution was drop-wise added to the zinc acetate solution. After mixing the stirring was continued further for 2 h. A brownish-white material was deposited at the bottom of the beaker. The precipitate was then filtered and then dried under filament bulb for further characterization.

### *Characterization of ZnO nanoparticles*

UV-visible absorption and transmission spectra were collected in Systonic UV-VIS spectrophotometer over the wavelength range 200-800 nm. The absorption data were taken by dispersing the synthesized nanoparticles in methanol.

## Results and discussions

Typical UV-visible absorption spectrum of the ZnO nanoparticles synthesized in apple extract is shown in Fig. 1. The material shows low absorbance in the visible region. The transmission spectrum is also shown in Fig. 2. It is just the opposite nature of the absorbance curve as obvious. The radius *(R)* of the ZnO nanoparticles (assuming monodispersed) can be calculated from the following relation [20]:

$$R(nm) = \frac{-0.3049 + \sqrt{-26.23012 + \dfrac{10240.72}{\lambda_o(nm)}}}{-6.3829 + \dfrac{2483.2}{\lambda_o(nm)}}$$

Here, $\lambda_o$ denotes the wavelength corresponding to the peak value of absorption which is 363 in our case. This yields the particle size $D = 2R = 4.7\ nm$.

Optical absorption and transmission properties depend on the nature of interaction of incident photons with the molecules of the material. This leads to the development of electric displacement vector $\boldsymbol{D}\ (\boldsymbol{r}, t)$ corresponding to the electric field $\boldsymbol{E}\ (\boldsymbol{r}, t)$ and are connected by the relation [21]:

$$\boldsymbol{D}\ (\boldsymbol{r}, t) = \iint \in (\boldsymbol{r}, t) \boldsymbol{E}\ (\boldsymbol{r}, t) d\boldsymbol{r} dt$$

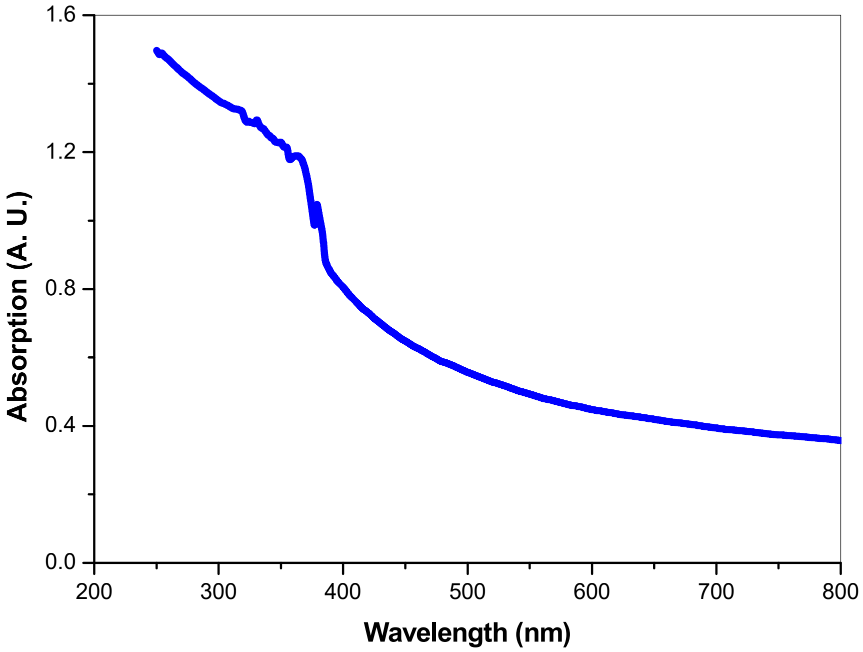


Figure 1: UV-visible absorption spectrum of synthesized ZnO nanoparticles

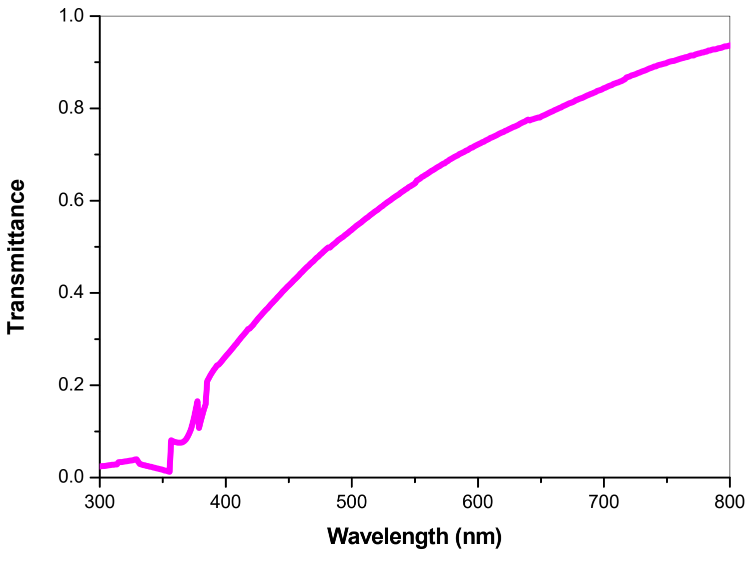


Figure 2: UV-visible transmission spectrum of synthesized ZnO nanoparticles

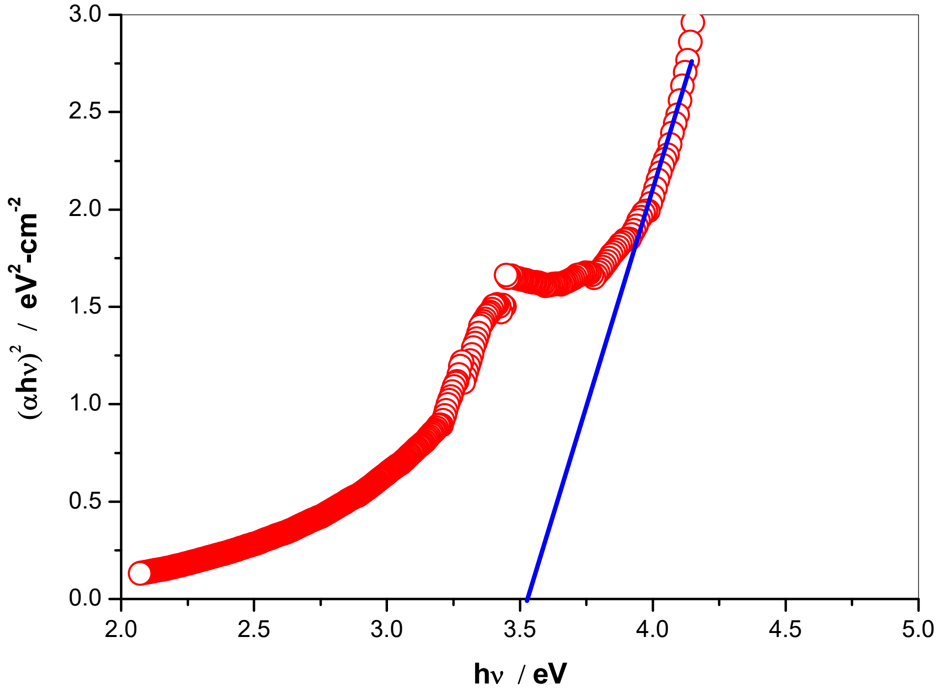


Figure 3: Tauc plot from UV-visible absorption spectrum to calculate band gap of synthesized ZnO nanoparticles.

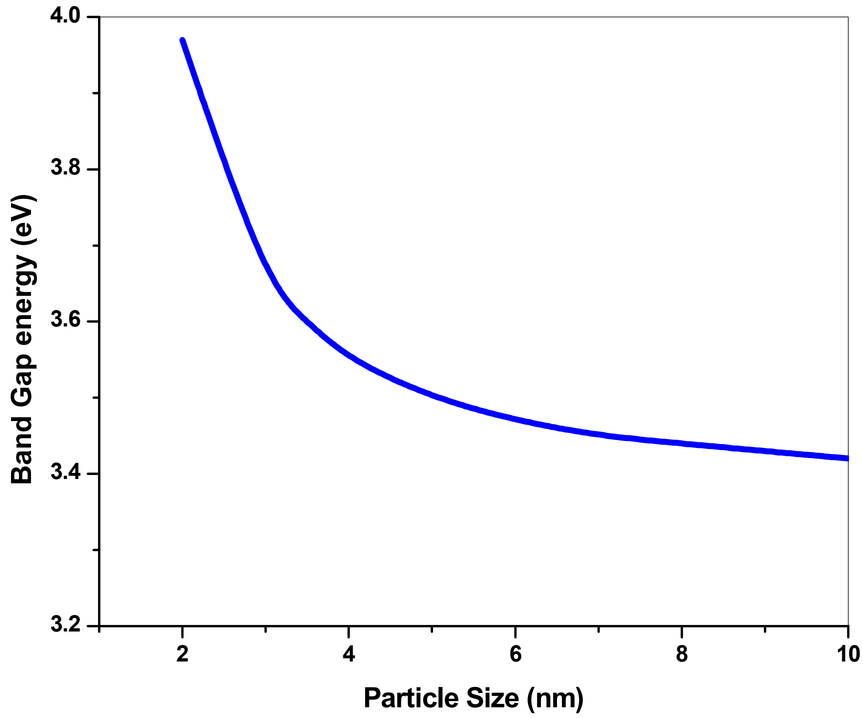


Figure 4: Variation of band gap energy with size of ZnO nanoparticles theoretically generated from effective mass model.

The inter-relation between the dielectric constant and conductivity can be obtained by solving the Maxwell's equations. The band gap of the material can be calculated from the absorption data by using Tauc's equation given by [22]:

$$\alpha h\nu = C\left(h\nu - E_g\right)^n$$

Where, C is a constant, α is the absorption coefficient and ν is the frequency of the incident radiation. The exponent assumes value ½ for direct band gap semiconductor as in our case. The plot of $(\alpha h\nu)^2$ against $h\nu$ is shown in Fig. 3. Now the intercept of the curve in high absorption region to $h\nu = 0$ line will give the band gap of the material. In our case the band gap of the synthesized ZnO nanoparticles was calculated to be 3.53 eV. This value is much higher than the bulk value of 3.4 eV. This band gap enhancement occurs due to strong quantum confinement of carriers withing the small dimension of the crystal. In nanocrystal the band gap depends on the size of the nanoparticles. Amongst various existing model effective mass model is widely accepted model to corelate the particle size and band gap under quantum confinement of electrons withing the narrow potential of quantum dots considering the Coulombic interaction. According to this model the band gap can be expressed by the equation [21, 23]-

$$E_g^{nano} = E_g^{bulk} + \frac{\hbar^2\pi^2}{2er^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) - \frac{1.8e^2}{4\pi\epsilon\epsilon_0 r}$$

Where, $E_g^{bulk}$ is the band gap energy of bulk system, $m_e$ and $m_h$ are the effective masses of electrons and holes within the material, $\varepsilon$ is the relative permittivity, $r$ is the radius of the nanoparticles. For ZnO nanoparticles, $E_g^{bulk} = 3.35\ eV, m_e = 0.24m_o, m_h = 0.45m_o$ and $\varepsilon = 3.7$ [23]. The term particle size here refers to the diameter of the nanoparticles. The variation of band gap with particle size using effective mass model is shown in Fig. 4. Using this curve, the band gap corresponding to a particle size of 4.7 nm is 3.51 eV. In our case we obtained the band gap 3.53 eV. Hence the obtained result is in accordance with the theoretical model.

## Conclusions

In conclusion, a simple environment friendly green approach has been followed to synthesized ultrafine ZnO nanoparticles. The particle size was 4.7 nm as calculated from the absorption spectrum. The band gap was also calculated to be 3.53 nm. This enhancement of band gap from the bulk ZnO is due to the strong quantum confinement effect of carriers within narrow potential well of the nanocrystal. The material exhibits high transparency in the visible region and hence can be used as transparent coating. This protocol being a green approach, the synthesized ZnO nanoparticles are expected to be non-toxic and can be used for various biological applications.

## Acknowledgements

The author sincerely acknowledges the instrumental facility provided by Prabhat Kumar College, Contai, India. The author also acknowledges UGC-DAE-CSR Kolkata for financial support to carry out this research work.

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