

Green synthesis of ZnO using citrus sinesis peel extract and its influence on morphology and optical properties

Srimathi Krishnaswamy¹, Veena Ragupathi¹, Puspamitra Panigrahi¹, SenthilKumar S² and Ganapathi Subramanian N*³

¹Centre for Clean Energy and Nano Convergence (CENCON), Hindustan Institute of Technology and Science (HITS), Padur, Kelambakkam, Chennai, India

²Advanced Materials Research Centre, Marutham Nagar Ext, Vadavalli, Coimbatore, India

³Quantum Functional Semiconductor Research Centre, Dongguk University-Seoul, Korea

Abstract

An eco-friendly green mediated synthesis of inorganic nano particle is a fast and growing needed research in the area of nano technology. This study reports the synthesis of Zinc oxide nano particle (ZnOp) using bio-solvent without the use of toxic chemicals. Optimization of synthesis condition for ZnOp via. Green route is carried out by modifying of bio solvent concentration. As synthesized ZnOp was analysed using X ray diffraction (XRD), Scanning electron microscopy (SEM) and UV-Visible spectroscopy. XRD confirmed hexagonal wurtzite structure and a reduction in the particle size of ZnO was observed for higher concentration of Bio-solvent. Enhancement of light absorption was observed for higher concentration of Bio-solvent.

Keywords: Green synthesis, Zinc oxide, nano particles, citrus sinesis

Introduction:

Transition metal oxides and semiconductors with dimensions in the nanometer realm have attracted considerable interest in many areas of chemistry, physics, material science, biotechnology and environmental technology [1].

In recent years, zinc oxide (ZnO) an interesting semiconductor have developed with tremendous scientific and technological interest, due to its unique properties like direct wide gap (3.37 eV, 387 nm, deep violet/borderline ultraviolet (UV)) and a large exciton-binding energy (60 meV). Due to its unique optical and electrical properties, it is regarded as a potential material in optoelectronic applications operating in the visible and near ultraviolet spectral regions. ZnO nanoparticles also find applications in many industrial areas such as solar cells, UV light-emitting devices, gas sensors, photocatalysts, pharmaceutical and cosmetic industries [2].

Furthermore, ZnO appears to strongly resist microorganisms [3] and some reports show considerable antibacterial activity of CaO, MgO and ZnO, which is attributed to the generation of reactive oxygen species on the surface of these oxides. The greatest advantage of ZnO is that it absorbs over a larger portion of the solar spectrum than TiO₂ [4].

To date, various methods have been adopted for the preparation of ZnO crystallites including sol-gel method, evaporative decomposition of solutions, gas-phase reaction, wet chemical synthesis, and

hydrothermal discharging-gas method[5]. However, in order to obtain ZnOnano-powders with appropriate chemical and optical properties for their intended applications, control of morphology, chemical composition, purity and particle size during synthesis are very important. Several studies have demonstrated that a Sol-gel has many advantages in obtaining highly crystallized nano-powders with a narrow grain size distribution, high purity and low calcination temperature.

Wide spread synthesis protocols used for nano particle often require the use of harsh organic solvents/surfactants[6] and strong reducing agents, which typically generate large quantities of hazardous reagents. With emerging application of nanotechnology a greener and cost effective synthesis procedure is a highly desirable eco-friendly solution.

Increasing awareness towards green chemistry and other biological processes has led to the development of an eco-friendly approach for the synthesis of nanoparticles. Green chemistry principles 3-5,7 and 12 less hazardous chemical synthesis ,safer solvents and auxiliaries ,using renewable resources are highly recommended by safe environment.

Naturally available resources containing phytochemicals such as honey ,soyabean extract, alfalfa lemon grass, green tea and Aloe vera leaf extract[7] serve as both reducing and stabilizing agents for synthesizing metal oxide nano particles.

Here we demonstrate green synthesis of Zinc oxide nano particle from bio extract. Bio-extract serve as homogenser and Dimineralised water as solvent.

This paper reports a simple route for the preparation nanoparticles of Zinc oxide using citrus x sinensis (orange) peel extract via sol-gel method.

Experimental

Chemicals.

All the chemicals and reagents used for synthesis of ZnOnp are of analytical reagent grade and glassware of Schott-Duran make.

Characterization of ZnO Synthesized from Citrus sinuesisextract :

XRD analysis were done using (SEIFERT – 2002 Model, DYEFLAX, Germany) with $Cu\alpha$ radiation ($\lambda=1.5412 \text{ \AA}$) in the range of 10–70 θ with 1 θ /min scanning rate. SEM (FESEM S-4800 Hitachi Model Scanning electron Microscope),Dongguk University, Optical absorption spectra were recorded using Shimadzu double beam monochromator spectrometer (UV-2540) equipped with an integrated sphere assembly ISR-240A in the range of 190-900nm.

Synthesis of ZnOnano particles:

In the typical experiment for the synthesis of “green-ZnO”, 0.1M of zinc nitrate hexahydrate was dissolved in 10 ml of water and subjected to hydrolysis using the different “green-solvent”[8] and distilled water. To get homogeneous solution, the mixture was stirred using magnetic stirrer at a very slow rate for 12 h to form sol. A transparent gel was observed and the gel was dried at 120 °C for 24 h to get a white precipitate. The dried precipitate was calcined at 500 °C for 2 h to obtain ZnO particles. The as-synthesized ZnO by different concentration was labeled as Z- 10, Z- 15, Z-20 and Z-25, respectively and are characterized.

X ray Diffraction studies:

All the peaks in fig 1 are in good agreement with hexagonal wurtzite structure of ZnO and well matched with a standard data (JCPDS 36-1451). The peaks at 2 theta 30.78, 34.41, 36.24 and 47.45 corresponds

to the planes (100), (002), (101) and (102), respectively, suggesting the hexagonal wurtzite structure of ZnO, supported by JCPDS 36-1451, JCPDS 89-7102, JCPDS 65-3411[9].

No other diffraction peaks were detected, indicating that no impurity existed and the precursor had completely transformed in to the ZnO phase. The width of XRD peaks is related to crystallite size. The crystallite size was calculated from the well known Debye Scherrer equations. It was used to determine the average diameter from half width of the diffraction peaks

$$D = K \lambda / (\beta \cos \theta) \dots\dots\dots (1)$$

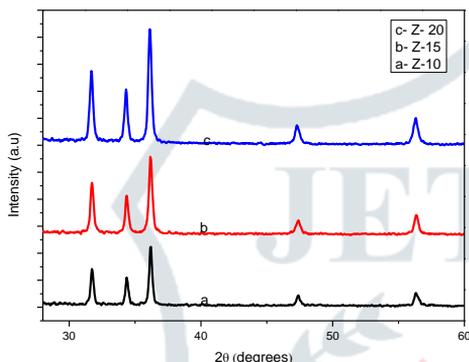


Fig. 1. XRD of ZnO synthesized from different concentration of Biosolvent a) Z-10 b) Z-15 c) Z-20

Where D – Crystallite size of the powder, λ – Wavelength of CuKalfa irradiation (1.5406Å), β - Full width at half- maximum width, θ- Bragg Diffraction angle, K – Constant (0.9). The calculated crystallite size of ZnO prepared from different concentration of Bio extract Z-10, Z-15, Z-20 and were given in table 1. The particle size decreases from Z-10 to Z-20. A reduction in the particle size of ZnO was observed for higher concentration of Bio-solvent.

Table 1: Particle size of Z-10, Z-15 and Z-20

Concentration of Extract	Z-10	Z-15	Z-20
Particle size (nm)	27.3	26.35	25.2

The XRD pattern was analyzed and reported in Table 2. The crystallite size is inversely related to the full width half maximum (FWHM) of an individual peak in the diffraction pattern. If the peaks are narrow, the FWHM decreases and hence the crystallites sizes are larger. The FWHM of Z-20 is more when compared to Z-10, Z-15, so that the particle size is smaller when compared to Z-10, Z-15. Thus, it is obviously confirmed that the FWHM of the diffraction peak is related to the size of the nanomaterials.

Table 2: 2θ and FWHM of Z-10, Z-15 and Z-20

Z-10		Z-15		Z-20	
2θ	FWHM	2θ	FWHM	2θ	FWHM
31.7357	0.306	31.7296	0.32	31.6891	0.344

34.3756	0.308	34.36	0.312	34.31	0.318
36.1639	0.293	36.17	0.314	36.1254	0.326

The formation of crystals involves a nucleation and a growth process. Particles of a smaller size are usually obtained when the rate of nucleation is faster than that of their growth. In our present study, formation of smaller crystallite sizes of ZnO in present due to the presence of Bio-extract .Bio-extract could adsorb onto the surface of the ZnO particles and could thus inhibit the diffusion of growth species from the surrounding solute atoms onto the surface of the growing particles (diffusion limited growth). So, the growth rate of the ZnO crystals was inhibited [10] and smaller crystallites size of ZnO formed.

Scanning electron Microscopy(SEM)

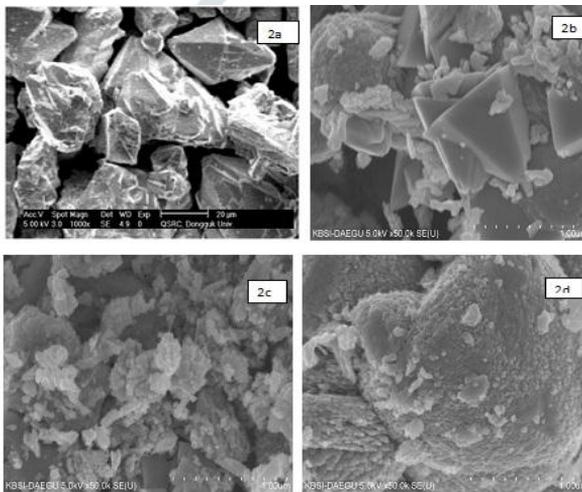


Fig. 2. SEM images of 2a) ZnO nano particles synthesized from Alcohol. ZnO nano particles synthesized from different concentration of Bio solvent 2b) Z-10 , 2c) Z-15, 2d) Z-20

For comparison purpose , SEM picture of ZnO synthesized from ethanol was given in fig 2a.

The morphology of the samples was studied by SEM. SEM images of Z-10, Z-15 and Z-20, samples are shown in Fig 2b to 2d. From Fig 2b, the shape is pyramidal with average grain size in range of 0.5-1.0 μ m. From fig 2c which shows for Z-15 where the particle size has reduced. From Fig 2d which shows for Z-20, the particles has agglomerated. Agglomeration of nanoparticles is usually explained as a common way to minimize their surface free energy; however some investigators suggest that agglomeration is due to the presence of organic radicals that act as binders.

Optical studies

The optical transmission spectra of Z-10, Z-15 and Z-20 was recorded as a function of wavelength in the wavelength range 200–900 nm as shown in figure 3. Transmittance spectra revealed that the transmittance of Z-10, Z-15, Z-20 were 89%, 90.4% and 95.8% respectively. Z-20 shows the higher transmittance when compared to other concentration.

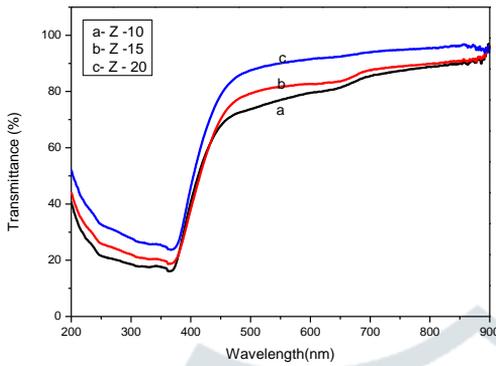


Fig. 3. Transmittance of ZnO synthesized from different concentration of Biosolvent a) Z-10 b) Z-15 c) Z-20

The optical absorption spectra of ZnO prepared from different concentration of Bioextract samples was done by UV-Vis spectrometer in the range of 190-900nm were presented. The absorption spectra of Z-10, Z-15, Z-20 are shown in fig 4. The absorption edge for all the samples is around 366nm. ZnO generally shows a characteristic absorption band around 366nm due to excitation of electron from valence band to conduction band [11].

It can be seen that the adsorption spectra of other ZnO exhibit blue shift to a certain extent with respect to different concentration of ZnO and the blue shift increases with the decrease of ZnO particle size. Similarly, the light absorption ability of ZnO also gets enhanced with decreasing particle size.

The energy band gap is determined using equation (2)

$$(\alpha h\nu)^2 = A(h\nu - E_g) \dots \dots \dots (2)$$

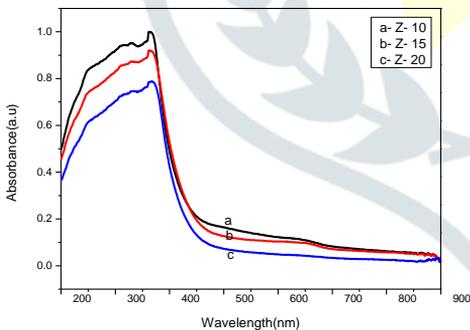


Fig. 4. Absorbance of ZnO synthesized from different concentration of Biosolvent a) Z-10 b) Z-15 c) Z-20

Where $h\nu$ = Photon energy, α =absorbance, E_g = Energy band gap, A = constant. The band gap is obtained by extrapolating the straight line portion of $(\alpha h\nu)^2$ vs $h\nu$. The band gap is calculated from the equation. The band gap is given in table 3.

Table 3:Band gap of Z-10, Z-15 and Z-20

Different conc of ZnO	Z-10	Z-15	Z-20
Band gap(eV)	3.27	3.16	2.99

The band gap decreased for Z-10 to Z-20 . This result is consistent with XRD result where the particle size decreased from Z-10 to Z-20.

Therefore, the optical band gap can be defined as the difference between the valence band and conduction band in momentum space. The optical band gap is dependent upon the particle shape, particle size and defect concentration in the crystal. It has been observed that the optical band gap of ZnO nanoparticles decreased when the crystallite size decreased.

Earlier studies[12] reported that as crystallite size decreases the band gap also decreases.It might be due to a lower defect concentration in the crystals of ZnO.

It was reported in the literature[13] that post annealed ZnOnano structures showed lower band gap and it falls in red shift which can be attributed to oxygen vacancies.

Thus, it could be concluded that in our present work,theEg value of all samples was smaller than that of the Eg value of a ZnO single crystal (3.37 eV), this might be because the Eg values in these experiments were due to the electronic transition from the filled valence states to energy levels of defects instead of the electronic transition from the filled valence band to the empty conduction band as usual. Further studies like Photoluminescence can be done to proof the defects in ZnO.

Conclusion

Zinc oxide nano particles was synthesized by simple and economical greener way. Extraction of bio waste was used for synthesis of ZnONp. Effect of concentration of bio solvent on synthesis of ZnO was done. ZnONp was analysed by XRD, SEM. Optical studies was observed for Z-10 to Z-20. Z-20 showed higher transmittance when compared to other concentration. So this concentration can be used for optoelectronic devices. The absorption spectra shifted to lower wavelength or blue shifted due to decrease in particle size . The band gap also decreased as the particle size decreased.

Acknowledgement

This work is mainly supported by the research funds from the management of Hindustan University through CENCON. One of the authors NGS acknowledges research funding from Dongguk University though QSRC and NITA. This research was also supported by Leading Foreign Institute Recruitment Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (MEST) (No.2013-044975). This research was also supported by the International Research &Development Program of the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (MEST) of Korea (Grant number: 2012-033431).

References:

1. Kuo TJ, Lin CN, Kuo CL, Huang MH, Chem Mater.19 (2007) 5143
2. Keem K, Jeong DY, Kim S Nano Lett. 6 (2006) 14543
3. Rockotpal et al, Colloids and Interfaces. 84 (2011) 338- 345
4. A.Fujishmia et al. J.Photochem.Photobiol: C Photochem.Rev 1(2000)1-21
5. Aleksandra B. Djurišić , Xinyi Chen , Yu Hang Leung and Alan Man ChingNg , J. Mater.Chem., 22(2012) 6526-65356

6. M.-L. Wu and L.-B. Lai, Colloids and Surfaces A, 244(2004) 149–157
7. G. Sangeetha ,S.Rajeshwari , R. Venckatesh, Materials Research Bulletin 46 (2011) 2560–2566
8. R.Sudarkodi et al ,J.Photochem.Photobiol:Article in press
9. Bora Akin, MuallaOner, Research on Chemical Intermediates , 38(2012)1711-1525
10. PhuriwatJitti-a-porn et al ,Journal of Ceramic Processing Research. Vol. 12(2011) 85-89
11. Liqiao Qin, Christopher Shing, ShaylaSawyer ,Partha S. Dutta,Optical Materials 33 (2011) 359–362
12. SumethaSuwanboon et al,Journal of Ceramic Processing Research. 11(2010) 547-551
13. Debabrata Pradhan1, Mater. Express, Vol. 1, 2011

