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A COMPARATIVE APPROACH FOR THE SYNTHESIS AND CHARACTERIZATION OF ZnO NANOPARTICLES: GREEN AND CHEMICAL METHOD

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Abstract— **Nanomaterials play a very important role in today's material world. Nanoparticles are extensively studied for their optical, electronic, catalytic, magnetic, antimicrobial properties. In this present study, ZnO nanoparticles were synthesized using eco-friendly green method and conventional chemical method and the effect of green and chemical synthesized ZnO nanoparticle on structural and optical property were analyzed. The bio-solvent is extracted from citras sinuesis peel extract and analyzed by Fourier transform infrared spectroscopy (FTIR) and Gas chromatography Mass spectroscopy (GS-MS).**

Structural, morphological and optical properties of the synthesized nanoparticles were characterized by X–ray diffraction analysis (XRD), Scanning electron microscopy (SEM) and UV–Vis spectroscopy (UV-Vis) and Room temperature photoluminescence spectroscopy (RTPL). XRD result confirms the formation of hexagonal wurztile structure and enhanced crystallinty is observed for green synthesized ZnO nanoparticles. The synthesized nanoparticles produced by both methods have different size and morphology. Results revealed that the ZnO nanoparticles synthesized by green route shows enhanced structural and optical properties than chemically synthesized ZnO nanoparticles. Green synthesized nanomaterial finds extensive applications in photovoltaic and photocatalytic field.

Index terms- **Comparative studies, bio-solvent, Chemical method, Green method, ZnO Nanoparticles, Optical properties.**

I. INTRODUCTION

Nanomaterials have wide range applications in various fields such as electronics, optics, materials science, and the biomedical sciences due to their size and morphology[1,2]. The nanomaterials exhibit unique and different physical, chemical and biological properties when compared to their macro scaled i.e. bulk counterparts[3].

Zinc Oxide (ZnO) is a versatile semiconductor material and has attractive properties like wide band gap (3.2eV), large exciton binding energy (60 meV), high stability and environment friendly material. These unique properties make ZnO is a promising candidate for the applications in optoelectronic, photovoltaic and bio sensing fields[4-6].

Synthesis of ZnO nanomaterials with the desired quality and properties is one of the key issues in cutting edge Nanotechnology world. Synthesis techniques change the optical, electrical and magnetic properties of nanomaterials. Currently, a large number of physical, chemical methods are available to synthesize ZnO nanoparticles[7-9]. Most of the synthesis techniques use organic solvents and reducing agents. They are highly toxic and pose potential environmental and biological risks. Hence, an environmentally benign "green" synthesis method will be the possible and promising alternative. The green synthesis techniques received lot of advantages over physicochemical methods because of its clean, non-toxic chemicals, environmentally benign solvents, and user-friendly nature[10-12].

In this work, ZnO nanoparticles were synthesized by chemical and green method. The effect of green solvent on the structural and optical properties of ZnO nanoparticle was analyzed.

II. EXPERIMENTAL

A. Synthesis of ZnO Nanoparticles by Green Method:

Conventional Sol gel method was adopted for both chemical and eco-friendly green synthesis method.

B. Synthesis of bio-solvent:

In the present studies, bio–solvent was extracted from the family of Rutacea with a genus citrus. Peels of Citrus sinuesis were collected and rinsed with double distilled water to remove the dirt and surface impurities. The cleaned bio-mass was cut into small pieces and ground well using a mechanical mixer at room temperature until medium viscous slurry was obtained.

The viscosity of the above slurry was decreased with known volume of double distilled water and extracted at70^{0}C

for 1 hr. A distillate containing purified concentrated essence from the slurry was collected and labeled as green solvent.

Zinc nitrate hexa hydrate (98% sigma aldrich) is used as precursors. An appropriate amount of precursors were dissolved in double distilled water. The bio extract was added to the precursor solution drop by drop and stirred overnight at constant speed. Then the solution was dried at 150^0C for 12 hrs. The dried white precipitate was calcined at 500^0C for 2 hrs to obtain ZnO nanoparticles.

C. Synthesis of ZnO Nanoparticles by Chemical Method

In Chemical method, instead of bio-extract, ethanol was added to the precursor solution and all other synthesis procedure was same.

D. Characterization:

Gas Chromatography Mass Spectrometry (GC-MS) was done by JEOL GCMATEII and Fourier transform Infrared Spectra were recorded using FT-IR Spectrometer (JASCO, Model 6300). Phase and crystalline orientation of the ZnO nanoparticles were characterized by an X-ray diffractometer (SEIFERT – 2002 Model, DYEFLAX, Germany) with Cukα (λ=1.5405Å) radiation. The morphology of the synthesized ZnO nanoparticles was analyzed by JEOL, JSM 6360 Scanning Electron Microscopy (SEM). Elemental compositions were analyzed using Energy dispersive X–ray spectroscopy (EDS). The optical studies were carried out using UV – Vis Spectroscopy (Shimadzu UV-2450) with an integrating sphere spectroscopy (ISR2200). Room temperature photoluminescence measurements were carried out using UV-VIS-NIR Spectrofluorometer (JASCO FP 8600**).**

III. RESULTS AND DISCUSSION

A. Characterization of Bio-extract

Bio-extract was analyzed using Gas Chromatography Mass Spectrometry (GC-MS) and Fourier transform Infrared Spectroscopy (FTIR). Fig.1 shows the GC-MS spectra of bio extract and the result exhibited a retention time around 9.038 minutes, corresponding to a compound, $C_{10}H_{13}O_4$ with molecular weight of 136.24. The compound, $C_{10}H_{13}O_4$ corresponds to D-limonene which is the characteristic molecule present in the citrus sinuesis species[13].

Insert Fig.1 shows the FTIR spectra of bio-solvent. The spectra exhibited a prominent OH peak around 3363 cm^{-1}. The peak around 2854 cm^{-1} corresponds to presence CH group in the limonene compound. The peak around 2906 cm^{-1}, 2954 cm^{-1}, 2306 cm^{-1} and 1633 cm^{-1}corresponds to alkaloid structure. Earlier reports also confirm the same peak for the *Citrus sinensis*[14]. The fragmentation pattern of the green solvent shown in GC-MS and FTIR spectra matched well with the characteristic spectrum of D- limonene[15]. The FTIR and GC-MS results confirm that the bio-solvent synthesized from Citrus Sinuesis peel contains mainly of limonene compound.

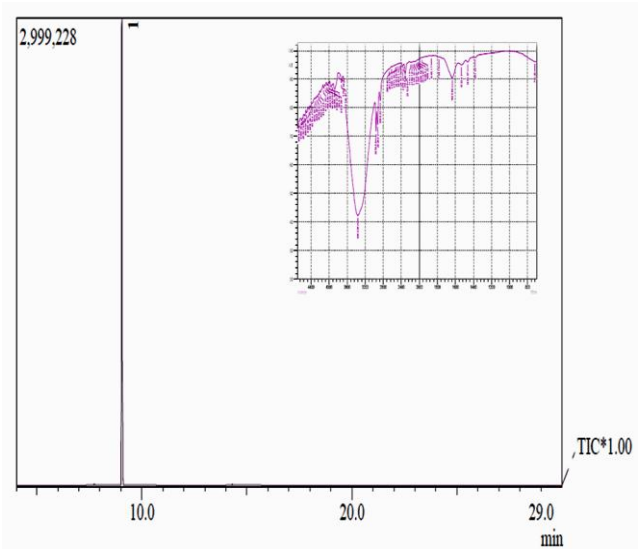

Fig.1 a) GC-MS and insert FTIR spectra of bio-solvent

B. Structural Analysi:

The crystal structure and purity of ZnO nanoparticles were characterized by X- ray diffraction (XRD) studies. Fig.2a shows XRD pattern of ZnO nanoparticles synthesized from green and chemical method. From the Fig.2a, it was inferred that all the peaks are in good agreement with hexagonal wurtzite structure of ZnO and well matched with standard data (JCPDS 36-1451). Sharpe intense diffraction peaks were observed for eco-friendly green method and no secondary peak were observed. The XRD result indicates green synthesized ZnO nanoparticles has enhanced crystalintity than chemical method. Enlarged version of XRD patterns is shown in Fig. 2b. It is obviously seen from the figure (Fig.2b) that the predominant peaks (100), (002), and (101) are shifted towards lower angle side for ZnO synthesized from green route. This may be due to increasing lattice strain and inter planar spacing[16,17]. Reduction in peak intensity and lattice strain increased in chemically synthesized ZnO nanoparticles.

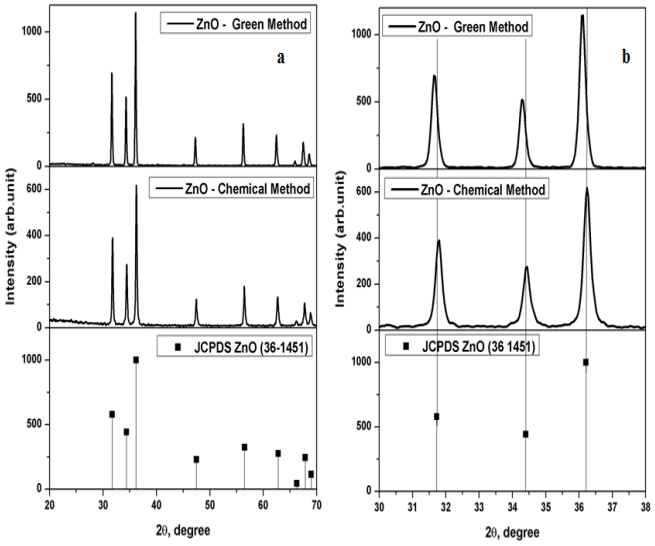

Fig .2a XRD spectra of ZnO nanoparticles synthesized by green and chemical method, b – Enlarged view

The crystallite size of ZnO nanoparticles were calculated using Debye-Scherrer equation[17]

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

Where D is the crystallite size, k is a constant taken to be 0.9, λ is the wavelength of X-Ray used (1.5405 Å), β is the full width half maximum, θ is the Bragg diffraction angle.

The strain-induced broadening in powders due to crystal imperfection and distortion was calculated using the formula[18]

$$\varepsilon = \frac{\beta}{tan\theta}$$

The lattice parameters, crystallite size, d–spacing and lattice strain of ZnO nanaoparticles synthesized from chemical and green method are summarized in Table 1. Calculated crystallite sizes of ZnO nanoparticles in green and chemical route were found to be 31.14 nm and 37.61 nm respectively.

Samples	Lattice parameter (Å)		Volume (cm^3)	d-spacing	Lattice Strain	Crystallite size (nm)
	a	c				
JCPDS (36 -1451)	3.253	5.209	47.73	-		-
ZnO - Green method	3.247	5.206	47.557	2.4769	0.1954	34.14
ZnO – Chemical Method	3.279	5.252	48.91	2.4988	0.1789	37.61

Table1. Crystallographic parameter of ZnO nanoparticles synthesized from green and chemical method

The reduction in particle size was observed for green synthesized ZnO nanoparticles. It is expected that the bio-solvent facilitate the formation of ZnO nuclei and allow growing to some extent leads to reduction in the crystallite size.

1) Morphology analysis:

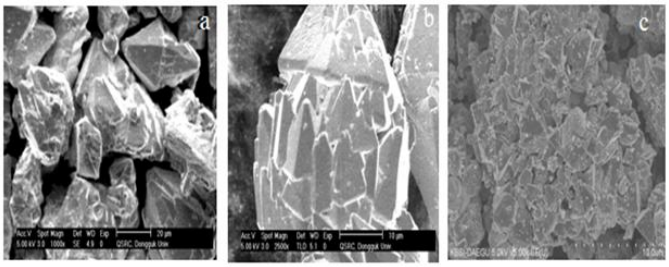

Fig. 3a&b SEM and magnified images of chemically synthesized ZnO nanoparticles and c. green synthesized ZnO nanoparticles

The Morphology of synthesized ZnO Nanoparticles was investigated by scanning electron microscopy (SEM) and elemental composition is analyzed by Energy dispersive X – ray spectroscopy (EDS). In Fig 3 (a–c) shows the SEM image of ZnO synthesized from chemical and green me thod.

ZnO synthesized from Chemical method shows (fig.2a&b), interesting pyramid shaped nanoparticle, diameter ranging from 83 nm to 98 nm. ZnO nanoparticle synthesized from green method (fig. 2c) shows triangular shape and the particles are highly agglomerated. As seen from the SEM images, green ZnO nanoparticle has lower particle size than the chemically synthesized ZnO nanoparticle as well as change in morphology is observed due to bio-solvent.

EDS results indicate 65% of Zinc and 35% Oxygen element was present in the green synthesized ZnO Nanoparticles. In chemical method, 73.8% Zn and 26.8% Oxygen was observed. No additional elements were detected in EDS analysis in both synthesis procedures, indicate the purity of ZnO nanoparicles.

2) . Optical Analysis

a) UV – Visible Spectroscopy:

Fig. 4a shows absorbance spectra of ZnO Nanoparticles synthesized from chemical and eco-friendly green method. Both samples shows sharp absorption edge near to 395 nm in the UV region and these adsorption edges slightly shift to longer wavelength. This might be due to the quantum confinement effect.

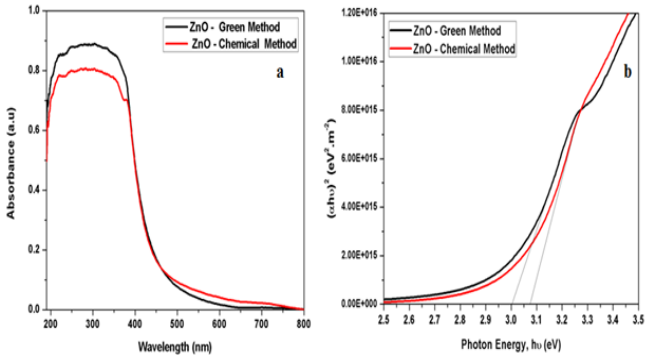

Fig. 4a Absorbance spectra and b) Tauc plot of ZnO nanoparticles synthesized by green and chemical method

The optical band gap of ZnO nanoparticles is determined from absorbance spectra by applying Tauc equation[19,20]

$$(\alpha h\upsilon)^2 = C\,[(h\upsilon - Eg)]^n$$

E_g is the optical bandgap, C is the constant and h^{υ} is the incident photon energy. n can be the value n=1/2 the transition data provide the linear curve in the plot of $(\alpha h^{\upsilon})^2$ Vs photon energy (h^{υ}). Fig. 4b Shows the plot of $(\alpha h^{\upsilon})^2$ Vs photon energy (h^{υ}) of the ZnO nanoparticles synthesized by chemical and green method. It has been observed that the linear over the wide range of photon energies indicating a direct type of transition. The intercepts (extrapolations) of theses plots (straight lines) on the energy axis reflect the energy bandgap. The band gap decreases from bulk ZnO (3.2eV) to 3.07 and 3.0 eV for chemical and green route synthesized ZnO nanoparticles. The decrease in band gap value could be due to the Size effect[21].

b) Photoluminescence Spectroscopy:

Photo luminescence studies are powerful tools for investigating energy states existing between valence and conduction bands. Fig. 5 shows the room temperature photoluminescence RTPL emission spectra of ZnO nanoparticles synthesized by green and chemical method exited at 240 nm.

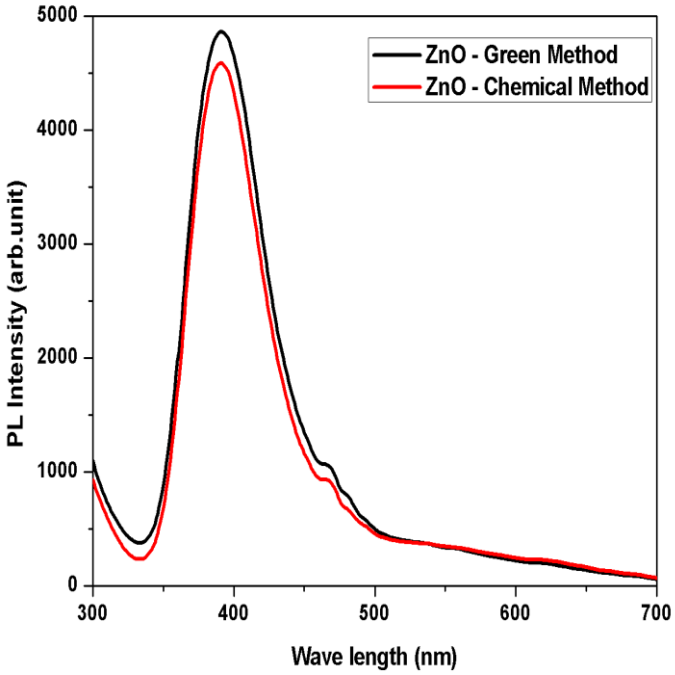

Fig. 5 RTPL Spectra of ZnO nanoparticles synthesized by green and chemical method

The emission spectra consist of two main peak, a sharp peak at 393 nm in the UV region and the other peak around 470 nm in the visible region. The observed UV emission is attributed to excitonic recombination of near band edge emission of ZnO and the blue emission may be due to lattice defects related to Zn interstitial / surface defects[22]. Sachin D. Kshirsagar et al reported the blue emission in ZnO due to acceptor bound exciton[23]. J. Lü et. al., has reported that the blue emission is associated with Zn vacancy and Zn interstitial defects[24]. In the present study, reduction in PL emission intensity is observed for chemically synthesized ZnO nanoparticles, Enhanced PL intensity was observed for green synthesized ZnO nanoparticles, which clearly indicates the enhanced crystalline quality and the results are well matched with XRD results.

IV. CONCLUSION

In this work, ZnO nanoparticles were synthesized by sol gel method through Chemical and Green method. XRD results revealed that all the samples are polycrystalline and hexagonal wurtzite structure. Enhanced crystallinity has observed for green synthesized ZnO nanoparticles. SEM results shows, pyramid shaped nanoparticles for chemically synthesized ZnO, while green synthesized ZnO nanoparticles exhibit triangular shape. SEM results clearly indicate the change in particle size and morphology due to the effect of bio- solvent. The optical measurement results shows shift towards higher angle was observed for green synthesized ZnO nanoparticles. Reduction in bandgap and particle size was observed in eco-friendly green method. From the above interesting results we concluded, ZnO nanoparticles synthesized by greener way, can find application in Optoelectronics.

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