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Effect of temperature on the structural and optical properties of Zinc Oxide nanoparticles prepared using Green synthesis method

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Abstract

Green technology for nanoparticles' synthesis is gaining a substantial interest among researchers as an eco-friendly technique to eliminate the employment of nephrotoxic chemicals. The present study reports the fabrication of Zinc oxide nanoparticles (ZnO-NPs) using Betel leaf extract and Zinc acetate synthesized by Co-Precipitation method in different temperatures (400 °C & 500 °C). The betel leaf assisted ZnO particles were investigated through X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray spectroscopy (EDS) ans Photoluminescence (PL) studies. Hexagonal (wurtzite) shaped ZnO-NPs with average size of 50 nm were synthesized. EDS showed the chemical compositions (Zn, O) ZnO NPs. At the room temperature, PL spectra of ZnO Nano crystalline particles was measured at an excitation wavelength of 329 nm. Annealing at 400 °C and 500 °C emission wavelength showed two weak violet peaks (416 nm & 437 nm). As the temperature was increased from 400 °C to 500 °C, the violet peaks in the emission spectra disappeared and strong blue emission was modified to strong super blue band at 461 nm. This is useful to blue LEDs applications.

Key words: ZnO-NPs, Green synthesis, Characterization Analysis (XRD, SEM, EDS, PL) and Temperature effect.

1 Introduction

Zinc oxide has many and very impressive properties like large binding energy, wide band gap, and high piezoelectric property etc. It is used in large number of applications like laser devices, optoelectronic devices, electromagnetic coupled sensor, and surface acoustic wave devices [1-6]. ZnO, also known as Zincite, is a wide and direct band-gap semiconductor "~3.7 eV" at room temperature[7,8]. Nanoparticles exhibit atom-like behaviors due to high surface energy resulting from high and huge specific area, high fraction of surface atoms and wide gap between valence and conduction band once divided to close to atomic size [9-11]. Zinc oxide nanoparticles have been used to eliminate sulphur, arsenic from water because bulk ZnO cannot remove arsenic because nanoparticle have great surface area than bulk material [12]. Zinc oxide NPs have amazing applications in diagnostics, bimolecular detection & microelectronics [13]. The plant extract mediated synthesis of nanoparticles is efficient [14]. In this work, green synthesis of ZnO nanoparticles was achieved by using extract of betel leaves. To the best of our knowledge, the use of leaf extract of betel leaf plant for green synthesis of ZnO nanoparticles has not been revealed. Hence, the present research was carried out on synthesis and characterization of ZnO nanoparticles using leaves extract of betel leaf plant. The leaf of betel plant was used in extract preparation.

2 Experimental

2.1 Synthesis of ZnO-NPs

Betel leaves were collected from the plants in and around Pulivendula area, Andhra Pradesh, India. Zinc acetate was purchased from Sigma Aldrich chemicals, India. The Betel fresh leaves were washed thrice with distilled water to get rid of mud. After that, it was chopped and the extract from the leaves was collected. The water was added to the extract in 1:3 ratio and boiled at 80 °C for 45 min. After that, the solution was cooled at room temperature for 6 hrs. Zinc acetate was taken (0.1 M) (1 gm of Zinc acetate was dissolved in 50 ml distilled water) and added to the water. The extract solutions were stirred on the magnetic stirrer and added the prepared Zinc Acetate solution drop wise. The stirring process was continued for 11 – 12 hrs. After stirring, final solution was placed in room temperature for one day. Next day, the solution was put into the Muffle furnace for 7 hrs. The solid type Zinc oxide was available and the solid ZnO from the furnace was then grinded with mortar pestle. The prepared powder of ZnO nanoparticles was annealed at 400 °C and 500 °C.

3 Results and Discussion

3.1 Structural Properties (XRD)

Table 1 XRD calculations of ZnO NPs at 400 °C and 500 °C

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Sample	2θ (101) degrees	d_{hkl} spacing	FWHM β radians	Lattice constant (A^0)		Volume (V)	Density $\delta = \frac{1}{D^2} \times 10^{-4}$	Strain $\varepsilon = \{\frac{\beta cos\theta}{4}\} \times 10^{-3}$	Particle size (nm)
				a(A^0)	c(A^0)				
ZnO (400°)	31.728	2.820	0.2952	3.253	5.635	154.91	3.840	0.07098	50.99
ZnO (500°)	31.739	2.819	0.2952	3.253	5.635	154.91	3.844	0.07098	51

The **Fig.-1** shows that the powder X-ray diffraction analysis of ZnO nanoparticles recorded in the glancing angle range of 10° to and 80°. ZnO Nanoparticles have purity, crystallinity and particle size in the nanosize (50 nm) as evidenced in the pattern. The narrow peaks indicate the purity and crystallinity of Nanoparticles. The XRD Peaks are consistent with the JCPDS data cord 79-207 hexagonal phase and primitive geometry of ZnO Nanoparticles. The detected peaks corresponded with those of hexagonal phase Zincite were found at the lattice plains of (100), (002), (101), (102), (110), (103), (112) and (202) in the 2θ value: 31.77^0, 34.45^0, 36.25^0, 47.53^0, 56.54^0, 62.83^0, 67.89^0, 76.87^0, respectively.

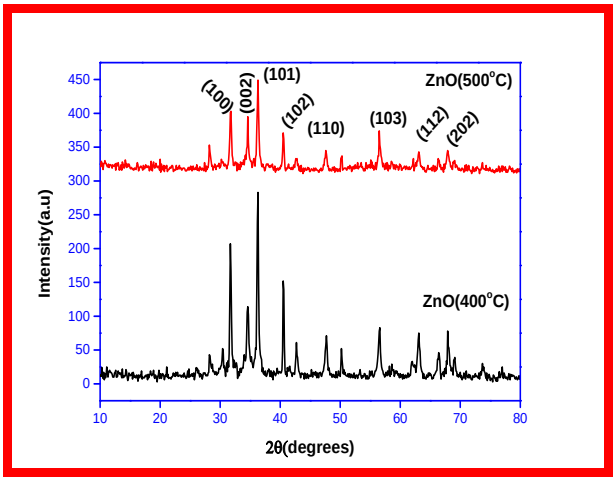

Fig. 1. PXRD pattern of ZnO NPs at 400 °C and 500 °C

$$D = \frac{0.9\lambda}{\beta Cos\ \theta}$$

where D is the average crystallite size in Å, K is the shape factor (0.9), ƛ is the wavelength of X-ray (1.5406 Å) CuKα radiation, θ be the Bragg angle, and β is the FWHM of the NPs. The average crystalline size of the most intense plane (101) of both temperatures were 50 nm, determined by Debye-Scherer's equation. The XRD profile shows that as the temperature increases, automatically the intensity decreases. Nano sized ranges of ZnO suggests that Betel leaves extract can be active as the hydrolytic and precipitating agent for the formation of ZnO Nanoparticles. Broadening of XRD patterns can be attributed to size of the nano particles, while sturdy and slim peaks indicate that the product has a smart crystallinity [15-17].

3.2 SEM–EDXS analysis

3.2.1 SEM

The SEM micro graphs of ZnO Nano particles showed that the particles are nearly spherical in shape and the particles are agglomerative to kind sponge like bunch of particles. Fig. 2(a) shows that the particles was agglomerated and between the space is small to compare the Fig. 2(b). The agglomeration could be evoked by densification leading to the slim area between the particles. When gas was escaped with high pressure, pores shape with the concurrent formation of little particle was observed. Fig. 2(a) shows that the particles are highly agglomerated when raising the temperature to 500 °C. The Fig. 2(b) shows that small agglomeration of the particles are responsible for forming the small size.

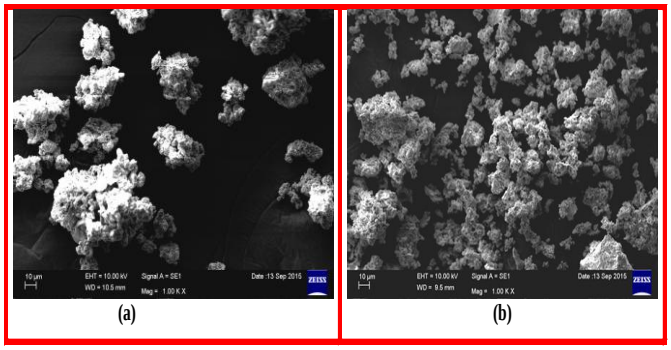

Fig.2. SEM image of ZnO NPs (a) 400 °C and (b) 500 °C.

3.2.2 EDS

EDS of the sample indicated the presence of Zinc and Oxygen at stoichiometric ratio in the EDS Spectra shows the presence of helpful agents that were originated from plant extract. The Fig - 3(a) and Fig - 3(b) indicating that bioactive compounds were absorbed by Betel leaves of ZnO nanoparticles at 400 °C and 500 °C. The Tables 1 & 2 represents the atomic and weight percentages of ZnO NPs at 400 °C and 500 °C.

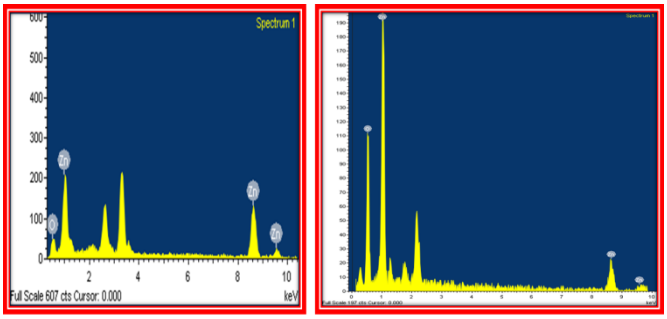

Fig.3. EDX spectrum of ZnO NPs (a) 400^{0}C and (b) 500^{0}C.

Table 2: Atomic and weight percentages of ZnO NPs at 400°C

Element	Weight%	Atomic%
O K	14.23	40.39
Zn K	85.77	59.61
Totals	100.00	

Table 3: Atomic and weight percentages of ZnO NPs at 500 °C

Element	Weight %	Atomic %
O K	34.76	67.46
Zn K	65.24	32.54
Totals	100.00	

3.3 Photo Luminescence study

At the room temperature, PL spectra of ZnO Nano crystalline particles was measured at an excitation wavelength of 329 nm (Fig.4). The ZnO Nano particles annealed at 400 ^{0}C from the Fig.5 shows that emission wavelength have three peaks centered at 416 nm, 437 nm, and 475 nm with the first two board peaks corresponding to violet emission and the sharp peak corresponding to the blue emission. When annealed at 500^{0}C, the emission wavelength shifted to (Fig. 6) blue band and centered at 461 nm. The PL of ZnO nanostructures has been studied extensively for their potential use as optical material. The super blue emission is possibly due to surface defects in the Nano crystalline particles of ZnO. The blue emission corresponds to the singly ionized O vacancy in ZnO. This emission results from the recombination of a photo generated hole with the only ionized charge state of the precise defect [18, 19]. Intersetingly, in this present work, as the temperature was increased from 400 °C to 500 °C, violet peaks in the emission spectra are disappeared and strong blue emission is modified to strong super blue band centered at 461 nm. This is useful to blue LEDs applications.

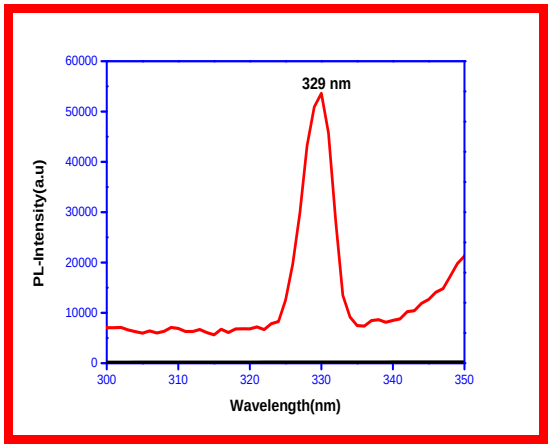

Fig.4.PL Excitation spectra of ZnO NPs

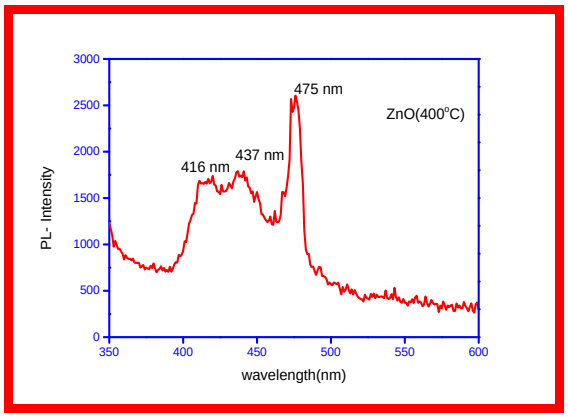

Fig.5.PL Emission spectra of ZnO NPs at 400°C

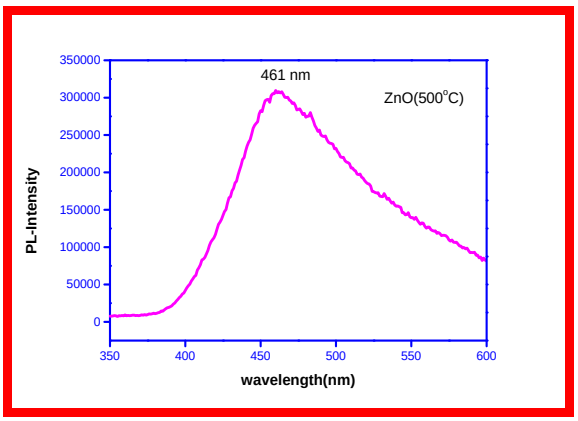

Fig.6.PL Emission spectra of ZnO NPs at 500°C

4 Conclusions

Green synthesis of hexagonal (wurtzite) ZnO-NPs at different temperatures (400 °C and 500 °C) has been achieved by exploitation leaf extract of Piper betel leaves. The SEM analysis reveals that the particles are collective to kind sponge like bunch of particles and increasing the temperature reduced the agglomeration. EDS shows that the presence of Zinc and Oxygen at stoichiometric ratios. At the room temperature, PL spectra of ZnO Nano crystalline particles was measured

at an excitation wavelength of 329 nm. Annealing at 400 ^{0}C and 500 °C emission wavelength shows a two weak violet peaks (416 nm & 437 nm). In this present work, the temperature was increased at 400 °C and 500 °C of emission spectra and violet peaks are disappeared. The strong blue emission was modified to strong super blue band at 461 nm. This is useful to blue LEDs applications.

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