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Machine learning and size fit analysis of green hydro thermal method synthesized ZnO Nano particles using leaf extract of Raphanus Raphanistrum.

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Abstract: The novelty of this report is synthesis of Bilayer hexagonal disks and hexagonal rings using phytochemicals as reducing agents. Raphanus Raphanistrum(Radish) leaf extract is used as reducing agent and NaOH as stabilizing agent with Zinc Acetate as precursor. A facile synthetic route- Green Hydro thermal method is used for obtaining the structures without any usage of external surfactants. The structural analysis of calcinated ZnO powder is carried out by XRD and the average crystallite size is found to be 21.13nm. The optical properties is checked by UV-VISIBLE spectrophotometer and the band gap is 3.47eV. Presence of functional groups is confirmed by FTIR. Morphology studies is done by SEM and SEM observations confirmed the two different ZnO structures. From size fit analysis, the best fit for experimentation to obtain Nanostructured ZnO is 1.0M- 180^{0}C- 12hrs.

Keywords **Raphanus Raphanistrum, ZnO, Bilayer hexagonal disks, Hexagonal rings, Green Hydrothermal method.**

Introduction

Materials show unique behaviour when their size reduces from microns to Nano. The one example which paves a way to this statement is the usage of gold nanoparticles on church glasses. Nano particles are generally considered in the size range 1-100nm of which any one dimension satisfy the criteria [1-3]. Properties like optical, thermal, electronic, electrical, magnetic [4-6] show quirky behaviour and these characteristics led advancements in several fields of Nano Technology. The applications of Nano materials includes many sectors like agriculture, medical, pharmaceuticals, electronic, automobile, cosmetics are few named. In classifying the Nano materials, metals, metal oxides, sulphides, nitrides, cnt's are well known [7-12]. In the advancing technology several approaches and methods are used for synthesizing Nano materials. These includes physical methods, chemical methods, and green methods [13, 14, 15].

The physical methods for synthesizing Nano particles require good capital [16] and the chemical methods has and have considerable effects on environment and these effects are increasing day by day. The concern for protecting environment has key initiative from environment (protection) act 1972, and the enlarging industrial capacities of Nano technology has a concern to not invite the further chemical compounds which produce adverse effects in the environment. So, the good way to reduce environmental effects of producing Nano materials is usage of green constituents [17] of plants as reducing as well as stabilising agents by replacing chemical reagents. Some of the methods for synthesis of ZnO Nano particles lists sol-gel method [18], chemical reduction [19], micro-wave assisted method [20], and hydro thermal [21].

In the application point of view, ZnO Nano particles have significant role and researchers have keen interest in attempting ZnO Nano particles for varied applications. ZnO is a metal oxide semi-conductor with a broad band gap of 3.37eV [22] and exhibits piezoelectric, photo catalytic, optoelectronics are few mentioned properties. ZnO is widely used in applications like sun screens [23], solar cells [24], gas sensing mechanisms [25, 26], photo catalysts [27], coolants [28], anti-corrosion coatings [29], and anti-microbial activities [30].

For sustainable growth and eco-friendly products, synthesis of Nano particles using green methods is quite considerable. The main advantage is the materials are safe to human health, no issues of environmental problems, and also a new way to synthesis Nano particles using Green Nano Technology. Numerous publications in synthesis of ZnO Nano particles using either plant leaf or other parts are discussed. Aloe Vera leaf extract [31], lemon peel extract [32], Hibiscus rosasinensis [33], Azadirachta indica leaf extract [34]. Size and morphology are important parameters in enhancing or dwindling the properties of the application. Hydro thermal method has a huge scope in obtaining different morphologies of Nano particles by varying temperature and time combinations. ZnO Nano particles synthesized by Terminalia Arjuna bark extract has spherical shape which was confirmed by SEM results [35]. Wang et al [36] synthesized ZnO Nano particles by varying pH values from 8-11 and the micrographs of SEM confirms spindle like needle structures and flower shaped particles.

In this present article, synthesis of ZnO Nano particles by Green Hydro Thermal method using Raphanus Raphanistrum (RR) leaf extract is done. The leaf of RR contains Oxalic acid, Malic acid, Citric acid, Tocoferols and anti-oxidants. More over the leaf contains 14 phenolic compounds, and 12 flavonol derivatives, majority is flavonoid portion up to 99% [37, 38]. The flavonoids in leaf acts as reducing agents similar to chemical reducing agents. In this, the effects of temperature and time on morphology at constant pH were investigated and the evaluation of Nano particles were eventually done by powder XRD, SEM, FTIR, UV-VISIBLE.

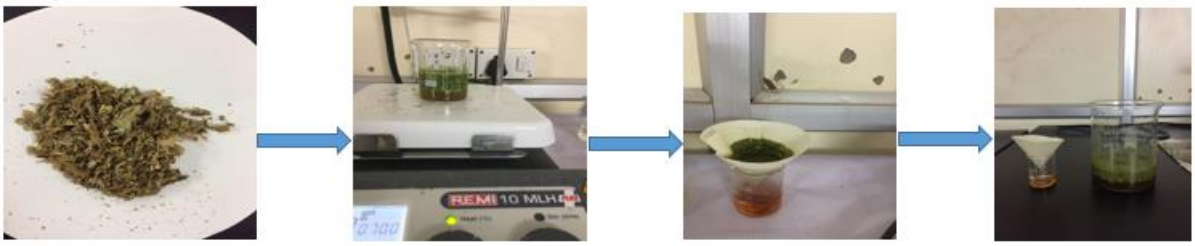
Experimental procedure

Materials and methods

For experimentation, chemical compounds were purchased from SD Fine-Chem Ltd and RR leaves were purchased from local market, Hyderabad. In this work, Zinc Acetate is used as precursor and Sodium hydroxide is used as capping or stabilizing agent, the leaf extract is used as reducing agent. Double distilled water (DW) was used in all experiments.

Leaf extract preparation

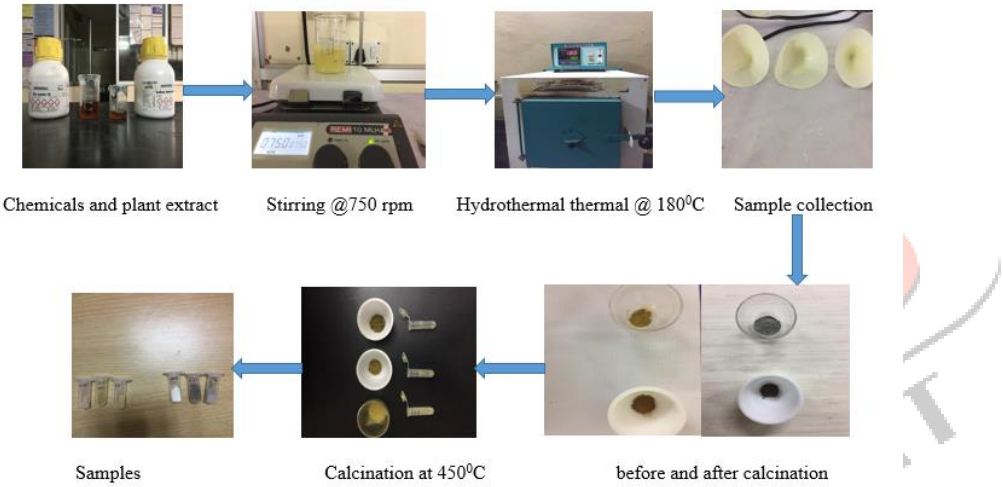
10 gms of air dried RR leaf powder was calibrated. In a beaker 200 ml of DW is taken and the dried powder is added. Now, the beaker is placed on a heat cum stir plate and heated for 45 min @ 70^0C. After nature cooling of the solution, it is filtered using Whatman filter paper and the concentrated solution is collected. This process is carried out for each experimentation and the prepared solution is stored in cold storage for future use.



RR leaf powder heated at 70^0C Filtration using Whatman filter paper and leaf extract

Synthesis of nanoparticles

Dry leaf powder – filtration of powder from liquid – leaf extract – X molarity Zinc Acetate – 4M NaOH – 20 ml leaf extract solution – Stirring up to 45 min – Transfer to Teflon autoclave for time t hrs. – Cooled to room temperature – cleaned the solution using D.I. water for 3 times– Filtered using whatman filter paper – Incubation for 2hrs – calcination is done for 2 hrs. at 450^0C.



Chemicals and plant extract Stirring @750 rpm Hydrothermal thermal @ 180^0C Sample collection

Samples Calcination at 450^0C before and after calcination

Characterization

Structural analysis of ZnO powder is carried out by XRD using Shimadzu XRD-7000 model (Cu K_α and λ= 0.15418nm). The optical properties was analysed by UV- VISIBLE spectrophotometer using Shimadzu 8400S. The functional groups present in the powder sample is investigated by FT-IR spectroscopy using Shimadzu 8400S. Morphology of the samples were observed by SEM using Hitachi S-3700N.

Results and discussion

Determination of size and structure

The figure 1 shows the XRD pattern of ZnO Nano particles. The diffraction angles are calculated from 10-80^0. The planes (100), (002), (101), (102), (110), (103), (112), (201), (202) coincides with JCPDS card no. 79-0207. It confirms hexagonal structure with lattice parameters a=b= 3.256, c= 5.212. The sharp peaks resembles crystalline nature of the material. The high intensity peaks are obtained at 36.1116, 31.6321, 34.2938 (degrees) and the corresponding planes are (100), (002), and (101). The average crystallite size is analysed by using Debye-Scherrer's equation [39] and obtained as 21.13 nm.

Crystallite size (D) = $\frac{K*\lambda}{\beta*cos\theta}$

Where K= Constant= 0.9, λ= XRD wavelength= 0.15406nm, β= FWHM (Full width at half Maximum intensity), θ= diffraction angle (degrees)

Determination of functional groups

Figure 2 shows FTIR spectrum of green synthesized ZnO Nanoparticle. The bands from FTIR spectrum are 3151.2, 1593.1, 1399.8, 570.6 cm^{-1} respectively. We observed that the peak at 570.6 cm^{-1} clearly shows Zn-O bond. Since, the peak in betweeen 400-600 cm^{-1} gives metal-oxygen bond. The peak at 1399.8 cm^{-1} gives a CH_3 bend. The peak at 1593.1 cm^{-1} gives aromatic bond of C=C. The presence of =C-H can be clarified by a peak at 3151.2 cm^{-1}. Apart from the dominating functional groups there are also some minute functional groups and the bands are 1080, 1120, 1260 cm^{-1}. The peak 1080 cm^{-1} gives C-N bond and the functional group is aliphatic amines. The bond at 1120 cm^{-1} is an alcohol/ esthers/ ethers functional group with C-O stretch. The 1260 cm^{-1} peak gives aromatic C-N bond.

Determination of optical properties

From wavelength vs absorbance graph Fig. 3(a), the peak at 382 nm clearly shows the presence of ZnO Nano particles. The confirmation of ZnO Nano particles by UV- Visible spectroscopy is cleared. ZnO is a direct band gap semi conductor and by using tauc plot, the band gap of the present material is found.

From tauc plot Fig. 3(b), the band gap of ZnO Nano particle synthesized using RR leaf extract is found to be 3.47 eV.

Tauc's relation

Tauc plot is adopted to find the optical band gap of the sample [39,40]. Tauc's relation is

$(\alpha h\nu)^n = B(h\nu - E_g)$

Where α= absorption coefficient, h= Planck's constant= $6.626*10^{-34}$ m^2 kg/s, ν= frequency= C/ λ, C= wavelength of light= $3*10^8$ m/s, λ= wavelength, n= 2 for direct band gap semi conductors, ½ for indirect band gap semi conductors, B is material constant

plotting $(\alpha h\nu)^2$ VS hν, hν on x-axis and $(\alpha h\nu)^2$ on y-axis, and extrapolating the linear portion on to x-axis gives direct gap of 3.24 eV.

SEM observations of ZnO

From the observations illustrated in Fig. 4 (a, b, c) the SEM images shows that as molarity increased from 0.4M to 1.0M the homogenity of the samples became better. The size distribution got widened while improving the structural quality of ZnO sample.

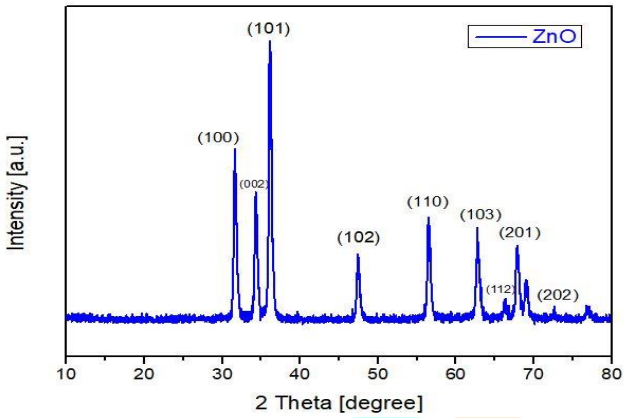


Fig. 1

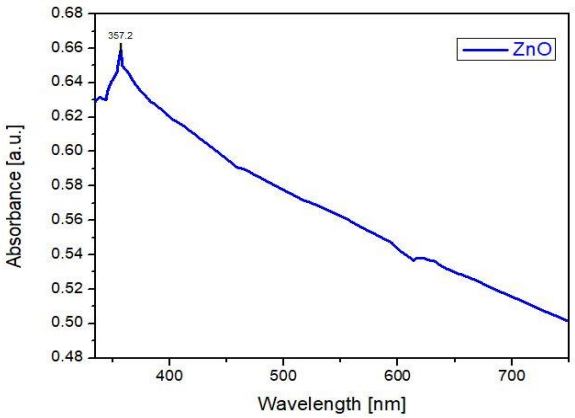


Fig. 3 (a)

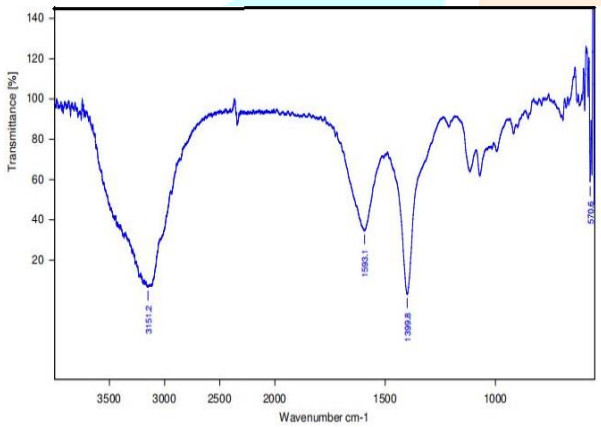


Fig. 2

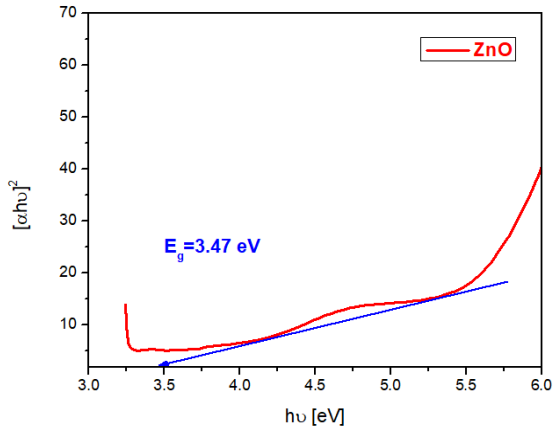


Fig. 3(b)

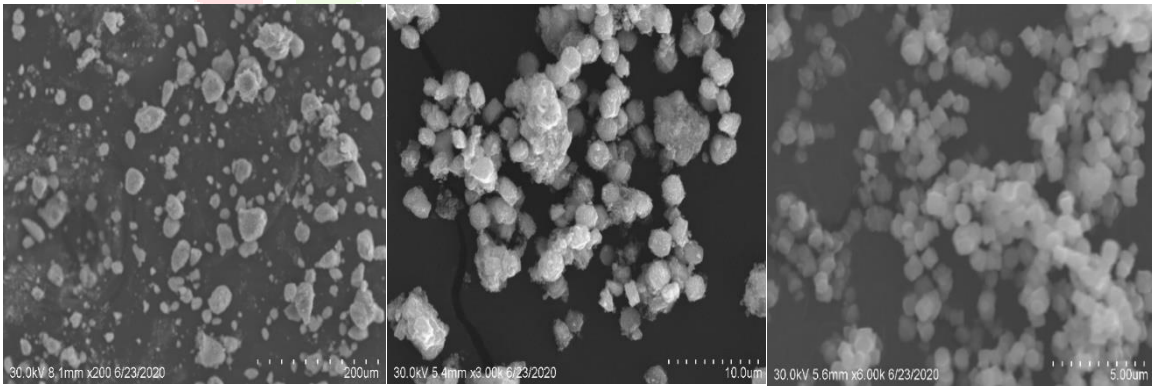


Fig. 4 (a) 0.4M (b) 0.7M (c) 1.0M

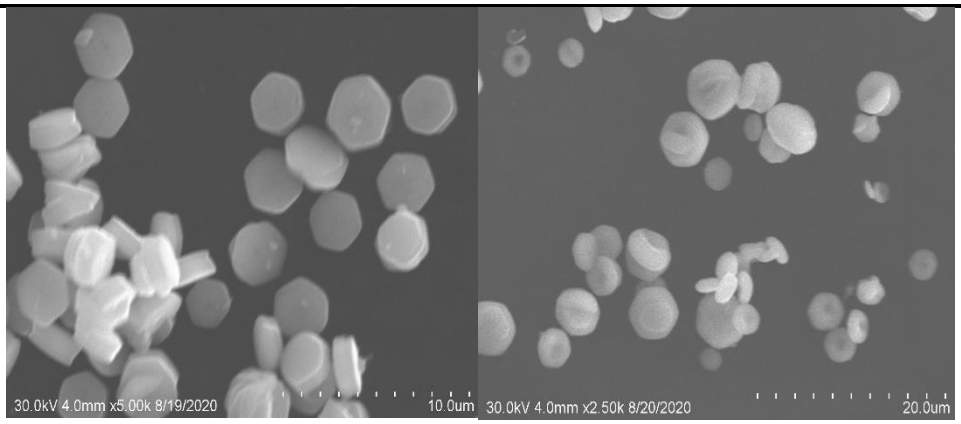


Fig. 5 (a) Bilayer hexagon disks (b) Hexagonal rings

In the synthesis of ZnO Bilayer hexagonal disks and hexagonal rings (Fig. 5 (a), (b)), temperature played a crucial role. The effect of time is limited to only formation of different size distributions of bilayer hexagonal disks. The functional groups present in RR leaf extract might be helpful in the formation of hexagonal rings. In this no surfactant is used for the formation of hexagonal rings. [41, 42].

Size data points of experimental results:

Considering all data points viz molarity, temperature, and time. The objective is to estimate a fit for obtaining best particle size. The obtained fit is

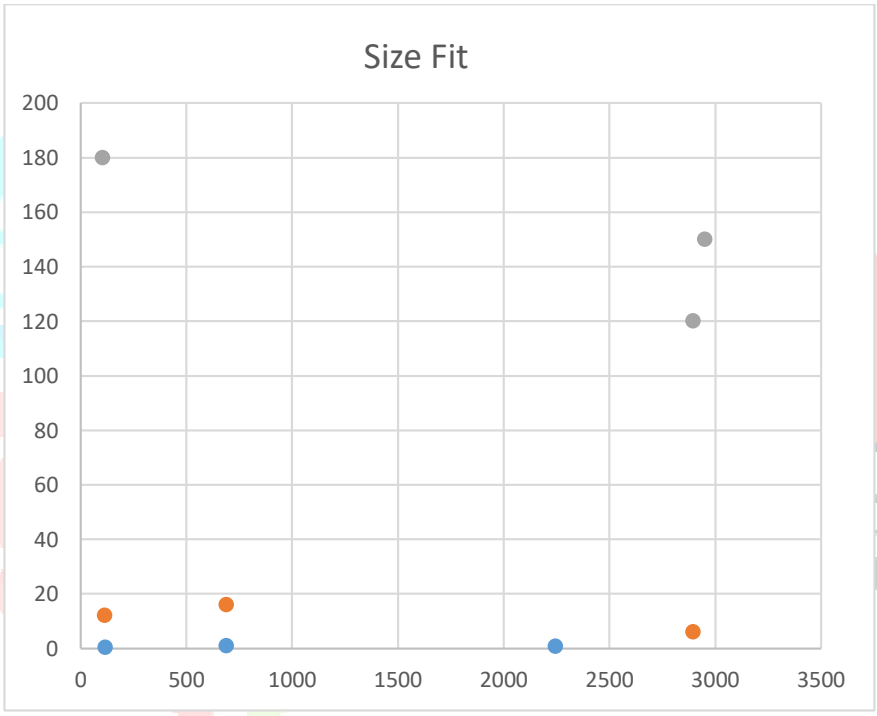


Fig.6 size fit data

Considering the first condition for fit, molarity, from three molarities (0.4M, 0.7M, 1.0M), to get Nano dimensional particles 0.4M is best but our aim is to get structural material. So, 1.0M is opted. The second condition for further fit is time, from three time estimates (6, 12, 16hrs), 12 hrs is best, since the median obtained is 113.5nm. The third condition is temperature, three temperature conditions are 120, 150, 180 ^{0}C. The best condition for fit is 180^{0}C. The median is 104nm. From the above three conditions, to fit a best set for obtaining structural rich ZnO nano structures is 1.0M- 180^{0}C- 12hrs.

Conclusion

Zno Nano structures are prepared using RR leaf extract by green hydrothermal method. It is found that temperature and molarity of precursor plays an important role in formation of different ZnO structures. Autoclave set time is limited to only size distribution and it has no influence on morphology. The different structures obtained by varying the parameters are Bilayer Hexagonal disks and Hexagonal rings. The optimum conditions from size fit analysis is 1.0M, 12hrs and 180^{0}C.

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