Green and chemically synthesized ZnO nanoparticles: A comparative study

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Abstract: Green synthesis of ZnO nanoparticles using plant extract is an alternative method to traditional chemical synthesis method. In the present work, we report the synthesis of zinc oxide nanoparticles (ZnO) synthesized by two methods, first by green synthesis by using zinc acetate and leaves extract of Ocimum Tenuiflorum (Tulsi leaves) and secondly by chemical route method using organic capping agent. The effect of synthesis methods on structural, optical, and photoluminescence property of ZnO nanoparticle were analyzed. Formation of zinc oxide nanoparticles has been confirmed by UV-Visible absorption spectroscopy, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and Scanning Electron Microscope (SEM). The Scanning Electron Microscope reveals non spherical morphology of nanoparticles. The particle sizes of nanoparticles were calculated experimentally using XRD and SEM. The particle size measured by XRD pattern was found to be 63nm for chemically synthesized ZnO and 38nm for ZnO sample prepared by green synthesis. SEM images showed interesting flower like structure and agglomeration of nanoparticles. The blue-shift in absorption spectra was observed with reducing size of the nanoparticles. The FTIR spectra inferred that the stabilizing agent passivated the surface of the particles. The PL spectra showed blue shift for the sample prepared by green synthesis. The results suggest that ZnO sample synthesized by green route is better in comparison to the chemically synthesized samples.
Keywords: Photoluminescence, Optical Characterization, ZnO nanoparticles, FTIR, Green synthesis.

1. Introduction

Nanomaterials play a very important role in today’s material world. The nanomaterials exhibit unique and different physical, chemical and biological properties when compared to their macro scaled counterparts [1]. Nanoparticles are extensively studied for their optical, electronic, catalytic, magnetic, antimicrobial properties. In the last few decades, inorganic nanoparticles, whose structures showed significantly new and improved physical, chemical, and biological properties and functionality due to their nanosize was much studied. Several types of inorganic metal oxides have been synthesized and remained in recent studies like TiO$_2$, CuO, and ZnO. Among the metal oxide, ZnO NPs are of maximum interest because they are inexpensive to produce, safe and can be prepared easily. Zinc oxide nanoparticles have drawn the attention of many researchers for their unique optical and chemical properties that can be easily tuned by changing the morphology. Zinc oxide nanoparticles belong to the class of metal oxides, which is characterized by photocatalytic and photo-oxidizing capacity against chemical and biological species [2]. Zinc Oxide 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. ZnO nanoparticles have been used in various cutting-edge applications like electronics, communication, sensor, cosmetics, environmental protection and biological applications like biological sensing, biological labeling, gene delivery, drug delivery and nanomedicines etc. [3–8].

There are many conventional physical and chemical methods that have been used for the synthesis of ZnO nanoparticles, such as, chemical vapor synthesis, laser ablation, solvothermal and sol-gel method [9-12]. However, these methods are usually expensive, labor-intensive, and are potentially hazardous to the environment and living organisms. The chemical method involves the use of toxic chemicals which can prove to be hazardous for the environment and the person handling it[13]. In physical and chemical methods, additional capping and stabilizing agent are needed. Most of the synthesis techniques use organic solvents and reducing agents [14–17]. Thus, there is an obvious need for an alternative, cost-effective and at the same time safe and environmentally sound method for synthesizing nanoparticle. Therefore there is a need for “green synthesis” that offers numerous benefits of eco-friendliness, where toxic chemicals are not used for the synthesis process. In green synthesis method plants, bacteria, fungi, algae etc are used. This method involves a biological approach in which different types of microorganisms/ plant extracts are used to synthesize different metallic NPs and has many advantages over other chemical methods as they are greener, energy saving and cost-effective. Various researchers studied the biosynthesis of zinc oxide nanoparticles using agricultural wastes, plants and their parts and fungal cultures that has emerged as an alternative to chemical synthetic procedures because it does not require elaborate processes and provide natural capping agents[18–23]. But, some problems that are often experienced in synthesizing metal nanoparticles by green synthesis are stability and aggregation, control of crystal growth, morphologies, sizes, and distribution, which are important issues and continue to be solved. In present study, we have synthesized samples of ZnO nanoparticles both by chemical (chem) and green method and compared the structural and optical properties of them. The structural characterization by XRD, SEM and optical characterization by UV-VIS spectrometry, FTIR was made. 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. The present work shows that, the green synthesis of ZnO sample have better results in comparison to the chemically synthesized samples.
2. Experimental
The samples of ZnO nanoparticles were synthesized by two methods.

(i) Green Synthesis

For the preparation of leaves extract of ocimumtenuiflorum leaves was first washed many times with water and dried in sunlight. 10 gm of dried leaves with 100 ml distilled water were taken in a 250 ml borosil beaker and was boiled for 10 min. until solution turns in reddish colour. The mixture solution was then cooled to room temperature. The leaves extract filtered utilizing filter paper 50 ml of ocimumtenuiflorum leaf extract was boiled to 60-70°C using magnetic stirrer heater. Then 5 gm of zinc nitrate was added to the leaf extract, when temperature reaches to 70°C it reduces to deep reddish paste. This paste was then dried at temperature 100- 130°C for 40-45 minutes. The dried light yellow powders of zinc oxide nanoparticles were obtained. The ZnO nanoparticles so obtained were preserved in the air-tight bottles for characterization purpose.

(ii) Chemical method

Zinc acetate (Zn (CH₃COO)₂, 2H₂O), thiourea ((NH₂)₂CS) and ammonia (25% NH₃) was used as the starting materials, for the preparation of the ZnO samples. The samples were prepared by dissolving zinc acetate, thiourea and ammonia in deionised water, separately. The chemical bath technique was used. Zinc acetate, thio-urea and ammonia solutions were mixed at ratio of 1:1:1 and rapidly heated to 80°C stirring it continuously. The prepared ZnO nanoparticles were washed with acetone, ethanol and deionized water. All the reagents of AR-grade were used without further purification.

The morphologies and sizes of as prepared ZnO nanoparticles were determined by X-ray diffraction using Cu Kα radiation (λ = 1.5418 Å). Rigaku Rotating Anode (H-3R) diffractometer was used for X-ray diffraction patterns. XRD data were collected over the range 20°– 70° at room temperature. For scanning electron microscope (SEM), JSM – 5,600 LV was used. Absorption spectra of the samples prepared was recorded with the help of Perkin Elmer Model Lambda 950 UV-VIS spectrophotometer. The FTIR spectra were recorded by the help of FTIR spectrometer (SHIMADZU) in the range of 500 cm⁻¹ to 4,000 cm⁻¹. For PL measurements Perkin Elmer spectrofluorophotometer Model LS 45 was used.

3. Results and Discussions

Figure.1 (a) XRD of nanoZnO by Chemical method (b) XRD spectra of nano ZnO by green method.
The crystal structure and purity of ZnO nanoparticles were characterized by X-ray diffraction (XRD) studies. Figure 1a shows the XRD pattern of the nano ZnO synthesized by chemical method. From the above figure it could be inferred that the synthesized ZnO nanoparticles are in pure phase, i.e. no impurities are seen in the XRD pattern. The peaks obtained at 2θ values of 31.62, 34.33, 36.12, 47.33, 56.31, 62.64, 66.03, 67.64, and 68.73 can be attributed to the planes (100), (002), (101), (102), (110), (103), (200) and (112), (201) respectively. All the peaks are in good agreement with hexagonal wurtzite structure of ZnO well matched with standard data (JCPDS 36-1451). Broadening in the XRD peaks could be seen very clearly, which confirms the nanocrystalline nature of zinc oxide. Figure 1b shows XRD pattern of ZnO nanoparticles by green synthesis method. Broad diffraction peaks were observed for eco-friendly method with one extra peak attributed to plane (001) obtained at 2θ value of 27.82, rest all other peak are slightly shifted towards lower angle side, which may be due to increasing lattice strain and interplanar spacing [24,25]. The broadening occurs in all the peaks. This is due to the smaller particle size and large number of crystal planes. The intensity in the signal of their diffraction patterns is reduced due to broadening of peaks. The XRD result indicates green synthesized ZnO nanoparticles have enhanced crystallinity than chemical method.

For both the samples the average crystallite size was determined from the XRD pattern parameters using Debye Scherrer equation \( D = \frac{k\lambda}{\beta \cos \theta} \), where \( D \) is the average crystallite size, \( k \) is Scherrer's constant equal to 0.90, \( \beta \) is the full-width at half-maximum (FWHM), and \( \theta \) is the Bragg's angle [26]. The broadening in peaks due to crystal imperfection, distortion and strain was calculated using the formula \( \varepsilon = \beta \tan \theta \) [27].

| Samples          | Lattice Parameter (Å) | d spacing | Lattice Strain | Crystallite Size |
|------------------|-----------------------|-----------|----------------|-----------------|
| Chemical Method  | 3.264 Å               | 5.228 Å   | 2.4992         | 0.1782          | 63nm            |
| Green Method     | 3.243 Å               | 5.209 Å   | 2.4763         | 0.1964          | 38nm            |

Table 1 shows the lattice parameter, crystallite size, d-spacing and lattice strain of ZnO nanoparticles synthesized from chemical and green method. The crystallite size of the chemically synthesized ZnO was found to be 63nm, whereas, the size of ZnO synthesized by green method was found 38nm.

The Morphology of synthesized ZnO nanoparticles was investigated by scanning electron microscopy. Figure 2 (a and b) shows the SEM image of ZnO synthesized from chemical and green method respectively. The sample of ZnO synthesized the chemical method shows the distinctive and abundant flower-shaped structure, which were principally the ZnO nanoparticles. There are huge hexagonal arrays of nanoparticles assimilated to form flower-shaped bundles. It can be seen that many of the particles are agglomerated, this is due to the formation of ZnO nanoparticles during first few minute of the experiment and later these particles agglomerates and their size becomes larger. The average particle sizes obtained from SEM images was ~ 65 nm. The SEM patterns agree well with the XRD results in terms of both size and shape. In the figure 2(b), highly agglomeration of particles is clearly seen. The average size of these synthesized non spherical powder ZnO nanoparticles is ~ 40 nm. Many of the particles are in the range less than 30nm. The hexagonal structure is not clearly visible for the sample prepared by green synthesis. As seen from the SEM images, green ZnO nanoparticle has lower particle size than the chemically synthesized ZnO nanoparticles. The change in morphology observed is due to green synthesis and natural capping agent.
Figure 2. (a) SEM of ZnOnano by Chemical method, (b) SEM of nanoZnO by green method.

![SEM images](image)

Figure 3 Absorption spectra of samples synthesized by Chemical and Green method.

![Absorption spectra graph](graph)

The UV–visible absorption spectra of ZnO nanoparticles synthesized by chemical method and by green synthesis as a function of wavelength are shown in Figure 3. In both the cases, the absorption band shows a blue shift due to the quantum confinement effect, as compared with the bulk. This optical phenomenon indicates that these nanoparticles have a quantum size effect [28]. Figure 3 shows the optical absorption spectra of the nanoZnO measured between 240 nm- 400 nm. It was found that the spectra are featureless and very less absorption occurs in the visible region. The absorption peak for the synthesized nanoZnO by chemical method was recorded at 284 nm. The excitonic absorption peak of ZnO nanoparticle synthesized by green method was found at 274 nm, which lies much below the band gap wavelength of 388 nm of bulk ZnO [29]. The peak at ~274 nm is due to inter band transition of electrons from the more inner shell to the uppermost shell. It is possible that, due to aggregation and agglomeration, particle size...
increases and material settled down at the bottom of container causing decrease in the absorbance [30]. This type of behavior is typical for many semiconductors due to internal electric fields within the crystal and inelastic scattering of charge carriers by phonons [31, 32].

Absorption coefficient ($\alpha$) associated with the strong absorption region for both the samples of nanoZnO were calculated from absorbance ($A$) and the sample thickness ($t$) using relation $\alpha = \frac{2.303A}{t}$. The Tauc relation $\rightarrow (\alpha h\nu)^{1/n} \approx (h\nu - E_g)$, was used to calculate optical band gap of ZnO nanoparticles, where, $\alpha$ is the absorption coefficient, $h\nu$ is the energy of incident photons and the value of $n$ depends upon the type the transition which may have $1/2$, $2$, $3/2$ and $3$ values corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively. The characteristic absorption edge reflects the band gap of the material. The band gap calculated from the above data was $\sim 4.36$ eV for the sample prepared by chemical method and the band gap for ZnO nanoparticles synthesized by green method was found to be $\sim 4.52$ eV. In both cases the optical band gap was found higher than standard value $3.54$ eV. The increase in the band gap of the ZnO nanoparticles with the decrease in particle size may be due to a quantum confinement effect.

FTIR is an effective method to reveal the composition of products. The composition of the samples and the presence of various bonds were studied. Figure 4 (a) and 4(b) shows the FTIR spectra of the ZnO nanoparticles prepared by chemical and ZnO nanoparticles by green synthesis respectively. Both the figures show a smooth similar curve having little difference. The peak around 501 and 540 cm$^{-1}$ are assigned to the Zn-O band in both the cases. In figure 4a bands around 1200 cm$^{-1}$ and 1100 cm$^{-1}$ are due to the characteristic frequency of inorganic ions. The absorption peak of the S-H vibration at 2,450–2,465 cm$^{-1}$ is not observed in the IR spectrum of green synthesis (Figure 4b), indicating that the thiourea molecules were bound to the ZnO nanoparticle surface. A comparative strong peak was observed at 1086 cm$^{-1}$, which is because of C-O stretching of the capping agent. The broad peak in the higher energy region at 3439 cm$^{-1}$ is due to OH stretching and the peak at 1625 cm$^{-1}$ is due to OH bending of adsorbed moisture in the sample and all the other peaks are attributed to the characteristic of the material.

Figure 4 (a) FTIR of ZnO nano by Chemical method, (b) FTIR of nano ZnO by green method.
Figure 4(b) show characteristic peaks at 511, 591, 671, 712, 826, 921, 1,058, 1,146, 1,386, 1,460, 1,638, 1,787, 2,448, 2,801, 3,450 cm–1 and some other associated peaks. The bands around 501 and 640 cm–1 are assigned to the Zn-O band. Similar investigations reported earlier shows that metal oxides give absorption bands in the fingerprint regions below 1000 cm–1 arising from inter-atomic vibrations [33]. A strong intensity band at 1,058 cm–1 may be due to S-O-C stretching. The stretching vibrations assigned to the C-S linkage occur in the region of 800–600 cm–1 and the weak S-S stretching vibration falls between 600 - 400 cm–1. The peak at 1600-1700 cm–1 may be due to nitrogen–oxygen interaction. The distinct peaks at 1386 cm–1 and 1146 cm–1 are due to phosphorus–oxygen interaction, establishing the presence of covalently bonded phosphates on ZnO nanoparticles. The broad absorption peak at 3450 cm–1 can be attributed to the characteristic absorption of hydroxyl group.

Figure 5. Photoluminescence spectra of samples by Chemical and Green synthesis.

Study of the photoluminescence (PL) is an interesting property of material that can provide valuable information on the purity and quality of the material. Luminescence studies provide information regarding defect states. PL studies may reveal the shift in defect states or the change in the density. Figure 5 shows the room temperature PL spectrum of the ZnO nanoparticles prepared by chemical method as well as by green synthesis method recorded in the range 420 nm-700 nm. The PL measurements were recorded at excitation wavelength of 370 nm. Only one broad peak was found for both the samples. Stoke’s shift in the peak was observed, the PL peak was obtained at 445 nm for green synthesis sample, whereas, the peak at 469 nm was found for chemically synthesized sample. This PL emission shifts towards smaller wavelength is due to the decrease in the size of the sample, which are in good agreement to the XRD and SEM results. This PL spectra may be because of the electron–hole recombination at a deep level emission in the band gap caused by intrinsic point defects and surface defects, e.g., oxygen vacancies, zinc interstitials, and the incorporation of hydroxyl groups in the crystal lattice during solution growth [34]. The broad band luminescence for both ZnO nanoparticles is related to transitions from donor states to deep acceptor states.
4. Conclusions
The nanoparticles of ZnO have been successfully synthesized by a simple chemical reaction using aqueous medium; in which thiourea was used as the capping agent and by green synthesis using leaves extract of OcimumTenuiflorum (Tulsi). The XRD pattern indicated the growth of the ZnO nanoparticles in hexagonal phase. The crystallite size measured by XRD pattern was found to be 63nm by for chemically synthesized ZnO and 38nm for ZnO sample prepared by green synthesis. SEM images showed interesting flower like structure and agglomeration of nanoparticles prepared by chemical synthesis. The SEM photograph also shows that the particle sizes are bigger for chemically synthesized samples. The blue-shift in absorption spectra was observed for the sample prepared by green synthesis. The solid-state theory based on the delocalized electron and hole within the confined volume explains the blue-shifted optical absorption spectra. The FTIR spectra inferred that the stabilizing agent passivated the surface of the particles. Prominent IR peaks were analyzed and assigned. The PL spectra showed blue shift for the sample prepared by green synthesis. Results revealed that the ZnO nanoparticles synthesized by green route shows enhanced structural and optical properties than chemically synthesized ZnO nanoparticles.

References
[1] Chaturvedi S, Dave P N and Shah N K 2012 J. Saudi Chem. Soc. 16 307 -325
[2] Sharma D, Rajput J, Kaith BS, Kaur Mohinder and Sharma Sapna 2010 Thin Solid Films 519 1224–1229
[3] Hussein J, El-Banna M, Razik T A and El-Naggar M E 2018 Int. J. Biol. Macromol 107 748-754
[4] Wang L, Kang Y, Liu X, Zhang S, Huang W and Wang S 2012 Sens. Actuators B: Chem. 162 237–243
[5] Cross SE, Innes B, Roberts MS, Tsuzuki T, Robertson TA and McCormick P 2007 Skin Pharmacol. Physiol. 20 148–154
[6] Zhou J, Xua N and Wang Z L 2006 Adv. Mater. 18 2432–2435
[7] Rasmussen J W, Martinez E, Louka P and Wingett D G 2012 Exp. Opin. Drug. Deliv. 7 1063–1077
[8] Shaheen T I, El-Naggar M E, Abdelgawad A M, Hebeish A 2016 Int. J. Biol. Macromol. 83 426-32
[9] Lobiak E V, Shlyakhova E V, Bulusheva L G, Plyusnin P E, Shubin Yu V and Okotrub A V J. Alloys and Compounds 621 351-356
[10] Cho J M, Song J K and Park S M 2009 Bulletin Korean Chem. Soc. 30 1610-1618
[11] Wang C, Shen E, Wang E, Gao L, Kang Z, Tian C, Lan Y and Zhang C 2006 Current Appl. Phys. 6 499-502.
[12] Hasnidawani J N, Azlina HN, Norita H, Bonnia N N, Ratim S and Ali E S Procedia Chemistry 19 211-216
[13] Kharisssova OV, Rasika HV, Kharisov D B I, Perez B O and Jimenez Perez V M 2013 Trends in Biotechnology 31 240-248
[14] Kumari B, Sharma S, Singh N, Verma A, Satsangi V R, Dass S and Shrivastav R 2014 Int. J. Hydrogen Energy 39 18216–18229
[15] Ambika S and Sundrarajan M 2015 J. Photochem. Photobiol. B Biol. 149 143–148
[16] Kavitha K, Paulpandi M, Ponraj T, Murugan K, Sumathi S 2016 Karbala Int. J. Mod. Sci. 2 46–55
[17] Ravikumar S, Gokulakrishnan R and Boomi P 2012 Asian Pacific J. Trop. Dis. 2 85–89
[18] Kumar B, Smita K, Cumbal L and Debut A 2014 J. Saudi Chem. Soc. 21 605–609
[19] Haverkamp RG and Marshall AT 2009 J. Nanoparticle Research 11 1453-1463
[20] Kumar B, Smita K, Cumbal L and Debut A J. Saudi Chem. Soc. 18 364-369
[21] Raliya R, Tarafdar J C 2013 Agric. Res. 2 48–57
[22] Kadhim Q A, Alwan R M, Ali R A, Jassim A N 2016 Nanosci. Nanotechnol. 6 1–5
[23] Jamdagni P, Khatri P, Rana J S 2016 *J. King Saud Univ Sci.* 30 168-175
[24] Kumar S, Asokan K, Singh RK, Chatterjee S, Kanjilal D, Ghosh A K 2014 *RSC Adv.* 4 62123 - 62131
[25] Bindu P and Thomas S 2014 *J. Theor. Appl. Phys.* 8 123 – 134
[26] Sharma R, Dhoble S J, Bisen D P, Brahme N and Chandra B P 2011 *Int. J. Nanoparticles* 4 64 - 76
[27] Varol S F, Babür G, Çankaya G, Kölemen U 2014 *RSC Adv.* 4 56645 -56653
[28] Huang M H, Mao S, Feick H, Yan H, Wu Y, Kind H, Weber E, Russo R and Yang P D 2001 *Science* 292 1897–1899
[29] Kumbhakar P, Singh D, Tiwary C S, Mitra A K 2008 *Chalcogenide Letters* 5 387-394
[30] Moss T S, Burrell G J and Ellis B 1973 *Semiconductor Opto-Electronics*, Butterworth & Co. Ltd.
[31] Honsi H M, Fayek S A, Al-Sayed S M, Roushdy M and Soliman M A 2006 *Vacuum* 81 54-58
[32] Sawby A, Selim M S, Marzouk S Y, Mostafa M A and Hosny A 2010 *Physica B, Physics of Condensed Matter* 405 3412-3420
[33] Kwon Y, Kim K, Lim C and Shim K 2002 *J. Ceramic Processes* 3 146–149
[34] Xu S and Wang Z 2011 *Nano Research* 4 1013- 1098