

## Journal of Pharmacognosy and Phytochemistry

Available online at www.phytojournal.com



E-ISSN: 2278-4136 P-ISSN: 2349-8234 JPP 2019; 8(3): 1095-1101 Received: 22-03-2019 Accepted: 24-04-2019

#### Manjunatha RL

Soil Health and Analytical Department, DSCiGN BIOSYS Pvt. Ltd., #91/2, Near Isha Cashew Factory, Kumbalagodu Industrial Area 2<sup>nd</sup> Phase Dodda Aladamara Road, Gerupalya, Bangalore, Karnataka, India

#### Usharani KV

Soil Health and Analytical Department, DSCiGN BIOSYS Pvt. Ltd., #91/2, Near Isha Cashew Factory, Kumbalagodu Industrial Area 2<sup>nd</sup> Phase Dodda Aladamara Road, Gerupalya, Bangalore, Karnataka, India

#### Dhananjay Naik

Soil Health and Analytical Department, DSCiGN BIOSYS Pvt. Ltd., #91/2, Near Isha Cashew Factory, Kumbalagodu Industrial Area 2<sup>nd</sup> Phase Dodda Aladamara Road, Gerupalya, Bangalore, Karnataka, India

Correspondence Manjunatha RL

Soil Health and Analytical Department, DSCiGN BIOSYS Pvt. Ltd., #91/2, Near Isha Cashew Factory, Kumbalagodu Industrial Area 2<sup>nd</sup> Phase Dodda Aladamara Road, Gerupalya, Bangalore, Karnataka, India

# Synthesis and characterization of ZnO nanoparticles: A review

#### Manjunatha RL, Usharani KV and Dhananjay Naik

#### Abstract

Zinc oxide is an inorganic compound and usually appears as a white powder. It also called a multifunctional material because of to its unique physical and chemical properties. Zinc oxide nanoparticles were successfully synthesized by a sol-gel method, precipitation method, green leaf extract, and microwave method, wet chemical and hydrothermal method. Different compositions of zinc oxides nano composites were characterized using X-Ray Diffractometer, Scanning Electron Microscope, Transmission Electron Microscope, Fourier Transform Infrared spectrometer and Photoluminescence Spectrofluorophotometer studies. The X-ray diffraction studies reveals that the synthesized ZnO nanoparticles have wurtzite structure and the particle size varies from 20 to 30 nm. Scanning Electron Microscopic investigation reveals that the surface morphology of ZnO nanoparticle is spherical in hydrothermal process and varies to flower like arrangement in sol-gel process. Crystalline oxide powders, combined with other materials, provide possibilities for obtaining improved chemical, mechanical, optical or electrical properties.

Keywords: Nanoparticles, zinc oxide (ZnO), synthesis, characterization

#### Introduction

Nano means one-billionth, thus nanotechnology deals with materials measured in a billionth of a meter. A nanometer is 1/80,000 the diameter of a human hair or approximately ten hydrogen atoms wide. Nanotechnology is the science of very small things. But nanotechnology is not just involved with small things. Nanotechnology is a multi-disciplinary science. It includes knowledge from biology, chemistry, physics and other disciplines. Nano technology as the manipulation or self-assembly of individual atoms, molecules or molecular clusters into structures to create materials devices with new or vastly different properties. Zinc oxide is an inorganic compound with the formula ZnO. It usually appears as a white powder, nearly insoluble in water. Zinc oxide, with its unique physical and chemical properties, such as high chemical stability, high electrochemical coupling coefficient, broad range of radiation absorption and high photo stability, is a multifunctional material. In materials science, zinc oxide is classified as a semiconductor in group II-VI, whose covalence is on the boundary between ionic and covalent semiconductors. A broad energy band (3.37 meV), high bond energy (60 meV) and high thermal and mechanical stability at room temperature make it attractive for potential use in electronics, optoelectronics and laser technology. The piezo- and pyroelectric properties of ZnO mean that it can be used as a sensor, converter, energy generator and photocatalyst in hydrogen production. Because of its hardness, rigidity and piezoelectric constant it is an important material in the ceramics industry, while its low toxicity, biocompatibility and biodegradability make it a material of interest for biomedicine and in pro-ecological systems.

#### ZnO Nanoparticles synthesis by Sol-Gel route

In the characteristic sol-gel method, the development of colloidal solution in the form of 'SOL' and their transformation into aqueous alkaline / acidic phase as 'GEL' takes place. This transformation is an important step in the development of particle formation, which is responsible for its vast tendency of various properties metamorphosized at nano-level. The different types of precursors, capping agents are used along with the presence of acidic or basic ion-carriers following with hydrolysis, stirring, condensation, etc during the process. Nipane *et al.* (2012) <sup>[19]</sup> obtained the ZnO-Nps of size about 50-100 nm. The spherical-flower shaped ZnO-Nps also exhibited admirable UV shielding and transparency properties. Chen *et al.* (2012) <sup>[10]</sup> produced blue-emitting ZnO Nanoparticles by sol-gel process at the optimal

annealing temperature and time of about 100 °C and 0.5 h, respectively. They claimed the

hexagonal wurtzite structure with diameter range from 17.42 to 25.8 nm.

Sharma et al. (2012)<sup>[31]</sup> synthesized the ZnO Nanoparticle via sol-gel route and also reported the effect of surface groups on the luminescence property of the synthesized ZnO-Nps. Liu et al. (2011)<sup>[17]</sup> developed the size controlled ZnO quantum dots (QD) using sol-gel technique by means of photo-induced desorption. Erol et al. (2010) [13] synthesized ZnO-Nps of diameter 10 nm and investigated the humidity adsorption and desorption kinetics by quartz crystal microbalance technique (QCMT). Tokumoto et al. (2003) [36] studied the chemical and structural behaviour of ZnO powders synthesized with sol-gel route and highlighted the dependency of temperature and nature of catalyst used in the hydrolysis step of the process. Cheetham et al. (1997)<sup>[9]</sup> reviewed the use of the in-situ methods for studying the materials syntheses from sol-gel precursors and he emphasized on the formation of the crystalline phases from solid gel precursors.

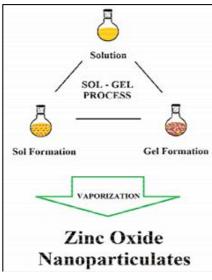


Fig 1: Sol-Gel Process

The sol-gel method was also used to obtain nanocrystalline zinc oxide by Ristic et al. (2005) [28] A solution of tetramethyl ammonium hydroxide (TMAH) was added to a solution of zinc 2-ethylhexanoate (ZEH) in propan-2-ol. The resulting colloidal suspension was left for 30 min (alternatively for 24 h), and was then washed with ethanol and water. TMAH is a strong organic base, which comparably with an inorganic base (e.g., NaOH) is characterized by a pH of ~14. This high pH means that metal oxides are not contaminated with the cation from the base, which may have an effect on the ohmic conductance of the oxide material. A determination was made of the effect of the quantity of ZEH used and the maturing time of the colloidal solution. TEM images showed that the ZnO particles obtained have sizes of the order of 20-50 nm. The quantity of ZEH has a negligible effect on the particle size. Zinc oxide nanoparticles synthesized by sol-gel method using zinc acetate and methanol as precursors. In the preparation, 16 g of zinc acetate was dissolved in 112 ml of methanol. After 10 minutes of magnetic stirring at room temperature the resultant solution was subjected to gellation at 80 °C with constant stirring for 5 hours, from which the zinc oxide nanomaterials in the form of powder was obtained. The resultant powder was annealed at 450 °C for 6 hours (Brintha and Ajitha, 2015)<sup>[8]</sup>. Alias et al. (2010)<sup>[1]</sup> reported that ZnO nanoparticles were processed at different pH values by the sol-gel process and centrifuged at 3000 rpm within 30 minutes. The ZnO powders agglomerate when synthesized in acidic and neutral conditions (pH 6 and 7). They stated that Fine powders were obtained when the pH of the sols was increased to 9. The maximum crystallite size of the ZnO powder was obtained at pH 9. The particles sizes of the ZnO synthesized ranged between pH 6 and 11 were in the range of 36.65–49.98 nm. Ultraviolet–visible studies (UV–vis) also revealed that ZnO processed ranging from pH 8 to 11 has good optical properties with band gap energy between 3.14 and 3.25 eV.

#### ZnO Nanoparticles synthesis by Hydrothermal route

In the characteristic hydrothermal method, the growth of crystallites occurs at high temperatures and at high pressures, performed in the presence of autoclaves. The different works related to ZnO Nanoparticles syntheses via hydrothermal route, performed by different groups. Sun et al. (2010) [34] reported the facile hydrothermal synthesis of ZnO structures with diverse morphologies viz. flower-like, hexagonal spherelike, oblate-like, and hexagonal biprism-like. They found this as a result of the change in molar ratios of the reactants and the surfactant, TEA used in an alkaline environment of reactions. They have also reported an enhancement in the photocatalytic behaviour to the synthesized ZnO structures against the dye, methylene blue (MB). The series of ZnO three-dimentional (3D) structures with star-like, sphere-like, flower-like and sea urchin-like morphologies via hydrothermal route, in the absence of catalyst/template. They reported the ZnO 3D structures with strong emission peak at 405 nm and also a high sensitivity and selectivity for ethanol. Yi et al. (2008) <sup>[40]</sup> also synthesized flower-like ZnO microstructures with an average diameter of 1µm via hydrothermal route. They investigated the effect of hydrothermal temperature, reaction time, concentration of NaOH and TEA on morphology and size of the final products. Brintha and Ajitha (2015)<sup>[8]</sup> reported that synthesis of ZnO nanoparticles by hydrothermal method using zinc acetate and methanol as precursors. Zinc acetate (0.1 M) solution was prepared in 50ml methanol under stirring. To this solution 25ml of NaOH (0.2M) solution was added under continuous stirring. The solution was transferred into teflon lined sealed autoclaves and heated at 100 °C for 6 hours under autogenous pressure. It was then allowed to cool naturally to room temperature. After the reaction was complete, the resulting white solid product was washed with methanol, filtered and then dried in air in a laboratory oven at 60 °C.

### ZnO Nanoparticles synthesis by Microwave assisted route

The microwave-assisted techniques have gained a significant interest in the field of Nanotechnology as far as Inorganic compounds including oxide syntheses are concerned. Without any sophistication, along with minimum power consumption, the desired products at good rates and at enhanced proportions. This all leads to a superior impact over different characteristic qualities of the developed nanostructures. The different works related to ZnO Nanoparticles syntheses by microwave route, performed by different groups worldwide are presented as: Bilecka et al. (2009) [7] presented the microwave-assisted synthesis of ZnO Nanoparticles from zinc acetate and benzoyl alcohol. They also presented the kinetics and thermodynamical aspects of ZnO synthesis along with the comparison of microwave route and the conventional heating and reported the performance level of prior one accelerated. Zhu *et al.* (2008) <sup>[42]</sup> reported various hierarchical nanostructures of ZnO via microwave-assisted route. The various ZnO nanostructures accounted were straw-bundlelike, wide chrysanthemum-like, and oat-arista-like

morphologies and microspheres. Cho et al. (2008) [11] exhibited the morphology-controlled growth of ZnO nanoand microstructures via microwave irradiation. The structures including nano-rods, nano-candles, nano-needles, nano-disks, nano-nuts, micro-stars and micro-balls of Zinc oxide were synthesized at 90 °C and about 50 W microwave heating along with subsequent aging process. Sutradhar and Saha (2016) <sup>[35]</sup> reported that green synthesis of zinc oxide nanoparticles by thermal method and under microwave irradiation using the aqueous extract of tomatoes as non-toxic and also nature-friendly reducing material. They concluded that microwave-assisted green chemistry has been used for the preparation of ZnO NPs. A facile approach has been reported using tomato extract, acting as reducing agent for the synthesis of ZnO NPs of well-defined dimensions in huge amount. This eliminated the need of toxic chemicals for the production of nanoparticles. The synthesis has been done by thermal process as well as under microwave irradiation using different power and the synthesized nanoparticles was successfully used to prepare nano-composites for photovoltaic application.

#### ZnO Nanoparticles synthesis by Precipitation method

Zinc sulfate (1.5 mol/l) and ammonium bicarbonate (2.5 mol/l) were prepared in distilled water and 100 ml ZnSO<sub>4</sub> solution was added to 126 ml NH<sub>4</sub>HCO<sub>3</sub> solution while stirring and the reaction mixture was kept at 45 °C. The slurry of basic zinc carbonate (BZC) in the form of a white precipitate was obtained. It was then filtered, washed and dried. Finally zinc oxide nanoparticle was prepared by calcining the precipitate at 500 °C for 1 hour. In this process, the reaction of Zn ions and ammonium acid carbonate proceeds according to the equation 1.

$$5ZnSO_4 + 10NH_4HCO_3 \longrightarrow Zn5 (OH)_6 (CO_3)_2 (S) + 5 (NH_4)_2SO_4 + 8CO_2 \uparrow + 2H_2O.... (1)$$

The complex formed decomposes upon calcining to ZnO according to the equation 2.

$$Zn5(OH)_6(CO_3)_2 \longrightarrow 5ZnO + 2CO_2\uparrow + 3H_2O\uparrow....(2)$$

#### ZnO Nanoparticles synthesis by Green method

Janjal et al. (2017) reported that zinc oxide nanoparticles were prepared by leaf extract of guava plant. For Preparation of leaf extract of guava plant: The leaves of guava (10 mg) were thoroughly washed, dried and then boiled in 100ml distilled water for 15 min. The resultant extract was cooled, filtered using Whatman No. 1 filter paper and used as the extract solutions. In this method, 0.02 M solution of zinc acetate (50ml) was taken and 2ml leaves extract was added drop-wise and the resulting mixture was stirred for 10 minutes. The pH of the mixture was maintained at 12 by adding 1M NaOH drop-wise and the solution was stirred continuously for 2 hr. A pale white precipitate resulted which is washed by distilled water 2-3 times followed by ethanol, filtered and dried at 50°C overnight in oven. Pale white powder of zinc oxide nanoparticles was store for characterization. Coriandrum sativum leaf was used for the synthesis and characterization of ZnO nanoparticles prepared by green and chemical technique. The average size was found to be 66 nm in green synthesis method while the size was 81nm in the chemical method. The ZnO nanoparticles prepared from Coriandrum leaf extract were expected to have more extensive application in biotechnology, sensors, medical, catalysis, optical devices, DNA labeling, drug delivery and water remediation Thambavani, [14] (Gnanasangeetha and 2013) The antibacterial activity towards human bacterial and plant pathogens showed good sensitivity towards the green synthesized ZnO-NPs at all concentrations. The size of the particles ranged from 100 to 200 nm. The study indicated that the C. procera ZnO nanoparticles had strong antimicrobial activity against the tested human and plant bacterial pathogens along with the fungal pathogens (Poovizhi and Krishnaveni, 2015) [22]. The synthesis of Zinc oxide nanoparticles was reported with the leaf extract of Oleaeuropea. The average size of particles was found to be 500 nm and the thicknesses was about 20 nm by SEM studies. FT-IR analysis of aqueous Olea europea leaf extract indicated the presence of phytoconstituents such as amines, aldehydes, phenols and alcohols which were the surface active molecules stabilizing the Zinc oxide nanosheets (Awwad et al., 2014)<sup>[3]</sup>.

The synthesized ZnO-NPs were evaluated for the antibacterial activity against *Bacillus thuringiensis*, *Escherichia coli*, *Staphylococcus aureus* and *Pseudomonas aeuroginosa*. The highest antimicrobial activity was observed against *Pseudomonas aeuroginosa* followed by *Staphylococcus aureus* (Bhumi and Savithramma, 2014)<sup>[5]</sup>. The synthesis of Zinc oxide nanoparticles with the leaf extract of *Adhatodavasica*. The Synthesized ZnO-NPs were found to be discoid in shape with an average size of 19 - 60 nm. Phytochemicals present in the plant were responsible for the quick reduction of Zn+ ion to metallic Zinc Oxide nanoparticles (Bhumi *et al.*, 2014)<sup>[6]</sup>.

Bala et al. (2015)<sup>[4]</sup> reported the synthesis of Zinc oxide nanoparticles from the leaf extract of Hibiscus subdariffa. The synthesized ZnO nanoparticles had potential anti-bacterial agents which have been studied on Escherichia coli and Staphylococcus aureus. The Zinc oxide nanoparticles were synthesized from the leaf extract of Tanners cassia (Cassia auriculata). The synthesized Zinc oxide nanoparticles were confirmed by SEM, UV- Vis Spectrophotometer and FTIR. The SEM studies revealed that the synthesized ZnO-NPs were spherical in shape (Ramesh et al., 2014a)<sup>[23]</sup>. The Zinc oxide nanoparticles were synthesized with the leaf extract of green tea (Camellia sinensis). Amrita et al. (2015)<sup>[2]</sup> reported that the plant leaf extract of Brassica oleraceae was used for the synthesis of Zinc oxide nanoparticles. The particles were spherical and sheet shape. The experimental results showed that the diameters of prepared nanoparticles in the solution had sizes between 1 and 100 nm. The whole plant body of Brassica oleraceae had possessed approdisiac activities, and it had a significant role in maintaining maleness. The nanoparticles showed antibacterial activity against both Gram-positive and negative bacteria. The antibacterial activities increased as the concentration of Zinc oxide nanoparticles increased. The synthesized Zinc nanoparticles were applied on Arachis hypogaea L (peanut) pot-culture to estimate soil microbial population, soil exo-enzyme activities and physiological growth parameters of the peanut plants. Zinc nanoparticles applied to the peanut pot-culture exhibited good soil microbial and enzyme activities by showing significant variations compared to the control and enhanced the physiological growth parameters of peanut plants (Sindhura *et al.*, 2015)<sup>[32]</sup>.

The Zinc oxide nanoparticles were synthesized with the leaf extract of Aloe vera. The particles were a hexagonal shape with an average size of 22.18 nm. Photodegradation and antibacterial activity of the nanoparticles were studied. The antibacterial studies of synthesized nanoparticles showed sensitivity to both Gram positive and Gram negative bacteria (Varghese and George, 2015)<sup>[38]</sup>. The green synthesis of Zinc oxide nanoparticles by using peel extract of Punica granatum. The particles were spherical and square in shape with a diameter range of 50-100 nm (Mishra and Sharma, 2015)<sup>[18]</sup>. The flower extract of Trifolium pratense was used for the synthesis of Zinc oxide nanoparticles. The synthesized ZnO nanoparticles were agglomerated with a particle size ranging from below 100 to 190 nm. ZnO nanoparticles synthesized from T. pratense flower extract showed effective antibacterial activity against all tested strains (Dobrucka and Dugaszewska, 2015) <sup>[12]</sup>. The Synthesis of Zinc oxide nanoparticles with the milky latex extract of Calotropis procera. The morphology of ZnO NPs embedded in calotropis matrix with little agglomeration having sizes about 5 nm throughout the carbon coated copper grid, and average particle size was in the range of 5-40 nm (Ravindra et al., 2011)<sup>[27]</sup>.

#### ZnO Nanoparticles synthesis by Wet chemical method

The Synthesis of zinc oxide nanoparticles by wet chemical method using zinc nitrate and sodium hydroxides precursors and soluble starch as stabilizing agent. Different concentrations of soluble starch (0.1%), were dissolved in 500 ml of distilled water by using microwave oven. Zinc nitrate, 14.874 g (0.1 M), was added in the above solution. Then the solution was kept under constant stirring using magnetic stirrer to completely dissolve the zinc nitrate for one hour. After complete dissolution of zinc nitrate, 0.2 M of sodium hydroxide solution was added under constant stirring, drop by drop touching the walls of the vessel. The reaction was allowed to proceed for 2 h after complete addition of sodium hydroxide. After the completion of reaction, the solution was allowed to settle for overnight and the supernatant solution was then discarded carefully. The remaining solution was centrifuged at 10,000 rpm for 10 min and the supernatant was discarded. Thus obtained nanoparticles were washed three times using distilled water.

Washing was carried out to remove the byproducts and the excessive starch that were bound with the nanoparticles. After washing, the nanoparticles were dried at  $80^{\circ}$ C for overnight. During drying, complete conversion of Zn(OH)<sub>2</sub> into ZnO takes place.

Raut and Thorat (2015) <sup>[25]</sup> studied on preparation, characterization and application of zinc oxide nanoparticles by leaves extract solution and boiled upto  $60^{0}$ -80 <sup>o</sup>C by using a stirrer-heater. When temperature of solution reached at  $60^{\circ}$ C then 5 grams of Zn(NO<sub>3</sub>)<sub>2</sub> were as added to the solution. The mixture was then boiled upto reduce to a deep yellow coloured paste. This paste then collected in a ceramic crucible. This paste heated in an air heated furnace at 300 <sup>o</sup>C for 120 min. A light yellow coloured powder was prepared and this was carefully collected. The powder was mashed in a mortar-pestle so as to get a finer nature for characterization. Sivakumar *et al.* (2011) worked on biosynthesis of silver nanoparticles from AgNO<sub>3</sub> solution and using *Calotrophis gigantean* leaf. In biosynthesis method *Calotrophis gigantean* leaf acted as a reducing agent. Vafaee *et al.* (2007) <sup>[37]</sup> worked

on synthesis and characterization of zinc oxide nanoparticles using sol-gel method. By using this method they synthesized spherical shape ZnO nanoparticles. They utilized first time triethanolamine (TEA) as a surfactant. Yiamsawas *et al.* (2009) <sup>[41]</sup> prepared zinc oxide nanostructures by using solvothermal method. They utilized PVP, ethanol, and zinc acetate dehydrate. All this chemical treated in sealed polypropylene vessel heated in autoclave.

## Characterization of ZnO Nanoparticles X-Ray Diffractometer (XRD)

X-ray diffraction is a versatile, non-destructive analytical method for identification and quantitative determination of various crystalline forms, known as 'phases' of compound present in powder and solid samples. Diffraction occurs as waves interact with a regular structure whose repeat distance is about the same as the wavelength. The phenomenon is common in the natural world, and occurs across a broad range of scales. For example, light can be diffracted by a grating having scribed lines spaced on the order of a few thousand angstroms, about the wavelength of light. It happens that Xrays have wavelengths on the order of a few angstroms, the same as typical inter-atomic distances in crystalline solids. That means X-rays can be diffracted from minerals which, by definition, are crystalline and have regularly repeating atomic structures. When certain geometric requirements are met, Xrays scattered from a crystalline solid can constructively interfere, producing a diffracted beam. The X-ray diffraction of prepared ZnO nanostructures were done with the help of an X-ray Diffractometer, BRUKER AXS D8 ADVANCE (Germany) using X-ray beam with nickel filtered CuKa radiations of wavelength equal to 1.54 Å and with a step dimension of 0.01° and scanning speed of 0.02 steps/second. A fixed power generation of 40 kV and 40 mA was used. The nanoparticulate sizes were further calculated with the help of spectral peaks by Debye-Scherer formula:

D = 
$$k\lambda/\beta cos\theta$$

Where,

D	=	Crystallite size
k	=	proportionality constant (0.9)
λ	=	X-ray wavelength (1.54178 Å)
β	=	FWHM of XRD peaks
θ	=	Braggs' angle

The Synthesized zinc oxide nanoparticles were characterized using XRD, UV–VIS spectrum and FTIR. The average size of the nanoparticles calculated using XRD data was 16 nm (Senthilkumar and Sivakumar, 2014)<sup>[29]</sup> whereas Shah *et al.* (2015)<sup>[30]</sup> reported on green tea and synthesized Zn nanoparticles were characterized by UV-Vis Spectroscopy, Particle size analyzer, and SEM. Particles size analyzer determined the size of the particles and was found to be 853 nm in diameter. *Coriandrum sativum* leaf was used for the synthesis and characterization of ZnO nanoparticles prepared by green and chemical technique. The characterization of ZnO-NPs was carried out by XRD, SEM, FTIR, and EDAX. The average size was found to be 66 nm in green synthesis method while the size was 81nm in the chemical method.

#### **Scanning Electron Microscope**

The Scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals

at the surface of solid specimens. The signals that derive from electron sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. The investigation of the surface morphology, dimensional characteristics of Zinc Oxide nanostructures have been done with the help of nondestructive instrument called Scanning electron microscope. It also provides the details of crystal structures of the developed Nanostructures. The scanning of samples is performed in the presence of high-energy electron beam and magnification power (upto 5 lakhs times) is monitored by variation of V-I supply. They studied the different parameters of the sample overheaded on the sample holder viz. lengths, widths, forms, orientations, etc of the single crystals or of the colonies. The samples were made more viable when coated with gold sputtering. The different morphological aspects were recorded with the help of Scanning electron microscopy, JEOL JSM-6510 LV.

The synthesized Zinc oxide nanoparticles were characterized using SEM, EDAX and FT-Raman Spectroscopy. The SEM results showed that the particles were spherical in shape with an average size of 23 to 57 nm. The synthesis of Zinc oxide nanoparticles with the leaf extracts of Azadirachta indica and Emblica officinalis. The formed nanoparticles were characterized by SEM, FTIR, and EDAX for their morphology, size, crystallinity and percentage composition. The synthesized nanoparticles were found to be in the range of 100-200 nm by SEM results. The qualitative examination of the aqueous extracts of the leaf samples of Azadirachta indica and Emblica officinalis showed the presence of phytochemical constituents such as Alkaloids, Carbohydrates, Glycosides, Steroids, Flavonoids, Terpenoids, Tannins, and Steroids (Gnanasangeetha and Thambavani, 2014)<sup>[15]</sup>. Raut et al. (2013) [26] reported that synthesis of Zinc oxide nanoparticles with the leaf extract of Ocimumt enuiflorum. Prepared ZnO nanoparticles were characterized by XRD, SEM and FTIR. The SEM image showed hexagonal shape and nanoparticle with diameter range of 11-25 nm. Calotropis gigantea leaf extract was used for the synthesis of Zinc oxide nanoparticles. The synthesized Zinc nanoparticles were characterized using SEM and XRD. The synthesized nano crystallites of ZnO were in the range of 30-35 nm (Vidya et al., 2013). [39] Citrus aurantifolia fruits were used for the synthesis of Zinc oxide nanoparticles. The morphology structure and stability of the synthesized ZnO nanoparticles were studied using SEM, UV- Spectrophotometer, and FTIR. The particles were spherical in shape, and the size ranged from 9 to 10 nm in diameter. Citrus aurantifolia extract revealed the presence of phytoconstituents like alcohols, aldehydes, and amines (Ramesh et al., 2014b)<sup>[24]</sup>.

The plant leaf extract of neem (*Azadirachta indica*) was used for the synthesis of Zinc oxide nanoparticles. The synthesized ZnO nanoparticles were characterized using FTIR spectroscopy and SEM analysis. The SEM results revealed that the particles were spindle-shaped and their size were 50  $\mu$ m (Noorjahan *et al.*, 2015)<sup>[20]</sup>. The leaf extract of *Pyrus pyrifolia* was used for the synthesis of Zinc oxide nanoparticles. The structural, morphological and optical properties of the synthesized nanoparticles have been characterized by using UV–Vis spectrophotometer, XRD, FTIR, AFM, and FE–SEM with EDX analysis. The synthesized ZnO NP's were found to be almost spherical in shape with a particle size of around 45 nm. The photo catalytic study concluded that the bio–ZnO NPs had the efficiency to dye degrade methylene blue under solar irradiation (Parthiban and Sundaramurthy, 2015)<sup>[21]</sup>.

#### Transmission Electron Microscope (TEM)

The morphological characteristics and the size of the particle of the fabricated Zinc oxide nanostructure were studied with the help of Transmission Electron Microscope (TEM) with model no. JEOL JEM-2100 (Japan), featuring ultra high resolution and rapid data acquisition. The instrument was well operational with high energy electrons of 200kV class analytical TEM with a probesize under 0.5 nm. The goniometer stage gives ease of use in tilting, rotating, heating and cooling. This analytical machine has also been equipped with Scanning Transmission Electron Microscopy (STEM), Electron Energy Loss Spectroscopy (EELS) and Charge Coupled Device (CCD) cameras, magnetic lenses which could provide better magnification of images at nano-levels. The scattered electrons give a characteristic diffraction pattern of the Nanostructure samples, which helps in analysing their crystal structure. The synthesized Zinc oxide nanoparticles were characterized using UV-Visible Spectroscopy, FTIR, Particle size analyzer, XRD, SEM, TEM, and Inductively Coupled Plasma-Optical Emission Spectrophotometer. The average particle size of synthesized Zinc nanoparticles was found to be 53 nm. TEM data revealed the presence of triangular shaped and poly-dispersed zinc nanoparticles with a grain size of  $50 \pm 5$  nm (Parthiban and Sundaramurthy, 2015) [21]

#### Fourier Transform Infrared spectrometer (FTIR)

The Fourier transform infrared spectra were taken with the help of model Thermo Scientific Nicolet. The FTIR spectra are collected after the absorption of electromagnetic waves with the frequency range from 400 to 4000 cm<sup>-1</sup>. The FTIR spectrometer gathers the spectral information of a broad spectral region. The identification of various functional groups and chemical structures in the nanoscaled ZnO is made possible by absorption of electromagnetic waves at distinctive frequencies and intensities. Hence the different groups and structures show a typical characteristic band arrangement and geometry for ZnO nanostructures.

#### Photoluminescence Spectrofluorophotometer (PL)

The non-destructive, room temperature photoluminescence (PL) spectral study of nanoscaled Zinc oxide is performed with the help of SHIMADZU Photoluminescence spetrofluoro photometer having model no. RF 5301pc. The photoluminescence (PL) study is carried out by using a light source 150W Xenon lamp with the operation temperature range of 15-35 °C, humidity range of 40-80% (below 70% with temperature higher than 30°C) and the wavelength range of 220-900 nm. The PL spectral study is extensively employed for the determination of different materials properties *viz.* material bandgap, defects, etc. Here, the study performed to get the PL details of Zinc oxide nanostructure synthesized at different parametric conditions.

#### Thermo gravimetric analysis

Thermo gravimetric analyzer (TGA, Q-50, and TA Instruments) was used to study the thermal stability of ZnO. Approximately 5 mg of the samples were heated at the rate of 20  $^{\circ}$ C/min to 800  $^{\circ}$ C.

#### Conclusion

Zinc oxide is a multifunctional material because of its many interesting properties (piezo- and pyroelectric), a wide range

of UV absorption, and high photostability, biocompatibility and biodegradability. ZnO can also be obtained with a variety of particle structures, which determine its use in new materials and potential applications in a wide range of fields of technology. Zinc oxide nanoparticles were synthesized by different methods such as wet chemical method, sol-gel method, green leaf extract method, microwave and hydrothermal methods and the prepared nanoparticles were characterized by XRD, SEM, EDX, and UV. The crystallite size of the prepared zinc oxide nanoparticles varies from 25-30 nm. All the prepared nanoparticles showed wurtzite structure. SEM analysis, suggested different morphological structures from flower like arrangement to spherical shape. Chemical purity and stoichiometry of the samples were investigated by EDAX Spectroscopy in order to confirm the presence of Zinc and Oxygen. UV- Visible spectrum show blue shift in all the synthesized nanoparticles. Crystalline oxide powders, combined with other materials, provide possibilities for obtaining improved chemical, mechanical, optical or electrical properties.

#### References

- 1. Alias SS, Ismail AB, Mohamad AA. Effect of pH on ZnO nanoparticle properties synthesized by sol–gel centrifugation. Journal of Alloys and Compounds. 2010; 499(2):231-237.
- 2. Amrita R, Reena SL, Mohammad J, Kapil L. Antibacterial activity of Zinc oxide nanoparticles prepared from *Brassica oleraceae* leaves extract. International Journal of Advance Research. 2015; 3(11):322-328.
- 3. Awwad AM, Albiss B, Ahmad AL. Green synthesis, characterization and optical properties of Zinc oxide nanosheets using *Oleaeuro pea* leaf extract. Advances in Material Letter. 2014; 5(9):520-524.
- 4. Bala N, Saha S, Chakraborty M, Maiti M, Das S, Basu R *et al.* Green synthesis of Zinc oxide nanoparticles using *Hibiscus subdariffa* leaf extract: effect of temperature on synthesis, anti-bacterial activity and anti-diabetic activity. *RSC* Advances. 2015; 5(7):4993–5003.
- Bhumi G, Savithramma N. Biological Synthesis of Zinc oxide Nanoparticles from *Catharanthus roseus* (I.) *G. Don.* Leaf extract and validation for antibacterial activity. International Journal of Drug Development Research. 2014; 6(1):208-214.
- 6. Bhumi G, Raju YR, Savithramma N. Screening of Zinc oxide nanoparticles for cell prolifertaion synthesized through *Adhatoda vasica nees*. International Journal of Drug Development Research 2014; 6(2):97-104.
- 7. Bileck I, Elser P, Niederberger M. Kinetic and Thermodynamic aspects in the Microwave-assisted synthesis of ZnO nanoparticles in Benzyl alcohol. ACSNANO. 2009; 3:467-477.
- 8. Brintha SR, Ajitha M. Synthesis and characterization of ZnO nanoparticles via aqueous solution, sol-gel and hydrothermal methods. Journal of Applied Chemistry. 2015; 8(11):66-72.
- 9. Cheetham AK, Mellot CF. *In-situ* Studies of the Sol-Gel Synthesis of Materials. Chemistry Materials. 1997; 9:2269-2279.
- Chen Z, Lix X, Chen N, Wang H, Du GP, Suen AYM. Effect of annealing on photoluminescence of blueemitting ZnO nanoparticles by sol–gel method. Journal of Sol-Gel Science Technology. 2012; 62:252-258.

- 11. Cho S, Jung SH, Lee KH. Morphology-Controlled Growth of ZnO Nanostructures Using Microwave Irradiation: From Basic To Complex Structures. Journal of Physical Chemistry. 2008; 112:12769-12776.
- 12. Dobrucka R, Dugaszewska J. Biosynthesis and antibacterial activity of ZnO nanoparticles using *Trifolium pratense* flower extract. Saudi Journal of Biological Sciences. 2015; 4:1-7.
- Erol A, Okur S, Comba B, Mermer O, Arikan MC. Humidity sensing properties of ZnO nanoparticles synthesized by sol–gel process. Sensors and Actuators. 2010; 145:174-180.
- Gnanasangeetha D, Thambavani SD. One pot synthesis of Zinc oxide nanoparticles via chemical and green method. Research Journal of Material Science. 2013; 1(7):1-8.
- 15. Gnanasangeetha D, Thambavani SD. Facile and ecofriendly method for the synthesis of Zinc oxide nanoparticles using *Azadirachta* and *Emblica*. International Journal of Pharmaceutical Science and Research. 2014; 5(7):2866-2873.
- Janjal SM, Rajbhoj AS, Gaikwad ST. Synthesis and characterization of zinc oxide nanoparticles using green method. Research Journal of Chemical Science. 2017; 7(4):40-42.
- Liu Y, Morishima T, Yatsui T, Kawazoe T, Ohtsu M. Size control of sol–gel-synthesized ZnO quantum dots using photo-induced desorption. Nanotechnology. 2011; 22:215605-215615.
- 18. Mishra V, Sharma R. Green synthesis of Zinc oxide nanoparticles using fresh peels extract of *Punica granatum* and its antimicrobial activities. International Journal of Pharmaceutical Research and Health Science. 2015; 3(3):694-699.
- Nipane D, Thakare SR, Khati NT. ZnO nanoparticle by sol-gel and its UV application in cosmetics formulation. International Journal of Knowledge Engineering. 2012; 3:168-169.
- Noorjahan CM, Shahina SKJ, Deepika T, Rafiq S. Green synthesis and characterization of Zinc oxide nanoparticles from Neem (*Azadirachta indicia*). International Journal of Science and Engineering Technology Research. 2015; 4(30):5751-5753.
- Parthiban C, Sundaramurthy N. Biosynthesis, characterization of ZnO nanoparticles by using *Pyrus pyrifolia* leaf extract and their photocatalytic activity. International Journal of Innovative Research and Science Engineering Technology. 2015; 4(10):9710-9718.
- 22. Poovizhi J, Krishnaveni B. Synthesis, characterization and antimicrobial activity of Zinc oxide nanoparticles synthesized from *Calotropis procera*. International Journal of Pharmaceutical Science and Drug Research. 2015; 7(5):425-431.
- 23. Ramesh P, Rajendran A, Meenakshi sundaram M. Green synthesis of Zinc oxide nanoparticles using flower extract *Cassia auriculata*. Journal of Nano Science Nano Technology. 2014a; 1(1):41-45.
- 24. Ramesh P, Rajendran A, Subramanian A. Synthesis of Zinc oxide nanoparticle from fruit of *Citrus aurantifolia* by chemical and green method. Asian Journal of Phytomedicine and Clinical Research. 2014b; 2(4):189-195.
- 25. Raut SB, Thorat PV. A Review on Preparation, Characterization and Application of Zinc Oxide Nanoparticles by Green Synthesis Method. International

Journal of Emerging Technology and Advanced Engineering 2015; 5(3): 521-524.

- Raut S, Thorat PV, Thakre R. Green synthesis of Zinc oxide nanoparticles using *Ocimum tenuiflorum* leaves. International Journal of Science and Research. 2013; 4(5):1225-1228.
- 27. Ravindra PS, Shukla VK, Raghvendra SY, Sharma PK, Singh PK, Pandey AC. Biological approach of Zinc oxide nanoparticles formation and its characterization. Advanced Material Letter. 2011; 2(4):313-317.
- 28. Ristic M, Music S, Ivanda M, Popovic S. Sol-gel synthesis and characterization of nanocrystalline ZnO powders. Journal Alloy Compounds. 2005; 39:1-4.
- 29. Senthilkumar SR, Sivakumar T. Green Tea (*Camellia Sinensis*) Mediated synthesis of Zinc oxide nanoparticles and studies on their antimicrobial activities. International Journal of Pharmaceutical Sciences. 2014; 6(6):461-465.
- 30. Shah RK, Boruah F, Parween N. Synthesis and characterization of ZnO nanoparticles using leaf extract of *Camellia sinesis* and evaluation of their antimicrobial efficacy. International Journal of Current Microbiology Application Sciences. 2015; 4(8):444-450.
- Sharma A, Singh BP, Dhar S, Gondorf A, Spasova M. Effect of surface groups on the luminescence property of ZnO nanoparticles synthesized by sol–gel route. Surface Science. 2012; 606:13-17.
- 32. Sindhura KS, Prasad TNVKV, Selvam P, Hussain OM. Biogenic synthesis of Zinc nanoparticles from *Thevetia peruviana* and influence on soil exo-enzyme activity and growth of peanut plants. International Journal of Applied Pure Science and Agronomy. 2015; 1(2):19-32.
- Sivakumar J, Premkumar C, Santhanam P, Saraswathi N. Biosynthesis of Silver Nanoparticles Using *Calotropis* gigantea Leaf. African Journal of Basic and Applied Sciences. 2011; 3(6):265-270
- 34. Sun Y, Hu J, Wang N, Zou R, Wu J, Song Y, Chen H, Chen Z. Controllable hydrothermal synthesis, growth mechanism, and properties of ZnO three-dimensional structures. New Journal of Chemistry. 2010; 34:732-737.
- 35. Sutradhar P, Saha M. Green synthesis of zinc oxide nanoparticles using tomato (*Lycopersicon esculentum*) extract and its photovoltaic application. Journal of Experimental Nanoscience. 2016; 11(5):314-327.
- 36. Tokumoto MS, Pulcinelli SH, Santilli CV, Briois V. Catalysis and Temperature Dependence on the Formation of ZnO Nanoparticles and of Zinc Acetate Derivatives Prepared by the Sol-Gel Route. Journal of Physical Chemical Biology. 2003; 107:568-574.
- 37. Vafaee M, Sasani M, Ghamsari J. Preparation and characterization of ZnO nanoparticles by a novel sol–gel route. Journal of Materials Letters. 2007; 61:3265-3268.
- Varghese E, George M. Green synthesis of Zinc oxide nanoparticles. International Journal of Advances Research and Science Engineering. 2015; 4(1):307-314.
- Vidya C, Hiremath S, Chandraprabha MN, Antonyraj LMA, Gopal IV, Jain A *et al.* Green synthesis of ZnO nanoparticles by *Calotropis gigantea*. International Journal of Current Engineering Technology. 2013; 1:118-120.
- 40. Yi R, Zhang N, Zhou H, Shi R, Qiu G, Liu X. Selective synthesis and characterization of flower-like ZnO microstructures via a facile hydrothermal route. Materials Science and Engineering. 2008; 153:25-30.
- 41. Yiamsawas D, Boonpavanitchakul K, Kangwansupamonkon W. Preparation of ZnO

Nanostructures by Solvothermal Method. Journal of Microscopy Society of Thailand. 2009; 23(1):75-78.

42. Zhu P, Zhang J, Wu Z, Zhang Z. Microwave-Assisted synthesis of various ZnO Hierarchical Nanostructures: Effects of Heating Parameters of Microwave Oven. Crystal Growth and Design. 2008; 8:3147-3153.