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Research Article

Biosynthesis of ZnO nano particles assisted by Euphorbia tirucalli (Pencil Cactus)

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Abstract

Green chemistry approach towards the synthesis of nanoparticles is in the lime light of modern nanotechnology due to growing concern to develop environment-friendly and sustainable methods. In this scenario, the focus is on development of new materials and methods for biosynthesis of nanoparticles. In the present study the ZnO nanoparticles are synthesized by biological reducing agent using Zinc Nitrate as precursor. Branches (stems) of Euphorbia tirucalli provide capping and reducing agents for the synthesis of Zno nano particles. The particle size, topography, and morphology of the synthesized ZnO product was characterized using X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The XRD peaks coincide with literature XRD pattern for hexagonal wurtzite ZnO. The zinc oxide particles obtained are spherical in nature and were agglomerates of nanocrystallites. The average size of synthesized ZnO nanocrystallites as calculated using Scherrer's Formula is 20 nm.

Keywords: *Green synthesis, Biosynthesis, X ray Difraction, Scanning Electron Microscopy, Green chemistry, Euphorbia milii, latex, ZnO, nano particles*

1. Introduction

The properties which cannot be obtained by coarse particles can be easily obtained by fine and nano particles. The strange and diverse properties can be obtained by smallness alone. That is the reason for nanotechnology which is the science of the tiny being so popular in last few decades. Date back to the middle age nanoparticles were used for their optical properties in some artwork. One of the first records of nanoparticles in the scientific literature date back to the middle of the 19th century, was about study of studying gold colloids in the nano meter range by Michael Faraday (M. Faraday, 1857). "The principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom." these are the words of famous physicist Richard Feynman in 1959. These words actually signify our complete control over the matter at atomic level and these words were the motivation to the scientific minds of researchers. Later in the early 1980's, Eric Drexler coined the powerful word nanotechnology. Nanotechnology is a broad field connected to basic sciences such chemistry, physics, medicine, material science as well as to applied technologies. The world of nanotechnology is implanting its footprint in the present decade very rapidly. Many products based on nanotechnology are in market but possible applications are wide and the potential benefit to technology and society are considered to be vast, hence the nanotechnology can still be considered as a young one.

The nanotechnology is the interesting area of research as many things are to be explored and explained.

Among all nano materials the metal oxides find application in wide areas like catalysis, adsorption etc. ZnO has been commonly used in its polycrystalline form over hundred years in a wide range of applications. Zinc oxide possessed many versatile properties for UV electronics and sensor applications.

Nano zinc oxide fascinates the researchers due to its diverse growth morphologies and wide range of applications. Wide range of nanostructures of ZnO, makes it best suited for nanoscale optoelectronics (M.H. Huang et al, 2001) and piezoelectric nanogenerators (J. Song et al, 2006)]. As Nano zinc oxide has antibacterial, antifungal properties it is been considered as efficient material in Medicine and Biotechnology field (Z.L. Wang et al; J.Sawai et al, 2004; J. Sawai et al, 2004). Unique optical, electrical and chemical properties of nano ZnO have increased its importance in electronic sector, solar cells, gas sensors, and photocatalytic degradation of chemicals (J. B. Baxter et al, 2005; Z. Ling et al, 2001; C. Y. Hsu et al, 2008; Y. Wang et al 2008).

Nano materials can be synthesized by two approaches namely bottom up and top down. In the bottom up method the small building blocks are produced and assembled into

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larger structures. The parameters like morphology, crystallinity, particle size, and chemical composition can be controlled in this method. Examples: chemical synthesis, laser trapping, self-assembly, colloidal aggregation etc.

In the top down method coarse materials are modified to give smaller features. For example: film deposition and growth, nano imprint /lithography, etching technology, mechanical polishing etc.

Various chemical methods such as hydrothermal (J. Zheng et al, 2009), precipitation (S. Suwanboon et al, 2008), sol–gel (X. Wei et al, 2006) and thermal decomposition (M Salavati-Niasari et al, 2009) have been employed for the synthesis nanostructured ZnO. Most of the synthetic physicochemical methods use organic solvents and toxic reducing agents majority of which are highly reactive and are unsafe to the environment. To avoid such implications and for sustainable synthesis of nano particles biological, biomimetic and biochemical approaches are desirable. Biosynthesis of nanoparticles is a kind of bottom up approach where the main reaction occurring is reduction/oxidation. Among the various biosynthetic approaches, the use of plant extracts has advantages such as easy availability, safe to handle and possess a broad viability of metabolites.

Plant extract has been used as reducing and capping agent for the synthesis of nanoparticles which could be advantageous over photochemical reduction, heat evaporation, electrochemical reduction, and chemical reduction methods (K. Mallick et al, 2005; S. Keki et al, 2000). Zinc oxide nano particles are synthesized by *Aloe barbadensis miller* leaf extract (G. Sangeetha et al, 2011) and *calotropis procera* (R. P. Singh et al, 2011). In the present work ZnO nanoparticles are synthesized using leaves of pencil cactus as reducing and stabilizing agent.

Euphorbia tirucalli (also known as Aveloz, Firestick Plants, Indian Tree Spurge, Pencil cactus, Pencil Tree, Sticks on Fire or Milk Bush) belongs to Euphorbiaceae family and Genus Euphorbia (Fig. 1.). It grows in dry areas, and is often used to feed cattle or as hedging and also finds some application in traditional medicine E. tirucalli is a hydrocarbon plant that produces poisonous latex.

Many pharmacological activities of *E.tirucalli* have been documented by many workers as molluscicidal activity (Jurberg *et al*., 1985; Tiwari *et al*., 2003), antibacterial activity (Lirio *et al*., 1998), antiherpetic activity (Betancur-Galvis *et al*., 2002) and anti-mutagenic (Rezende *et al*., 2004). The stem of *E.tirucalli* contains alcohol eufol, α-euforbol and taraxasterol, tirucallol (Costa, 2002; Almeida, 1993), hentriacontene, hentriacontanol, the antitumor steroid β-sitosterol, taraxerin, 3,3'-di-O-methylellagic acid, ellagic acid, and a glycoside fraction which hydrolyses to give kampferol and glucose. The whole plant contains 7.4% citric acid with some malonic and some Bernstein (succinic) acids (List and Horhammer, 1969). In the present study the stems of E. tirucalli are used as reducing agents for the synthesis of ZnO nano particles from zinc nitrate.

Fig. 1. *Euphorbia tirucalli* (Pencil cactus)

2. Materials and Methods

Analyitical grade Zinc nitrate was purchased from Vasa Chemicals, Bangalore India. Leaves of Pencil cactus plant were collected from campus of R V College of Engineering, Bangalore

2.1Preparation of stem extract.

Fresh stems (branches) of E. tirucalli were washed with water several times. Then they were cut into small pieces. 50 gm of cut stems were dispensed in 200 ml distilled water and boiled for one hour at 80^{o}C. The extract was collected in separate conical flasks. The extract was filtered using Whatman filter paper.

2.2 Procedure

The 50 ml stem extract is taken in a beaker was heated. 5 gm of Zinc nitrate was added to leaf extract when temperature of extract reaches 60°C. The solution was heated continuously to temperature 60-80 deg Celsius at a low heating rate. The solution starts evaporating and after continuous heating the yellow color paste is obtained. On further heating a white color powder was observed, this is the end point of synthesis process. The powder thus obtained is calcined in a crucible at 400 deg Celsius for 1.5 hrs.

3. Characterization

The product obtained was characterized by X Ray Diffraction (XRD), Scanning electron Microscopy (SEM) and Particle size distribution by zeta potential. Phase purity and grain size were determined by X-ray diffraction (XRD) analysis recorded on Shimadzu Maxima_ X XRD-7000 diffractometer operated at 40 kV and 30 mA with CuKα as the radiation source. The surface morphology was studied by Hitachi SU-1500 model no 150604-07. The particle size distribution was determined by Zetatrac NPA-152 Microtrac.

4. Results and Discussion

4.1 Surface morphology

The XRD pattern (Fig. 2.) showed noticeable peaks 2θ values 36.2 (101), 31.8 (002), 34.5 (100). The XRD pattern of the powder is studied with the dif- fraction angle 25° - 80°. The results coincide with literature XRD pattern for hexagonal wurtzite ZnO (JCPDs Card No 36-1451). There are no other characteristic impurities peaks were present which also confirm that the product obtained is in pure phase. The line broadening in the peaks determine the crystallite size of ZnO to be less than 20 nm.

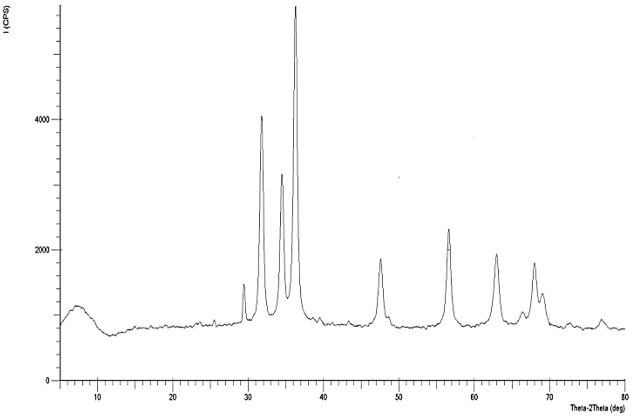

Fig. 2. XRD peaks of synthesized ZnO nano crystallites

4.2 Determination of crystallite size

The size of small particles can be estimated by using the peak broadening of the peaks in the XRD-pattern. This has been done according to the method of Scherrer (P. Scherrer, 1918), which is considered a standard method. The particle mean size, D, which is a volume average, is given by equation 1, where K is a shape factor, λ the wavelength of the x-rays, β the full with at half maximum in radians, and θ the angle between the x-ray source and the detector. The value of K depend on the shape of the particles and here the value 0.9 have been used which is a standard value for spherical particles.

$$D = \frac{K\lambda}{\beta \mathrm{Cos}\theta} \quad (1)$$

The full with at half maximum, FWHM or β, needs to be corrected for the instrumental broadening which is done according to equation 2, where βmeasured is the measured FWHM and where βinstrument is the peak broadening due to the instrument which is the measured FWHM for a bulk sample.

$$\sqrt{\beta^2{}_{measured} - \beta^2{}_{instrument}} \quad (2)$$

The particles obtained are spherical in nature and are agglomerates of nanocrystallites of 20 nm.

4.3 Scanning Electron Microscopy

The SEM images showed the formation of approximately spherical ZnO nanoparticles. The size of the primary nanoparticles was too small to conclusively determine the diameter from the SEM images; therefore, the crystal sizes obtained from the XRD results were used as the estimated diameters. The secondary ZnO particles as observed by SEM images (Fig. 3.) consist of primary ZnO nanocrystallites (~20nm). The primary nanocrystallites are combined to form a larger particle (secondary) by the following two routes: (1) Fusion of one primary crystallite into another. (2) Aggregation of the primary crystallites (Tammy et al, 2007).

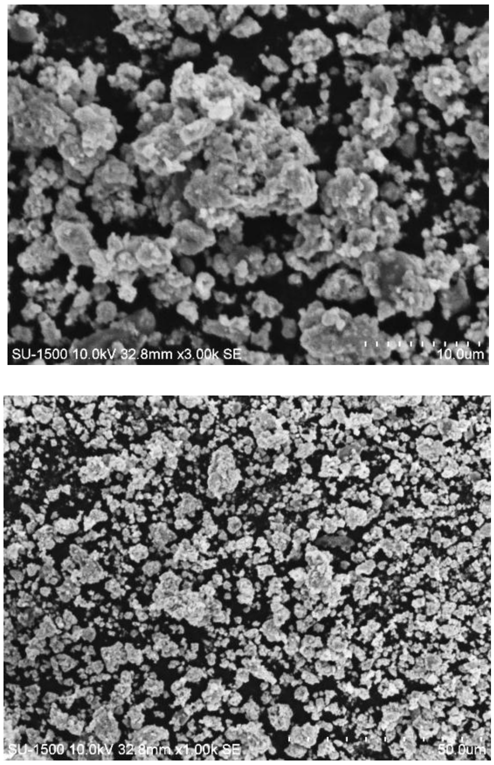

Fig. 3. Morphology of Synthesized ZnO particles ate different magniffications

4.4 Particle size distribution

Histograms, from the nanotrac analyzer, representing particle size distribution of the synthesized ZnO are shown in Fig .4. Approximately 90% of the particles are within 100nm.

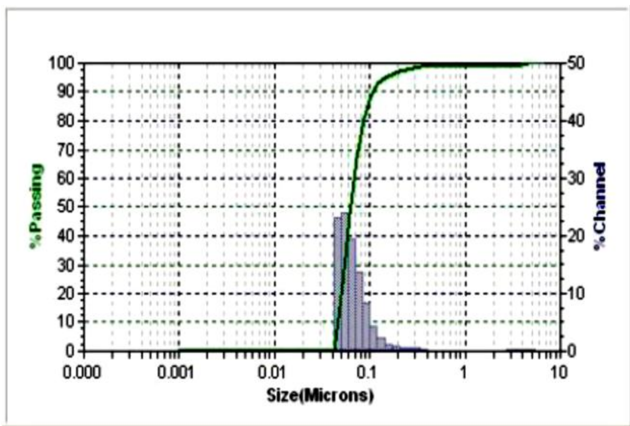

Fig. 4. Particle size distribution of synthesized ZnO nano particles

Conclusions

The biological synthesis of zinc oxide nano particles using stems of *Euphorbia tirucalli* avoids the usage of harmful reducing/stabilizing agents. The SEM morphology suggests that these nano-sized particles agglomerate together. The *Euphorbia tirucalli* stem assisted synthesis of ZnO nano particles is simple, fast, cheap, and efficient.
The product obtained could be targeted for the promising potential applications including dye removal, antibacterial, antifungal, biosensing devices, and nanoelectronic because of its pollution free and eco-friendly approach. Since biological reducing and capping agents have been used the product can best suit the medical applications. The studies for size selective synthesis and the application of the product are in progress.

References

A.F. Costa (2002). Farmacognosia. In: Fundac¸ao Calouste Gulbenkian. Lisboa, pp.788–790

C. Y. Hsu, T. F. Ko, Y. M. Huang (2008), Influence of ZnO buffer layer on AZO film properties by radio frequency magnetron sputtering, *Journal Eur Ceram Soc,* Vol. 28, No. 16, pp.3065-3070

E.R. Almeida (1993). Plantas medicinais brasileiras: Conhecimentos populares e cient´ıficos. In: *Hermus Editora. Rio de Janeiro*, pp. 70–71

G. Sangeetha, S. Rajeshwari, R. Venckatesh (2011), Green synthesis of zinc oxide nanoparticles by aloe barbadensis miller leaf extract: Structure and optical properties, *Materials Research Bulletin*, Vol. 46, pp.2560–256

J. B. Baxter, and E.S .Aydil (2005), Nanowire Based Dye Sensitized Solar Cells, *Appl. Phys. Lett*. Vol. 86, pp.53114

J. Sawai, and T.Yoshikawa (2004), Quantitative Evaluation of Antifungal Activity of Metallic Oxide Powders (MgO, CaO and ZnO) By an Indirect Conductimetric Assay, *J. Appl. Microbiol.* Vol. 96, No. 4, pp.803-80

J. Song, J. Zhou, and Z.L. Wang (2006), Piezoelectric and Semi conducting Coupled Power Generating Process of a Single ZnO Belt/Wire. A Technology for Harvesting Electricity from the Environment, *Nano, Lett.* Vol. 6, No. 8, pp.1656-1662

J. Zheng, Z. Y. Jiang, Q. Kuang, Z. X. Xie, R. B. Huang, and L. S. Zheng (2009), Shape-controlled fabrication of porous ZnO architectures and their photocatalytic properties, *Journal of Solid State Chemistry*, Vol. 182, No. 1, pp. 115–12

J.R. Rezende, S.B. Rodrigues, I.A.S. Jabor, J.A. Pamphile, C.L.M.S.C. Rocha, (2004.) Efeito antimutagenico do latex de Euphorbia tirucalli no sistema metioninaem Aspergillus nidulans. *Acta Scientiarum Biological Sciences,* Vol. 26, pp.481–48

J.Sawai, H. Igarashi, A. Hashimoto, T. Kokugan,c, and M.Shimizu (1996a), Antibacterial Characteristics of Magnesium Oxide Powder, *J. Chem. Eng. Japan,* Vol. 29, pp.556-561\

K. Mallick, M.J, M.S. Scurrella Witcombb (2005), Self-assembly of silver nanoparticles in a polymer solvent: formation of a nano-chain through nano-scale soldering, *Mater. Chem. Phys*., Vol. 90, pp. 221–224

J. Roldan (2002), Cytotoxic and antiviral activities of Colombian medicinal plant extracts of the Euphorbia genus, Memorias do Instituto Oswaldo Cruz, Vol.97, pp.541–54

L.G. Lirio, M.L. Hermano, M.Q. Fontanilla (1998), Antibacterial activity of medicinal plants from the Philippines, *Pharmaceutical Biology*, Vol. 36, pp.357–35

M Salavati-Niasari, N Mir, F Davar (2009) ZnO nanotriangles : Synthesis, characterization and optical properties, *Journal of Alloys and Compounds*, Vol. 476, No. 1-2, pp. 908-912

M. Faraday (1857). Experimental relations of gold (and other metals) to light, Philosophical transactions of the Royal Socieaty, Vol.147. pp. 145-181

M.H. Huang, S.Mao, H. Feick, H.Q. Yan, Y. Wu, H. Kind, E. Weber, R Russo, and P. Yang (2001), Room-Temperature Ultraviolet Nanowire Nanolasers, In *Sers. Science*, Vol. 292, No. 5523, pp.1897-189

P Jurberg, N. Cabral, J.B. V.T Schall (1985), Molluscicide activity of the 'avelos' plant (Euphorbia tirucalli, L.) on Biomphalaria glabrata, the mollusk vector of schistosomiasis, Memorias do InstitutoOswaldo Cruz, Vol.80,pp. 423–42

P. Scherrer (1918). Analysis of external and internal structure of colloidal particles by means of X-rays : Nachrichten vonder Konig. Gesellsch. Wissensch. zu Gottingen-Math.-Phys. Kl., Vol. 2, pp.98-10

P.H. List, L.Horhammer (1979), Hager's handbuch der pharmazeutischen praxis. *Springer*-Verlag, Berlin, edition 4, Vol. 6, pp.200-201

P.Tammy, Chou, Q. Zhang, E.Glen, Fryxell, C.Guozhong(2007), Hierarchically Structured ZnO Film for Dye-Sensitized Solar Cells with Enhanced Energy Conversion Efficiency, *Adv. Mater,* Vol. 19, pp.2 588–259

R. P. Singh, V. K. Shukla, R. S. Yadav, P. K. Sharma, P. K. Singh, A. C. Pandey (2011), Biological approach of zinc oxide nanoparticles formation and its characterization, *Advanced Materials Letters*, Vol. 2, No. 4, pp.313-317

S. Keki, J. Torok, G. Deak, J (2000), Silver nanoparticles by PAMAM-assisted photo-chemical reduction of Ag+, Colloid Interf. Sci. Vol. 229, pp.550–553

S. Suwanboon, A. Amornpitoksuk, A. Haidoux, J.C.Tedenac (2008), Structural and optical properties of undoped and aluminium doped zinc oxide nanoparticles via precipitation method at low temperature. *J Alloys Compd,* Vol.462, pp. 335-339

S.Tiwari, P.Singh, A. Singh (2003). Toxicity of Euphorbia tirucalli plant against freshwater target and non-target organisms, *Pakistan Journal of Biological Sciences*, Vol.6, pp. 1423–142

X. Wei, D. Chen (2006), Synthesis and characterization of nanosized zinc aluminate spinel by sol-gel technique, *Materials Letters*, Vol. 60, pp. 823-827

Y. Wang, Li X, Wang N, Quan, Y. Chen (2008). Controllable synthesis of ZnO nanoflowers and their morphology-dependent photocatalytic activities, *Sep Purif Technol,* Vol. 62, No. 3, pp. 727-732

Z. Ling, C. Leoch, R. Freer (2001). Heterojunction gas sensors for environmental NO_2 and CO_2 monitoring. J *Eur Ceram Soc*, Vol.21, No.(10-11), pp.1977-198

Z.L. Wang (2004), Functional Oxides Nanobelts Materials, Properties and Potential Applications in Nanosystems and Biotechnology, *Annu. Rev. Phys. Chem.,* Vol. 55, pp.159-196