www.vbripress.com, www.amlett.com, DOI: 10.5185/amlett.indias.204
"INDIAS 2010" Special Issue Published online by the VBRI press in 2011

Biological approach of zinc oxide nanoparticles formation and its characterization

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Received: 25 Dec 2010, Revised: 05 March 2011 and Accepted: 07 March 2011

ABSTRACT

Herein, we are reporting a novel biological approach for the formation of zinc oxide (ZnO) nanoparticles using Maddar (*Calotropis procera*) latex at room temperature. X-Ray diffraction (XRD) pattern reveals the formation of ZnO nanoparticles, which shows crystallinity. Transmission electron microscopy (TEM) suggested particles size and shape in the range of 5-40 nm. Scanning electron microscopy (SEM) image reveals that the particles are of spherical and granular nature. UV-Vis absorption shows characteristic absorption peak of ZnO nanoparticles. Photoluminescence (PL) studies were performed to emphasize its emission properties. This simple and cost-effective biological approach for the formation of ZnO NPs has a promising application in biosensing, electronics and photonics. Copyright © 2011 VBRI press.

Keywords: Biological approach; *Calotropis procera*; zinc oxide; nanoparticles; biosensing.

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Introduction

Nanomaterials have wide-ranging applications and implications in a variety of areas, including physics, chemistry, electronics, optics, materials science, and the biomedical sciences. Besides, the novel properties exhibited by the metal nanoparticles due to quantum size effects, their synthesis protocol pose a major environmental problem. The nanomaterials exhibit unique and considerably changed physical, chemical and biological properties when compared to their macro scaled i.e. bulk counterparts [**1-3**]. Nel et al. repoted the nanoparticles interaction with biological materials and established a series of nanoparticle/biological interfaces that depend on colloidal forces as well as dynamic biophysicochemical interactions. These interactions lead to the formation of new nanomaterial with control size, shape, surface chemistry, roughness and surface coatings [**4**]. Furthermore, evidences suggested that the inorganic nanoparticles are very immense material because of their high surface area, it is easy to enter in cells via pores of plasma membrane proteins at nanoscale size. Apart from this, they have potential properties for sensing and detection of various biological analytes. For instance, the presence of semiconductor metal zinc oxide nanoparticles (< 30 nm) in the biological system have ability to altered biological properties. Zinc oxide nanoparticles have potential applications in various areas including optical, piezoelectric, magnetic and gas sensing and also they exhibit high catalytic efficiency, strong adsorption ability, high isoelectric point (9.5), biocompatibility, and fast electron transfer kinetics for biosensing purposes [**5-13**]. Most of the synthetic physicochemical methods reported till date are heavily on the use of organic solvents and toxic reducing agents like thiophenol, mercapto acetate, sodium borohydride etc. Most of these chemicals are highly reactive and pose potential environmental and biological risks. With the increasing interest in minimization or elimination of such kinds of hazardous chemicals, the development of biological, biomimetic and biochemical approaches is desirable. Therefore, biological approach has advantages over physicochemical methods because of its clean, non-toxic chemicals, environmentally benign solvents, and user-friendly nature [**14**].

C. procera, is a desert plant known as Madar in Greeco-Arab medicine. This plant is widely distributed in tropical and subtropical Africa and Asia. The different parts of the plant are used in Indian traditional medicine for the treatment of painful muscular spasm, dysentery, fever, rheumatism, asthma and as an expectorant and purgative [**15, 16**]. *C. procera,* is a plant with good enough quantities of latex i.e. milky liquid, when any mechanical damages, their tissues are broken and secrete the milky latex, consisting of several biologically active compounds, including proteins, amino acids, carbohydrates, lipids, vitamins, alkaloids, resins, and tannins. Predominantly, milky latex contains several alkaloids of interest such as calotropin, catotoxin, calcilin, gigatin etc [**17**]. To the best of our knowledge, biological approach using milky latex of *Calotropis procera* has been used for the first time as a reducing material as well as surface stabilizing agent for the synthesis of spherical-shaped ZnO-NPs. The structure, phase, and morphology of synthesized product were investigated by the standard characterization techniques.

Experimental

The zinc acetate dehydrate, sodium hydroxide, was purchased from E. Merck Ltd., Mumbai, India. The other all the reagents are of analytical purity grade and have been received from commercial sources. ZnO nanostructures were prepared by co-precipitation method. 0.02 M aqueous solution of zinc acetate dihydrate was put into 50 ml of distilled water under vigorous stirring. After 10 min stirring, Latex of Maddar 0.25, 0.5 ml and 1.0 ml was added in three set into the above solution. After addition of milky latex, 2.0 M NaOH aqueous solution was introduced into the above aqueous solution, resulting in a white aqueous solution at pH 12, which were then placed on magnetic stirrer for stirring for 2 hr. The precipitate was then taken out and washed repeatedly with distilled water followed by ethanol to remove the impurities for the final products. Then a white powder was obtained after drying at 60 ^{o}C in vacuum oven overnight. The whole mode of proposed method for the synthesis of ZnO NPs mediated by milky latex of *Calotropis procera*, was illustrated in the **Fig.1**.

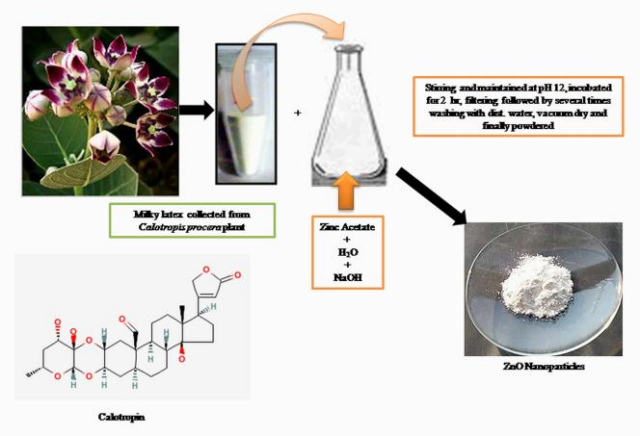

Fig. 1. Proposed procedure for the synthesis of ZnO nanoparticles formation.

Results and discussion

The biological approach for the formation of ZnO nanoparticles using Maddar (*Calotropis procera*) milky latex at room temperature was reported. The X-Ray diffraction (XRD) pattern reveals the formation of ZnO nanoparticles, which shows crystallinity. **Fig. 2** shows the XRD pattern of the heated and non-heated ZnO NPs powder embedded in calotropis matrix synthesized by co-precipitation method.

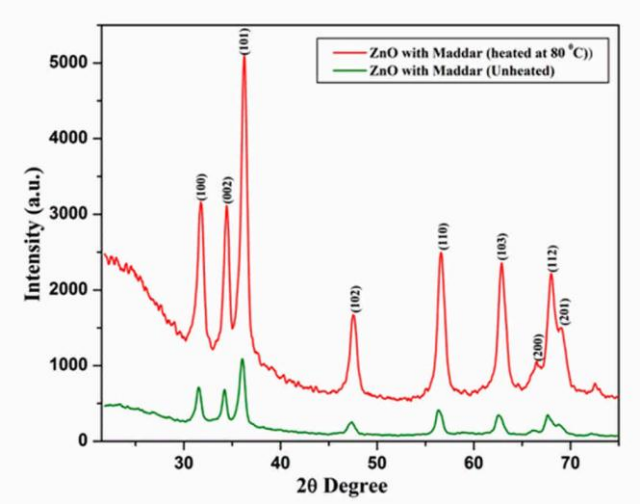

Fig. 2. XRD pattern of ZnO nanoparticles of heated and non heated sample.

When compare the both the samples, XRD Spectra showed strong diffraction peaks at 31, 34, 36, 47, 56, 62, 66, 67 and 68 degrees of 2θ which corresponds to (100), (002), (101), (102), (110), (103), (200), (112) and (201) crystal planes, which were in significant agreement with the JCPDS file 36145 (a = b = 3.249 Å, c = 5.206 Å) and indexed as the hexagonal wurtzite structure of ZnO having space group $P6_3$ mc. It can be seen that ZnO NPs embedded in calotropis matrix, XRD peaks were not as sharp as in the case of non-heated as-prepared ZnO sample when compared with the heated sample, it means that the slight decrease in crystallinity, which suggests the formation of smaller particle size.

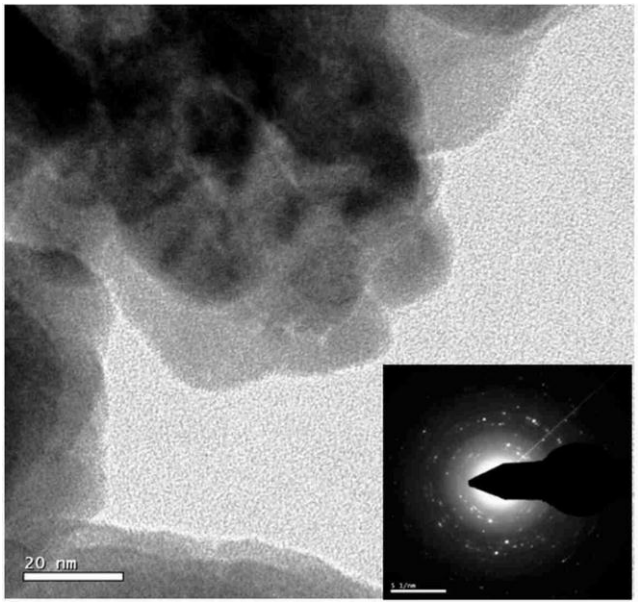

Fig. 3. TEM image shows ZnO nanoparticles in as-prepared sample with calotropis latex and inset shows selective area electron diffraction (SAED) pattern.

Fig. 3 TEM image shows ZnO nanoparticles with average size of 5-40 nm. Inset shows Selective area electron diffraction (SAED) pattern exhibits a set of rings containing spots suggesting that nanoparticles have a larger grain size, uniform shape and polycrystalline in nature. A TEM image was recorded by dissolving the as-synthesized powder sample in ethanol and then placed a drop ethanolic solution on the surface of copper grid.

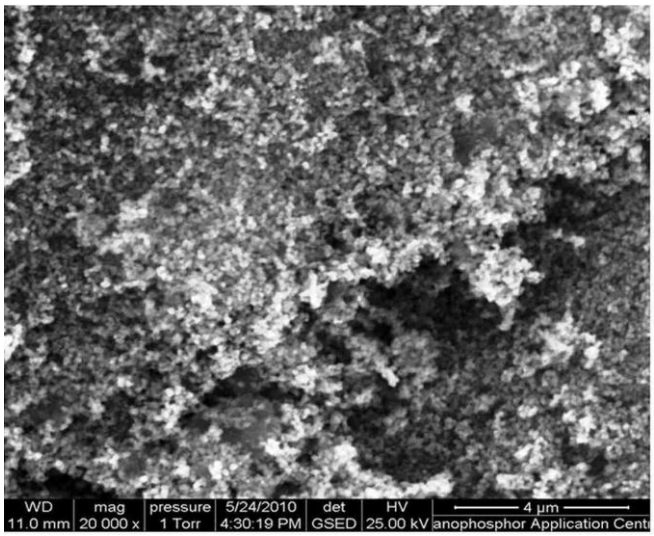

Fig. 4. SEM image shows the particles are of spherical and granular nanosized nature in as-prepared sample treated with calotropis latex.

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 particles size and shape in the range of 5-40 nm. Scanning electron microscopy (SEM) image reveals that the particles

are of spherical and granular nanosized in nature as depicted in the **Fig. 4**.

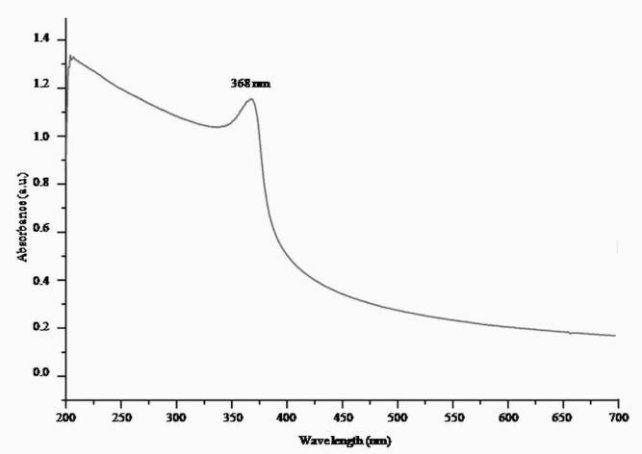

Fig. 5. UV-Vis absorption spectrum of as-prepared ZnO NPs, treated calotropis latex (Maddar) using optimal 0.5 ml volume in the proposed incubation cum precipitation method.

Optical properties of the as-prepared ZnO nanostructure sample was revealed by UV–Vis spectrum and photoluminescence spectroscopy at room temperature, as shown in **Fig. 5** and **6**, respectively. It can be seen from the **Fig. 5** that there was intensive absorption in the ultraviolet band of about 200-400 nm. The absorption wavelength at about 368 nm of ZnO suggested the excitonic character at room temperature.

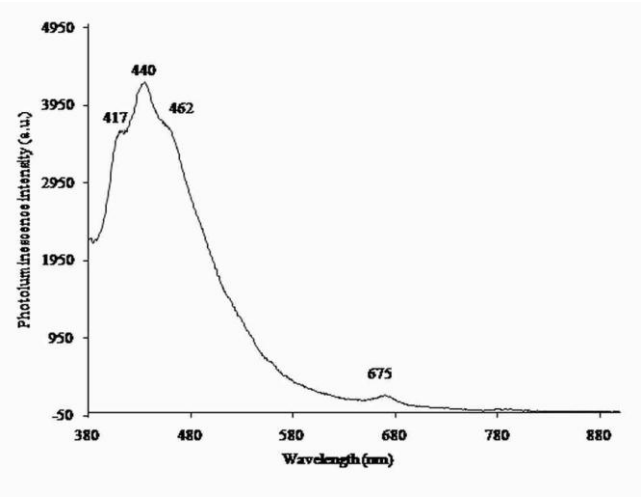

Fig. 6. PL spectrum of as-prepared ZnO NPs, treated calotropis latex (Maddar).

Photoluminescence (PL) studies were performed to emphasize its emission properties as shown in **Fig. 6**. The photoluminescence of ZnO sample suggested five emitting bands, including three blue bands at 417 nm 440 and at 462 nm, probable green band at 520 nm as well as one weak shoulder red band at around 675 nm have been observed in as-prepared ZnO sample. The PL of the ZnO sample in our case is considerably different from the typical observation in ZnO crystals, which usually exhibited UV emission at around 385 nm and yellow-green emission around 495 nm [18]. Vanheusden et al. described that the UV emission is attributed to the radiative recombination between the electrons in the conduction band and the holes in the valence band [19]. whereas Mahamuni et al. have described that the visible luminescence is due to defects related to deep level emission [**20**]. The blue band at 417,440 and 462 nm may be in correlation with the defect structures in ZnO crystal. The green band at 520 nm and shoulder red band at 675 nm may be correlated to a transition between the oxygen vacancy and interstitial oxygen respectively [**19, 21**]. There has been no totally accepted explanation about the visible luminescence until now but more researches are needed for luminescence mechanism of ZnO.

Conclusion

Our findings could be targeted for the promising potential applications including biosensing devices, and nanoelectronic because of its pollution free and eco-friendly approach. This green synthesis approach shows that the environmentally benign and renewable latex of *C. procera* can be used as an effective stablizing as well as reducing agent for the synthesis of zinc oxide nanoparticles. Zinc oxide nanoparticles synthesized by this approach are quite stable and no visible changes are observed even after a month. Synthesis of zinc oxide nanoparticles using milky latex is an alternative to chemical synthesis. We anticipate that the smaller particles are mostly stabilized by alkaloids and proteins. Further experiments for the systematic mode of mechanism of size selective synthesis of zinc oxide nanoparticles using this very useful milky latex are in progress.

Acknowledgement
Authors are grateful to DST Nano-Mission (SR/NM/NS-87/2008), Department of Science and Technology, Government of India for financial support.

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