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Green synthesis of zinc oxide nanoparticles by *aloe barbadensis miller* leaf extract: Structure and optical properties

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ABSTRACT

Biological methods for nanoparticle synthesis using microorganisms, enzymes, and plants or plant extracts have been suggested as possible ecofriendly alternatives to chemical and physical methods. In this paper, we report on the synthesis of nanostructured zinc oxide particles by both chemical and biological method. Highly stable and spherical zinc oxide nanoparticles are produced by using zinc nitrate and *Aloe vera* leaf extract. Greater than 95% conversion to nanoparticles has been achieved with *aloe* leaf broth concentration greater than 25%. Structural, morphological and optical properties of the synthesized nanoparticles have been characterized by using UV–Vis spectrophotometer, FTIR, Photoluminescence, SEM, TEM and XRD analysis. SEM and TEM analysis shows that the zinc oxide nanoparticles prepared were poly dispersed and the average size ranged from 25 to 40 nm. The particles obtained have been found to be predominantly spherical and the particle size could be controlled by varying the concentrations of leaf broth solution.

1. Introduction

Nanomaterials, controlled to nano crystalline size (less than 100 nm), can show atom-like behaviors which result from higher surface energy due to their large surface area and wider band gap between valence and conduction band when they are divided to near atomic size [1]. Transition metal oxides with nanostructure and semiconductors with dimensions in the nanometer realm have attracted considerable interest in many areas of chemistry, physics, material science, biotechnology, information technology and environmental technology as next generation technologies [2–4]. In recent years, zinc oxide (ZnO), an important semiconductor with tremendous scientific and technological interest, having a direct wide gap (3.37 eV, 387 nm, deep violet/borderline ultraviolet (UV)) and a large exciton-binding energy (60 meV) [5], is a highly preferred multitasking metal oxide having a vast list of attractive properties. Due to its unique optical and electrical properties [6,7], it is regarded as a potential material in optoelectronic applications operating in the visible and near ultraviolet spectral regions. ZnO nanoparticles have been widely used in many industrial areas such as solar cells, UV light-emitting devices, gas sensors, photocatalysts, pharmaceutical and cosmetic industries [8–12]. Additionally, metal nanoparticles have a surface plasmon resonance absorption in the UV–visible region. It is non-toxic, self-cleansing [13,14], compatible with skin, antimicrobial, dermatological and is used as an UV-blocker in sunscreens and many biomedical applications [15]. Furthermore, ZnO appears to strongly resist microorganisms [16] and some reports show considerable antibacterial activity of CaO, MgO and ZnO [17], which is attributed to the generation of reactive oxygen species on the surface of these oxides.

In spite of these merits, ZnO is bio-safe, biocompatible with unique ability like structure-dependent properties, electrical and thermal transport properties, which could be varied with respect to particle size, shape, morphology, orientation and aspect ratio, have resulted in increased interest in obtaining this nano metal oxide material [18–20]. Several physical and chemical procedures have been used for the synthesis of large quantities of metal nanoparticles in relatively short period of time. Approaches such as simple solution-based methods, chemical precipitation [21,22], sol–gel [23], solvothermal/hydrothermal [24–26], electrochemical and photochemical reduction techniques are most widely used [27,28]. Chemical methods lead to the presence of some toxic chemicals adsorbed on the surface that may have adverse effects in medical application [29]. Increasing awareness towards green chemistry and other biological processes has led to the development of an eco-friendly approach for the synthesis of nanoparticles. The use of environmentally benign materials like plant leaf extract [30], bacteria [31], fungi [32] and enzymes [33] for the synthesis of silver nanoparticles offers numerous benefits of eco-friendliness and compatibility for pharmaceutical and other biomedical applications, where toxic chemicals are not used for

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the synthesis protocol. Although biosynthesis of gold nanoparticles by plants such as *alfalfa* [34,35], *Cinnamomum camphora* [36], *neem* [37], *Emblica officinalis* [38], *lemon grass* [39], and *tamarind* [40] have been reported, the potential of plants as biological materials for the synthesis of nanoparticles is yet to be fully explored. The present investigation describes for the first time, synthesis, characterization and optical properties of ZnO nanoparticle prepared by both chemical and biological (green) techniques using *Aloe vera*. *Aloe vera* (*Aloe barbadensis Miller*) a perennial succulent belonging to the Liliceal family, is a cactus-like plant that grows in hot, dry climates [41]. *Aloe* gel is the mucilaginous jelly obtained from parenchyma cells of the *Aloe vera* plant. Different researchers have described different processing techniques of the gel with regard to its sterilization and stabilization, i.e., cold processing or heat treatment. For many years, *aloe vera* has been reported to possess immunomodulatory, anti-inflammatory, UV protective, antiprotozoal, and wound healing properties [42–45]. In order to find the efficiency of *aloe vera* plant in synthesis of nanoparticles, total leaf and gel broth extracts have been used for the study. The effect of reaction conditions (broth concentration) on synthesis rate and particle size of the zinc oxide nanoparticles has also been investigated.

2. Experimental details

2.1. Synthesis by chemical and biological method

Zinc nitrate (99% purity) and NaOH (pellet min. 99%) were used as the starting material and were supplied by Sigma–Aldrich Chemicals, India. The *Aloe vera* leaves were harvested from local agricultural fields, Coimbatore, Tamilnadu. *Aloe vera* extracted solution was prepared by two different processes. In the first process, about 250 g portion of thoroughly washed *Aloe vera* leaves were finely cut and boiled with de-ionized water in medium flame. The resulting product was ground to get complete extract. The solution was boiled, filtered and stored in refrigerator for further experiments. In the second process, the inner gel portion was extracted from the *aloe* leaves, crushed and ground to thin paste by adding enough de-ionized water and filtered by using fine mesh. The resulting extract was stored at 10 °C for further experiments.

Two different methods were used for synthesizing ZnO nanoparticles of varying particle sizes. In synthesis I (chemical method), zinc nitrate was dissolved in distilled water under constant stirring. While at room temperature, sodium hydroxide solution was added drop by drop. After completion of reaction, the solution was allowed to settle for overnight and the supernatant liquid was discarded. The white precipitate formed was washed thoroughly with double distilled water to remove all the ions and then centrifuged at 3000 rpm for 10 min. The obtained precipitate was dried in a hot air oven at 80 °C for 6 h. During drying, complete conversion of $Zn(OH)_2$ into ZnO took place. In synthesis II (biological method), a typical procedure was employed, where *aloe* leaf and *aloe* gel broth extracts at different concentrations (50%, 25%, 15%, 10%, 5%) were prepared with distilled water and the volume was made up to 250 ml. Later, zinc nitrate was dissolved in the *aloe* extract solution under constant stirring using magnetic stirrer. After complete dissolution of the mixture, the solution was kept under vigorous stirring at 150 °C for 5–6 h, allowed to cool at room temperature and the supernatant was discarded. The pale white solid product obtained was centrifuged twice at 4500 rpm for 15 min after thorough washing and dried at 80 °C for 7–8 h. The resulting dried precursor was crushed into powder and stored in air tight container for further analysis.

2.2. Characterization

Optical properties of ZnO nanoparticles were characterized based on UV absorption spectra and photoluminescence (PL). The sample was sonicated for uniform dispersion and the aqueous component was subsequently analyzed at room temperature for optical band gap (E_g) using UV–Vis spectrophotometer (UV-2450, Shimadzu). Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS-55 B. The chemical composition was studied by using FTIR spectrometer (Perkin-Elmer 1725X). The shape, size and microstructures of the products were characterized by using scanning electron microscopy (Model JSM 6390LV, JOEL, USA). The size and morphology were examined by TEM, JEOL model JEM 3010 Electron microscope. Size distribution and the average size of the nanoparticles were estimated on the basis of TEM micrographs with the assistance of Sigma-Scan Pro software (SPSS Ins, Version 4.01.003). Phase purity and grain size were determined by X-ray diffraction (XRD) analysis recorded by diffractometer (SEIFERT PTS 3003). All experiments were done in triplicates and the data were analyzed using Origin Pro 7.5 SRO software (OrginLab Corporation, USA) and the results were recorded for different *aloe* leaf broth concentrations (0–50%).

3. Results and discussion

The study reports the formation of nanoparticles when exposed to *aloe* extract by monitoring changes in colour as particle size increased. White precipitate formed was the end product in synthesis I whereas in synthesis II, pale white precipitate appeared. Fig. 1 shows the synthesis of nanoparticles by chemical and biological method with 25% *aloe* leaf and gel broth extracted solution. At a reaction period of 3 h, around 50–60% conversion was achieved for *aloe* leaf and gel broth, whereas only 20% conversion was noticed in chemical synthesis. Increasing the reaction duration to 5–6 h improved level of conversion to almost 100% in *aloe* gel broth and 95% in leaf broth, but in chemical synthesis the duration exceeded and only 50% conversion was noticed after 6 h. It was found >58% nanoparticle synthesis was achieved after 4 h. The average ZnO nanoparticle size achieved by using gel (35 nm) and leaf broth (34 nm) was more or less similar whereas the average size was found to be increased to 60 nm in chemical synthesis.

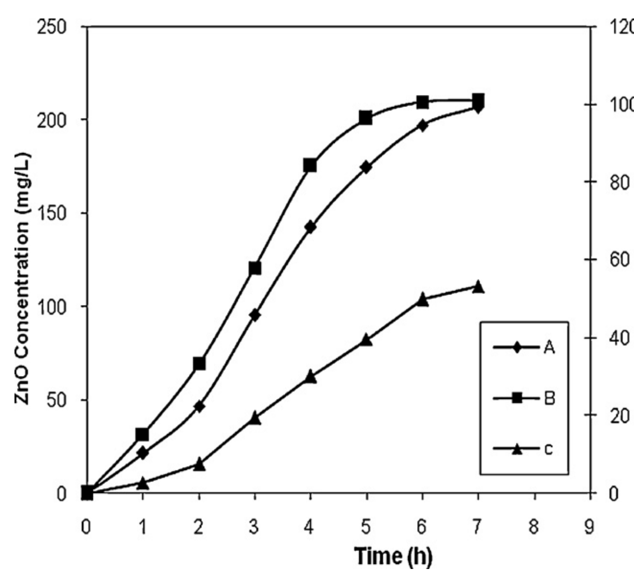

Fig. 1. Synthesis of ZnO nanoparticle by (a) 25% *Aloe* gel broth, (b) 25% *Aloe* leaf broth, (c) 0% *Aloe* broth.