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One-pot green synthesis of zinc oxide nano rice and its application as sonocatalyst for degradation of organic dye and synthesis of 2-benzimidazole derivatives

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ABSTRACT

In this paper, we report novel and green approach for one-pot biosynthesis of zinc oxide (ZnO) nanoparticles (NPs). Highly stable and hexagonal phase ZnO nanoparticles were synthesized using seeds extract from the tender pods of *Parkia roxburghii* and characterized by XRD, FT-IR, EDX, TEM, and N_2 adsorption-desorption (BET) studies. The present method of synthesis of ZnO NPs is very efficient and cost effective. The powder XRD pattern furnished evidence for the formation of hexagonal close packing structure of ZnO NPs having average crystallite size 25.6 nm. The TEM image reveals rice shapes ZnO NPs are with an average diameter of 40–60 nm. The as-synthesized ZnO NPs has proved to be an excellent sonocatalysts for degradation of organic dye and synthesis of 2-benzimidazole derivatives.

1. Introduction

Synthesis of semiconductor nanoparticles has been one of the most widely studied subjects for the researchers in material science due to their novel optical, photoelectrochemical, electronic and chemical properties which are different from that of bulk [1,2]. ZnO NPs has attained the remarkable attention, for its semiconducting properties, unique antifungal, antibacterial, wound healing and UV filtering properties, humidity sensing, photochemical and high catalytic activity [3–5]. Furthermore, ZnO NPs finds wide range of applications in pigments, gas sensors, rubber additive, optical devices and varistors [6,7]. The characteristics and application of ZnO nano powder depend on its size, shape and methods of preparation. There are several methods available for the preparation of nanosized ZnO, such as chemical microemulsion [8], wet chemical [9], hydrothermal [10], sol–gel method [11], electrochemical depositions [12], microwave assisted combustion [13], co-precipitation [14], chemical [15], and sonochemical [16] etc. All of these methods have their own advantages and drawbacks. For example in chemical methods, the synthesis can be carried out in large scale but use of toxic chemicals pose major environmental and biological problems. To avoid the use of toxic chemical and harsh reaction conditions for the preparation of nanoparticles, biosynthesis has proved to be a useful tool. Recently, green synthesis of nanoparticles has gained much attention due to its inexpensive, simplicity and eco-friendly procedure. Biosynthesis of metal or metal oxide NPs using plant extract, bacteria and fungi for is considered to be immense importance owing to modern legislation on clean environment. Therefore, the synthesis of nanoparticles using natural sources is an excellent strategy that could reduce the environmental impact. Such methods are also useful for large-scale synthesis of nanoparticles with well-defined size and shape of nanoparticles [17–20]. *Parkiaroxburghii*, which is traditionally used as food source among local communities in northeast Indian states, has proved to be an excellent extract for the biosynthesis of gold and silver nanoparticles [21,22]. Inspired by the efficiency of leaf extract of *Parkiaroxburghii* towards biosynthesis of gold and silver NPs, we contemplated to use seeds from the tender pods of *Parkiaroxburghii* for the synthesis of ZnO NPs. A comprehensive literature survey reveals that there is no report on the biosynthesis of ZnO NPs using the seed of *Parkiaroxburghii*.

It is important to mention that demand for good quality textile materials across the globe is rising consistently. Due to this a great deal of attention has been devoted in recent years for their removal from the environment particularly from wastewater [23–25]. Therefore tackling

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this problem is major concern for people in industry. Among the various known methods, photocatalytic techniques have been extensively considered as energy-saving and a "green" means to degrade the soluble dyes from wastewater. In degrading the organic pollutant ultrasound irradiation has been proved to be an useful tool in enhancing reaction rates, accelerating dissolution, renewing the surface of solid catalysts or reactants etc [26,27]. Thus combination of nanocatalysts with ultrasound irradiation in degradation reactions will certainly open up a new avenue for highly efficient environmentally friendly synthetic protocols [26–29].

Synthesis of 2-benzimidazole and its derivatives are important because such compounds find application in pharmaceuticals industries as anticancer, antifungals, antiulcer, antihypertensive, antiviral and antihistaminics agent [30,31]. For example, 2-benzimidazole derivatives act as important scaffold in the synthesis of drugs such as stemizole, lansoprazole, telmisartan, and albendazole drugs [32–34]. Thus 2-benzimidazoles and other related heterocycles are considered to be of utmost significance in pharmaceutical industries. A survey of recent literature reveals a number of works on their synthesis. Most of such procedures involve condensation of *o*-phenylenediamine and aldehydes over various oxidants or catalysts such as $VO(acac)_2$ [35], $In(OTf)_3$ [36], $FeCl_3$ [37], I_2 [38], NH_4OAc [39] and Dowex 50 W [40], etc. These methods have registered remarkable improvement over the previously reported procedures. However they still process some limitations from green chemistry perspective. It may be emphasized here that use of nanocatalyst might be a viable choice to replace the conventional catalyst in the synthesis of 2-benzimidazoles. In this connection one such catalyst that has attracted attention of researchers in recent past is zinc oxide nanoparticles. ZnO NPs have been proved to be remarkably efficient to catalyze synthesis of 2-benzimidazoles and the related compounds. For example D. O. Jang et al. have reported ZnO NPs catalyzed synthesis of benzimidazole, benzoxazole, and benzothiazole derivative using ball milling technique [41]. S Banerjee et al. have reported ZnO NPs as green and efficient catalyst for biologically active benzothiazole and benzoxazole derivatives [42].

Attention of the readers may be drawn to the fact that ultrasound irradiation in chemical reactions is proved to be an useful tool in accelerating dissolution, enhancing reaction rates, renewing the surface of solid catalysts or reactants etc. Thus combination of nanocatalysts with ultrasound irradiation in chemical reactions will certainly open up a new avenue for highly efficient environmentally friendly synthetic protocols. Keeping in mind the environmental legislations on the practice of processes for development of industrially important products including pharmaceuticals, one has to look to develop synthetic methods that are suitable for industry.

As a sequel to our current endeavour [10,21,25,43,44] on the synthesis and application of nanocatalysts, we report herein a green approach for the synthesis of ZnO NPs and their application as catalyst for ultrasound assisted degradation of organic dye and synthesis of 2-benzimidazole derivatives.

2. Experimental

2.1. Materials and physical measurements

ride ($ZnCl_2$), *o*-phenylenediamine (OPD), and all the aldehyde was purchased from Merck India Ltd. Sonication was performed in Qsonica Q700 sonicator with a frequency 20 kHz and at a nominal power of 250 W. FT-IR spectrum was recorded on KBr matrix with Bruker 3000 Hyperion Microscope with Vertex 80 FT-IR system. XRD measurements were carried out on a Bruker AXS D8-Advance powder X-ray diffractometer with Cu-Kα radiation (λ=1.5418 Å) with a scan speed of 2°/min. Transmission electron microscopy images were obtained on a JEOL, JEM2100 equipment. TEM grids were prepared using a few drops of the ethanol dispersed sample.

2.2. Synthesis of ZnO NPs

The seeds from the tender pods of *Parkiaroxburghii* were brought to laboratory cleaned thoroughly by distilled water and then shade dried for a week. The dried seeds were crushed into fine powder in a glass mortar. 10g of powder was mixed with 50 ml of water for two hours at 100 °C using soxhlet apparatus. The resulting extract was filtered using a pure cotton cloth followed by Whatman No. 1 filter paper. As collected filtrated was directly used as the hydrolyzing agent in the synthesis of NPs. 0.1 M stock solution of zinc nitrate hexahydrate were mixed with 25 ml of extract under vigorous stirring for 2 h. After the completion of the reaction, the dirty precipitate those formed was allowed to settle for 24 h, centrifuged, washed with deionized water and ethanol several times and dried in a hot air oven. The as-obtained precursor powder was then calcined in a muffle furnace for 4 h at 400 °C to obtain powders of ZnO NPs.

2.3. Catalytic performance test

Zno nanorice catalyst was investigated ultrasound assisted degradation of methylene blue (MB) and rhodamine B (RhB) dyes. In a typical catalytic reaction, 2 ml of freshly prepared sodium borohydride (SB) solution (0.2 M) was added to 50 ml (10 mg L^{-1}) aqueous solution of dye at room temperature (25 ± 1 °C) followed by addition of 1 mg of catalyst. The resultant mixture was irradiated with ultrasound. At a regular interval of time, 4 ml of the suspension was withdrawn and centrifuged immediately. The measurement of absorbance of the supernatant was carried out using UV–visible spectrophotometer. A blank reaction without the catalysts was also performed and its UV–visible measurement was conducted.

2.4. Synthesis of 2-benzimidazoles derivatives using ZnO NPs as catalyst

In a typical procedure, aldehyde (10 mmol) and *o*-phenylenediamine (10 mmol) was dissolved in 10 ml ethanol. To this 0.5 mol% of ZnO (4.1 mg) nanocatalyst was added to the solution. The mixture was sonicated at a room temperature (25 °C) with ultrasound irradiation for 10 min. After completion of the reaction as indicated by the TLC, the reaction mixture was poured in ice cold water. The solid was filtered and the product was washed with water twice, dried and then purified by recrystallization from ethanol.

3. Results and discussion

3.1. Catalyst characterization

The FT-IR spectrum of the ZnO NPs (Fig. 1(a)) shows a strong absorption peaks at 3415 and 16614 cm^{-1} could be assigned to O–H stretch and N–H bend functional groups respectively. The bands observed at 2927, 756 and 644 cm^{-1} can be assigned as –C–H stretch (alkanes), C–H (aromatics) and –C≡C–H (alkynes). The absorption peaks around 1525 and 1445 cm^{-1} can be attributed the C=C bending and C–C stretching of aromatic rings, whereas peaks around 1235, and 1031 cm^{-1} assigned to the C–N stretching mode in aliphatic amines [45]. An intense peak at 549 cm^{-1} which corresponds to hexagonal phase Zn-O stretching vibration [18].

The phases exhibited by the synthesized ZnO NPs were identification by powder XRD patterns. The XRD patterns of the synthesized ZnO nanoparticles is presented in (Fig. 1(b)). The diffraction peaks are found to be consistent with those of the reported data ZnO (JCPDS File no. 89-0511), which further indexed to a hexagonal ZnO NPs. No peaks of impurities were observed indicating a high purity of the NPs. The sharp, strong and narrow peaks shows the good crystallinity of the synthesized NPs. Debye-Scherrer equation [43,44] was used to evaluate