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# ECO FRIENDLY SYNTHESIS OF ZNO NANOPARTICLES USING SUBSTITUTED IMIDAZOLIUM IONIC LIQUIDS; CARACTERIZATION AND ANTIMICROBIAL ACTIVITY

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**Abstract:**
*In this work, ZnO nanoparticles were synthesized via wet chemical method using imidazolium based ionic liquids (ILs), its activity on microorganism pathogens was investigated. X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM) have been employed for the characterization of structure and morphology of the synthesized ZnO particles. Diffraction analysis confirms the formation of cubic form and hexangular structures of nanoparticle, SEM analysis conforms the blossom like shaped morphology with nanosize is observed for the ZnO nanoparticles to IL1 and flake like shaped morphologies with IL2. Pure Ionic liquids and the as synthesized ZnO nanoparticles were screened for their antibacterial activities. In view of the results, among the nanoparticles, it appeared that nanoparticles prepared in ionic liquids with $PF_6^-$ are the most effective products against the tested bacterial strains compared with nanoparticles prepared in ionic liquids with $BF_4^-$ anion.*

Key Words: *ZnO nano particles, ionic liquids, scanning electron microscopy, X-ray Diffraction, Antimicrobial activity.*

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## INTRODUCTION

Green chemicals are a class of compounds that are biodegradable, sustainable materials, environmentally preferable products and are developed in line with compliance to the twelve tenets of Green chemistry. Ionic liquids (IL) have been recognized as environmental benign green media alternative to volatile organic solvents. Application of ionic liquids in chemical processes has blossomed within the last decade. Indeed, these media have been used in replacement of volatile organic solvents in a wide variety of chemical processes, such as separation and purification, and reaction media in biochemical, and chemical catalysis [1]. Particularly room temperature ionic liquids (RTIL) have been widely studied in organic chemistry as new types of environmentally friendly reaction media, owing to their unique properties such as extremely low volatility, wide temperature range in liquid state, ionic conductivity and non-flammability [2-4], which are toxic and not easily degraded in the environment [5]. In some cases, ILs and the structurally related ionic liquid crystals combine these functions and serve as ‘‘all-in-one’’ solvent–reactant–templates, or ionic liquid (crystal) precursors (ILPs and ILCPs, respectively) [6,7]. Nanotechnology has an immense potential to create a wide range of novel, exciting and interesting applications for environment and other sectors like medicines, electronics and communication. The considerable antimicrobial activities of inorganic metal oxide nanoparticles such as ZnO, MgO, $TiO_2$, $SiO_2$ and their selective toxicity to biological systems suggest their potential application as therapeutics, diagnostics, surgicaldevices and nanomedicine based antimicrobial agents [8-11]. The advantages of using these inorganic oxides nanoparticles as antimicrobial agents are their greater effectiveness on resistant strains of microbial pathogens, less toxicity and heat resistance. In addition, they provide mineral elements essential to human cells and even small amounts of them exhibit strong activity [12].

ZnO nanoparticles has many significant features such as chemical and physical stability, high catalysis activity, effective antibacterial activity as well as intensive ultraviolet and infrared adsorption with broad range of applications as semiconductors, sensors, transparent electrodes, solar cells, photo-catalysts, optical materials, cosmetics, nanostructure varistors, UV absorbers, gas sensors, and industrial additives [13-15]. Also in recent years ZnO has received considerable attention because of its unique optical, piezoelectric, and magnetic properties [16]. In addition ZnO nanoparticles has the potential to impact many aspects of food and agricultural systems because of its antimicrobial efficacy especially with the growing need to find alternative methods for formulating new type of safe and cost-effective antibiotics in controlling the spread of resisted pathogens in food processing environment [17]. One of the most important environmental applications of nanomaterials is their use as sensors with enhanced monitoring capabilities for pollutants. They are used for treating contaminated water, soil or air and in green technologies to eliminate or decrease harmful emissions and wastes from industry using photo catalytic processes. Zinc oxide nanoparticles have been found to have superior UV blocking properties compared to its bulk substitute. This is one of the reasons, why it is often used in the preparation of sunscreen lotions. In general, three types of processes are applied for the synthesis of metal oxide particles in solution: the "classical" synthesis under reflux conditions, the autoclave synthesis and, the most recent microwave-assisted synthesis. In this paper, we report an effective method for the preparation of ZnO nanoparticles by using microwave irradiation. The microwave irradiation method considered herein is fast, mild, energy-efficient, and environment-friendly and, hence, it is not a weak substitute of the conventional method. Therefore, this paper focuses on these topics providing a state-of-the-art overview of new paradigms and challenges in research on ionic liquids as green solvents for the synthesis of nano particles and highlights the importance of this topic.

## EXPERIMENTAL

All chemicals used were obtained from BDH Chemicals (England) and used as such without purification. 1-butyl-2-ethyl-3-methylimidazolium bromides [BEMIM] Br, 1-butyl-2-ethyl-3-methylimidazolium tetrafluoroborate [BEMIM] BF4, 1-butyl-2-ethyl-3-methylimidazolium hexafluoro phosphate [BEMIM] PF6 were prepared according to the literature [18]. The ZnO nanoparticles were precipitated following the procedure described in the previous paper [19].

Antimicrobial activity of the as synthesized ZnO nanoparticles was carried out using Broth dilution technique. Briefly, a series of fifteen test tubes were filled with 0.5 ml sterilized nutrient broth. Sequentially, test tubes 2–14 received an additional 0.5 ml of the sample serially diluted to create a concentration sequence from 500 – 0.06 μg. The first test tube served as the control [20]. All the test tubes received 0.5 ml of inoculums. The test tubes were vortexed well and incubated for 24h at 37ºC. The resulting turbidity was observed, and after 24h, the minimum inhibition concentration (MIC) was determined where growth was no longer visible by assessment of turbidity by optical density readings at 600 nm.

The [1]H-NMR and [13]C-NMR spectra of the ILs were recorded in $CDCl_3$ and DMSO-$d_6$ on a Joel JNN ECX 400P spectrometer. The FT–IR spectra were obtained on a Varian 800 FT-IR as thin films or for solid samples. The phase, purity and crystalline size of the ZnO nanoparticles were characterized by powder X-ray diffraction (powder XRD) and Scanning Electron Microscope (SEM). The X-ray diffraction (XRD) patterns were recorded on a Philips Xpert X-ray diffractometer with Cu Kα radiation ($\lambda$ = 0.15406 nm) employing a scan rate of 1° / min in the 2θ range from 20° to 80°. Surface morphology and the distribution of particles were characterized by a LEO 1430VP scanning electron microscopy (SEM) using an accelerating voltage of 15kV. The samples used for SEM and EDX observations were prepared by transferring the particles, which were first dispersed in ethanol, to a glass substrate attached to the SEM stage. After the evaporation of ethanol from the substrate, the particles on the stage were coated with a thin layer of gold and palladium.

## RESULTS AND DISCUSSION:

### XRD analysis

The X-ray diffraction data of the ZnO nanoparticles synthesized in IL-1 (Figure 1a) were recorded by using Cu Kα radiation (1.5406 A°). The intensity data were collected over a 2θ range of 20 - 100°. The average grain size of the samples was estimated with the help of Scherrer equation [21] using the diffraction intensity of (200) peak. X-ray diffraction studies confirm that the synthesized nanoparticles are ZnO with cubic phase and all the diffraction peaks agree with the reported JCPDS data ( 62-2880 ) and no characteristic peaks are observed other than ZnO.

The XRD pattern of sample 2 (ZnO in IL-2) indicates that the surface nanostructures grown on the substrate show reflections indexed to hexagonal ZnO which are in good accordance with the values on the standard card (JCPDS 36-1451). The XRD results confirm the formation of well crystallized ZnO nano particles [22]. According to the full width at half maximum of the diffraction peaks, the average size of the particles could be estimated from the Scherer equation to be about 39 nm for IL1 and 12 nm for IL2.

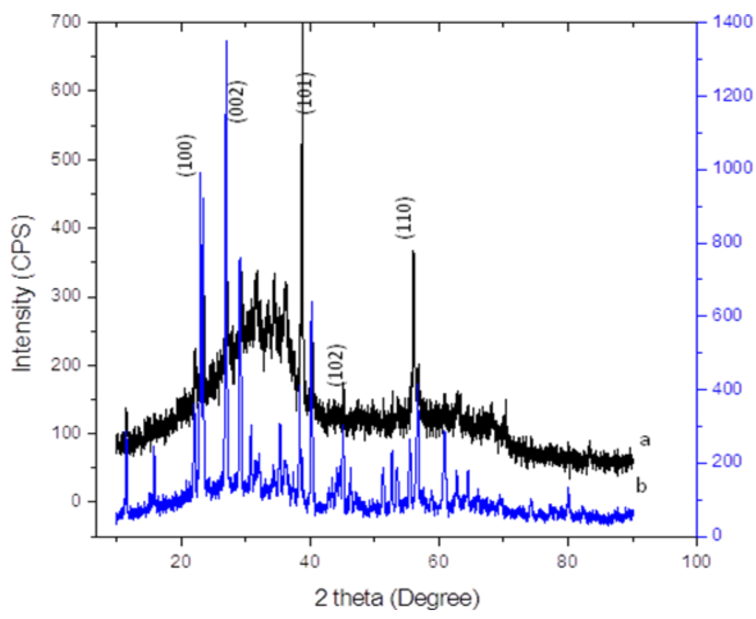


**Fig. 1: XRD images of synthesized ZnO nanoparticles from (a) IL1 and (b) IL2**

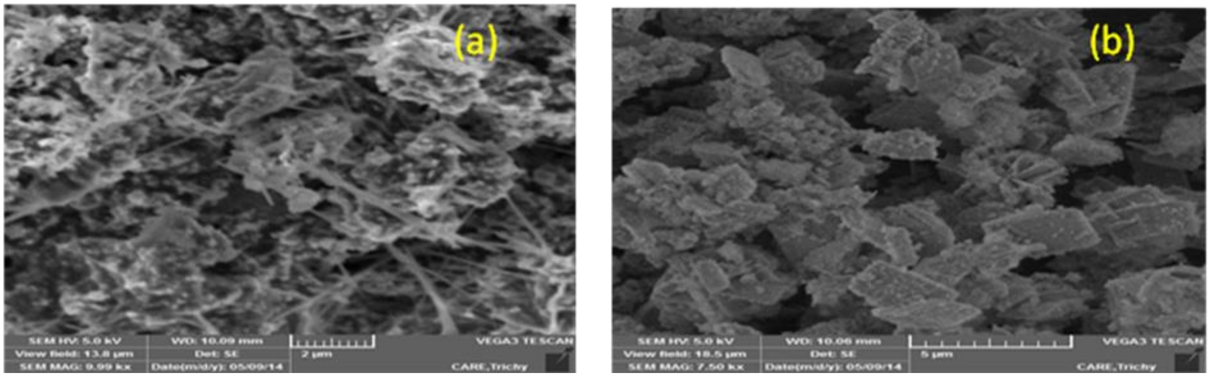


**Fig. 2: SEM images of synthesized ZnO nanoparticles from (a) IL1 and (b) IL2**

**SEM analysis**.
Morphology of the ZnO nanoparticles was investigated by scanning electron microscopy (SEM) which was recorded at different magnifications and one of these is shown in figure 2. Ionic liquids are particularly interesting species in green chemistry not only as they can act as template to control the particle shape and assembly behavior, but also their ionic properties can drastically enhance the efficiency of the nanoparticle production.

For that mean, we have performed the synthesis of ZnO from IL; the synthesized ZnO particles from IL1 exhibit the morphology of blossom shaped particles without any agglomeration (Fig. 2(a)). The mean diameter read from the nanoscale bar of SEM images of ZnO prepared from IL2 is around 38 nm. When the highly coordinated anion $PF_6^-$ is introduced instead of $BF_4^-$, the morphology and size of ZnO also tuned as flake shaped particles (Fig. 2(b)). SEM analysis clearly indicates that the different characteristic ionic liquids produced the ZnO particles with well-defined and extended ordered morphology without any agglomeration and aggregation.

**EDX analysis**
The purity and composition of the products (ZnO nanoparticle in [BEMIM] $BF_4$ and [BEMIM] $PF_6$ were studied by energy dispersive X-ray spectroscopy (EDX). The results are displayed in figure 3a-b. The other peaks in the figure corresponded to gold, palladium, and silicate which were due to sputter coating of the glass substrate on the EDX stage, and these were not considered in the elemental analysis of ZnO. It is clear that the ZnO nanoparticles prepared were sufficiently pure.

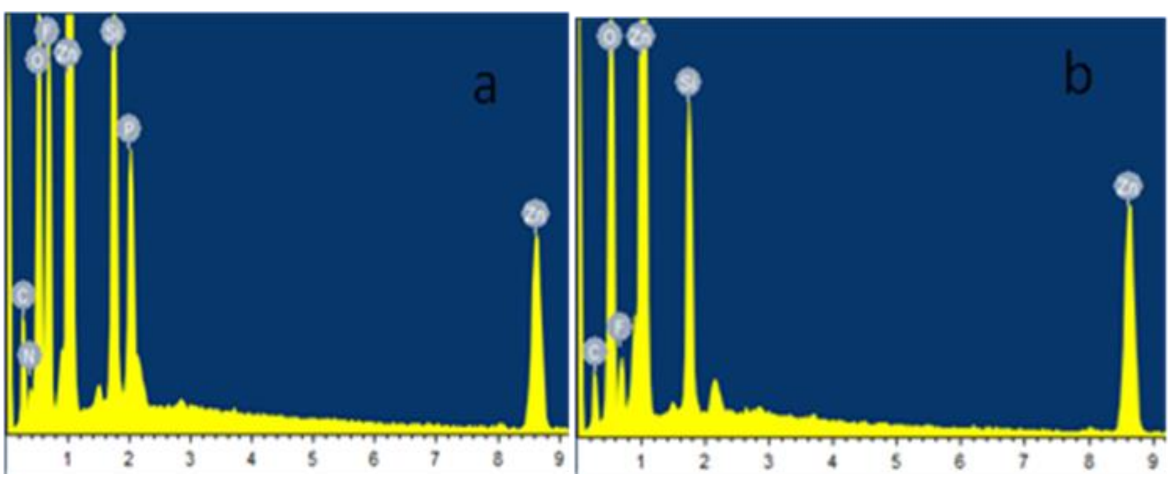


**Fig. 3: EDX pattern of as- prepared ZnO nanoparticles from (a) IL1 and (b) IL2**

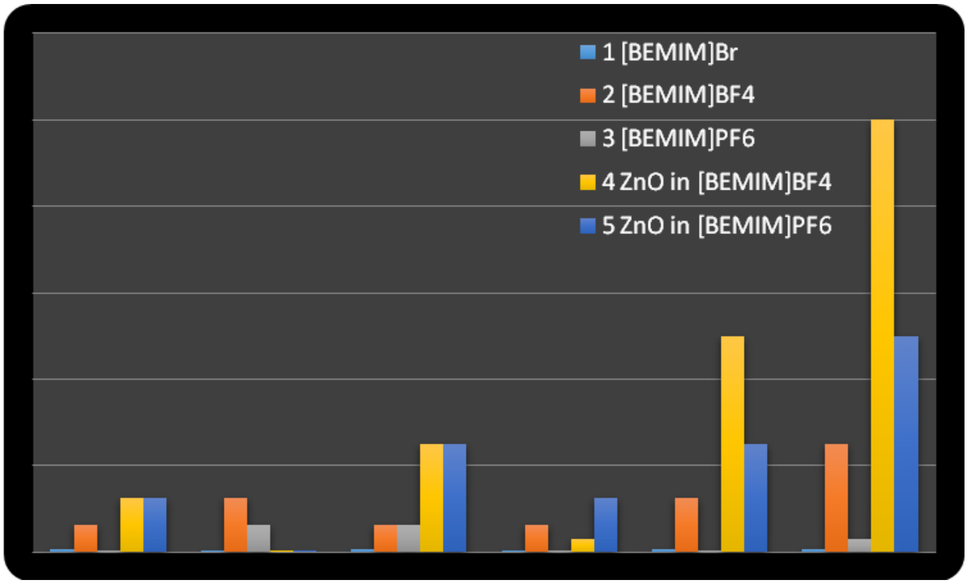


**Fig. 4: Comparative account of antibacterial activity of ZnO nanoparticle in ionic liquids and pure ionic liquids**

**Antimicrobial Activities**

Antibacterial activity of the ZnO nanostructures was compared with their pure ionic liquids against three gram positive bacteria (*Staphylococcusaureus*, *Micrococcusluteus* and *Bacilluscereus*) and three gram negative bacteria (*Escherichiacoli*, *Pseudomonasaeruginosa* and *Aeromonashydrophila*) by broth dilution method.

In view of the results, it appears that the all tested imidazolium ionic liquids stabilized ZnO nanoparticles are less effective products against the tested bacterial strains(except *Micrococcusluteus* gram positive bacteria) compared with the antimicrobial activity of pure ionic liquids. It is also noticed that ZnO nanoparticle has better antimicrobial activities on *Micrococcusluteus* than its pure ionic liquid. The toxic effect of ILs may be related to a common cellular structure or process. It is assumed that the toxicity mechanism of ILs is through interaction with the cell wall and membrane, leading to a membrane disruption [24].

ILs consisting of cation-anion pairs is similar to the structure of surfactants, pesticides and antibiotics that attack lipid structure, and induce polar narcosis due to their interfacial properties, and may cause membrane-bound protein disruption [23] . From the results, it appears that pure IL and nanoparticle with $PF_6^-$ are the most effective products against the tested bacterial strains compared with $BF_4^-$ anion containing ionic liquid and its nanoparticle. From the size of nano particles, it is obvious that the antibacterial activity of ZnO increased with decreasing size according to the previous reports [24]. The enhanced bioactivity of smaller particle probably is attributed to the higher surface area to volume ratio. According to the results, it can be concluded that ZnO nanoparticles are effective antibacterial agents both on Gram-positive and Gram-negative bacteria. Hence, lesser size ZnO nanoparticles with IL2 exhibits lower MIC Values than the ZnO nanoparticles from IL1, which holds the higher nanosize. ZnO inactivation of bacteria involves the direct interaction between ZnO nanoparticles and cell surfaces, which affects the permeability of membranes where nanoparticles enter and induce stress in bacterial cells, subsequently resulting in the inhibition of cell growth and eventually in cell death.

## CONCLUSIONS:

ZnO nanoparticles were synthesized using hydrothermal method; this process is a simple, feasible, fast and facile process without any use of external template or surfactants for the well-defined morphology with less nanosize. The as synthesized ZnO nano particles were characterized by XRD, SEM and EDX and also they were screened for their antimicrobial activities. The XRD pattern of ZnO nanoparticles showed the materials to be at the nanometeric size regime with cubic and hexagonal wurzite structure. SEM observations of ZnO nanoparticles exhibit the different structures of flake like and rods like shaped morphologies without any agglomeration for IL1 and IL2 respectively. From the antibacterial studies, it appears that the two tested imidazolium ionic liquids stabilized ZnO nanoparticles are the less effective products against the tested bacterial strains compared with the anti-microbial activity of pure ionic liquids.

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