# IONIC LIQUID ASSISTED SYNTHESIS AND CHARACTERISATION OF ZnO NANOPARTICLES

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**Keywords:** ZnO, Ionic liquids, XRD, TEM, FT-IR, UV-DRS and Particle Analyzer.

A green approach has been developed for the synthesis of nanocrystalline zinc oxide (ZnO) with the aid of room-temperature synthesized ionic liquids (RTIL's) as crystal growth modifiers by low-temperature precipitation technique. The role of RTIL's (propylammonium acetate (PAA), propylammonium formate (PAF), 3-hydroxy propylammonium acetate (3-HPAA), 3-hydroxy propylammonium formate (3HPAF) and their concentration effect on the particle size is studied in this protocol. The formed nanoparticles are characterized by XRD, TEM, FT-IR and UV-DRS. XRD spectra of nanoparticles exhibit typical diffraction peaks of hexagonal phase with wurtzite ZnO structure corresponding to JCPDS 36-1451. TEM results revealed that spherical nanoparticles obtained with an average particle size in the range of 5-20 nm. UV-Vis-DRS spectra of the ZnO nanoparticles shows blue shift compared to the bulk ZnO, attributed to quantum confinement effect.

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## Introduction

ZnO nanoparticles have been extensively studied over the past few years because of their size-dependent electronic and optical properties.[1] Zinc oxide (ZnO) has attracted immense research interest worldwide during the present decade. Its wide band gap (3.37 eV)[2] and high exciton binding energy (60 meV)[3] makes it a potential material for applications in blue light emitting devices (LED),[4] dye-sensitized solar cell,[5] gas sensors,[6] ceramics,[7] field emission devices,[8] luminescent materials,[9] biomedical[10] and photocatalysis.[11]

In this regard, developing a low-cost process to control the morphology and optical properties is the main challenge to building ZnO nanostructure-based technologies. It is well-known that by reducing the size of materials, their properties can be modified drastically.[12-16] Considerable efforts have been devoted to controlling the morphology and size of ZnO nanostructures.[17-20]

Room-temperature ionic liquids (RTILs) have received considerable attention due to theirs beneficial chemical and physical properties.[21,22] There is significant progress in the applications of RTILs to synthetic-organic chemistry, catalysis, separation, electrochemistry, biopolymers and molecular self-assemblies.[23,24] RTIL's have recently received a great deal of attention as potential new green media for nanomaterial synthesis.[25-28] In continuation of our investigations into nanomaterial preparation by using natural gums [29], the selection of the RTIL's was justifiable by the fact that it can be obtained at a relatively low price and its synthesis method is simple.[30]

The aim of this work is to report the green synthesis of zinc oxide nanoparticles via pressure vial method in different RTIL's. Through this technique, spherical nanoparticles can be synthesized by a precise variation of the concentration of RTIL's. The pressure vial process has proved to be a useful technique for generating various nanostructured materials. Our study shows that the nanostructures are of good crystalline quality with low structural and electronic defects.

## Experimental

All the reagents were of analytical grade and were used without further purification. Zinc acetate dihydrate and sodium hydroxide (NaOH) were obtained from SD Fine Chemicals, India.

All the solutions were prepared with deionized water. Zinc acetate dihydrate (1 mmol) was dissolved in 10 ml of distilled water and different concentrations of RTIL's (propylammonium acetate (PAA), propylammonium formate (PAF), 3-hydroxypropylammonium acetate (3 HPAA), 3-hydroxypropylammonium formate (3HPAF) (0.1 ml, 0.5 ml) was added and stirred for 10 minutes. After complete dissolution, 10 ml of NaOH (0.1 M) was slowly added dropwise to the above solution under magnetic stirring for 10 min. The precursor solution was transferred to a tightly fitted screw capped pressure vial, and the bottles were kept in an oil bath for 2 hrs by maintaining the temperature of 80°C.

The product was separated by centrifugation, washed thoroughly with deionized water followed by ethanol. The white precipitate dried in hot air oven at 60 °C for 2 hrs. The synthesized RTIL's are used for synthesizing ZnO nanoparticles which are listed below in Table 1.

**Table 1.** Synthesized Room Temperature Ionic Liquids (RTILs)

| Name | Chemical formula | Acronym |
|---|---|---|
| 3-Hydroxypropylam-monium formate | $C_4H_{11}NO_3$ | 3-HPAF |
| 3-Hydroxypropylam-monium acetate | $C_5H_{13}NO_3$ | 3-HPAA |
| Propylammonium formate | $C_4H_{11}NO_2$ | PAF |
| Propylammonium acetate | $C_5H_{13}NO_2$ | PAA |

**Characterization**

The structural properties of the obtained products were recorded using a Rigaku X-ray powder diffractometer (Cu radiation, λ = 0.1546 nm) running at 40 kV and 40 mA (Tokyo, Japan). TEM images were observed on TECNAI FE12 TEM instrument operating at 120 kV using SIS imaging software. The particles were dispersed in methanol, and a drop of it was placed on formvar-coated copper grid followed by air drying. UV-Vis-DRS spectra were recorded on a Perkin-Elmer Lambda 750 spectrophotometer. FT-IR spectra were recorded on Thermo Nicolet Nexus (Washington, USA) 670 spectrophotometer.

## Results and discussion

**Structural characterization of ZnO nanoparticles**

Figure 1 shows the crystallinity and phase of the synthesized nanocrystalline ZnO with different RTIL's via pressure vial method. The sharp diffraction peaks manifest that the synthesized ZnO nanoparticles have high crystallinity. The nanoparticles of ZnO were synthesised with four different RTIL's (PAA, PAF, 3HPAA, 3HPAF) and the XRD patterns show similar peak positions (Figure 1 a-d). The prominent peaks labelled at angles of 31.6°, 34.2°, 36.1°, 47.3°, 56.3°, 62.7°, 66.2°, 67.5° and 68.8° belong to the (100), (002), (101), (102), (110), (103), (200), (112), and (201) planes respectively. All the diffraction peaks show a very good agreement with the reported values of the Joint Committee on Powder Diffraction Standards data (JCPDS 36-1451) and confirm the formation of hexagonal phase with the lattice constants of $a = b = 3.2498$ Å, and $c = 5.2066$ Å.[31,32]

The results indicate that the synthesised powders consist of pure phase and no other characteristic peaks of other material were detected. The average crystalline size of the ZnO particles is estimated by using Debye–Scherrer's Equation.[33]

$$D = \frac{0.94\lambda}{\beta \cos\theta}$$

where

$D$ is the average crystalline size
λ is the X-ray wavelength of 1.54 Å,
θ is the Bragg diffraction angle, and
β is the FWHM.

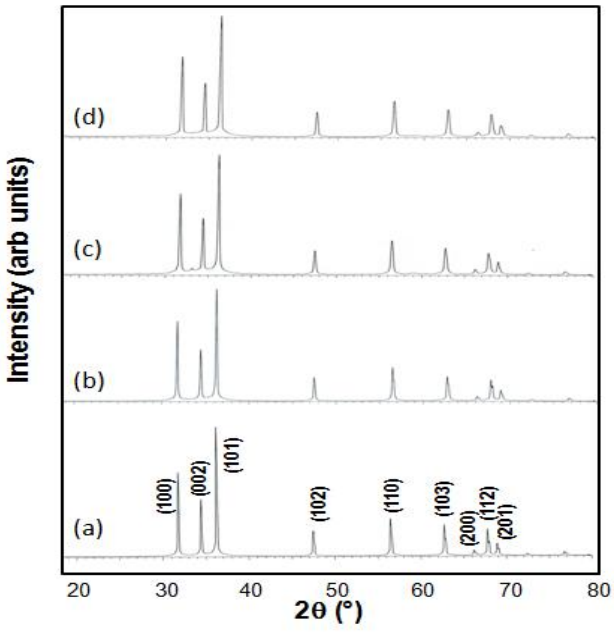


**Figure 1.** XRD patterns of ZnO nanoparticles synthesised in pressure vial with RTIL (a) PAA (b) PAF (c) 3 HPAA (d) 3 HPAF.

**Size control of ZnO nanoparticles**

To access the size of the as-synthesized samples, we performed TEM, and the images are presented in Figure 2. As they can be seen in Fig. 2a, ZnO particles synthesized without RTIL's are very large as well as in various shapes such as spheres (~ diameter = 40 nm and length in few microns) and cubes (~ in the range 30 - 210 nm). The influence of RTIL's on the formation of ZnO nanoparticles in pressure vial method was studied at two molar concentrations of IL's – 0.1ml and 0.5ml. At 0.1 ml RTIL's concentration, ZnO nanoparticles are not distinct, and they appear to be less in number. Increasing the concentration of RTILs to 0.5ml exhibited spherical ZnO nanoparticles of about 10-20 nm. It is likely that initially, $Zn^{2+}$ ions form bonds with the high number of coordinating functional groups of the RTIL's, leading to nucleation and preferentially crystal growth. In the most cases, the van der Waals interactions between the surface molecules of the formed nanoparticles form the driving force for self-assembly, and then ZnO nanocrystals can be assembled to form large ZnO spheres. In the presence of RTIL's, in pressure vial method, the produced sphere-like structures consisting of ZnO nanoparticles (Fig. 2b, c), are of nearly uniform size distribution between 5–20 nm (Fig. 2a), that compares well in accordance with the size – 21.6 nm estimated with XRD studies.

Particle size distribution shown in Fig. 2b clearly indicate a remarkable reduction in the average size of ZnO nanoparticles from 130 nm to 10 nm in the presence of 0.1 ml RTIL's. A small increase in the average particle size was

observed when the reaction was carried out in 0.5ml RTIL's (pressure vial method) that can be assumed due to the re-agglomeration of the nanosized particles in the pressure medium of higher concentration. The higher surface area is attributed to the formation of smaller particles.

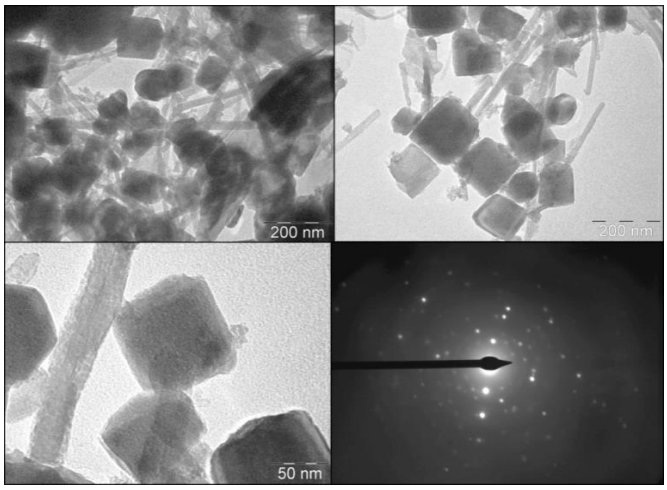


**Figure 2a.** ZnO particles synthesized without RTIL's

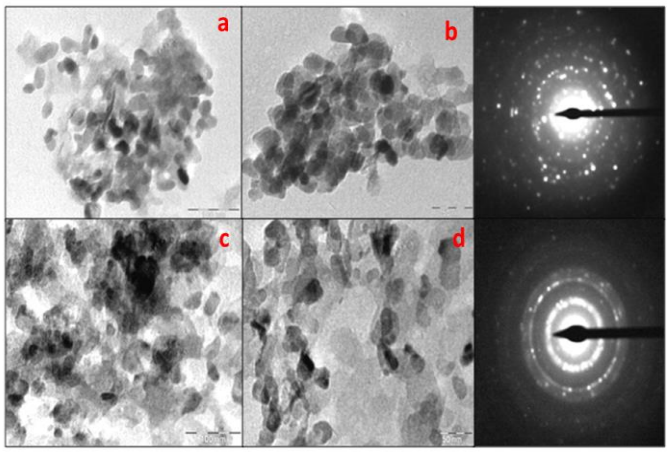


**Figure 2b.** ZnO particles synthesized with RTILs (a) PAA (b) PAF (c) 3 HPAA (d) 3 HPAF at 0.1 ml

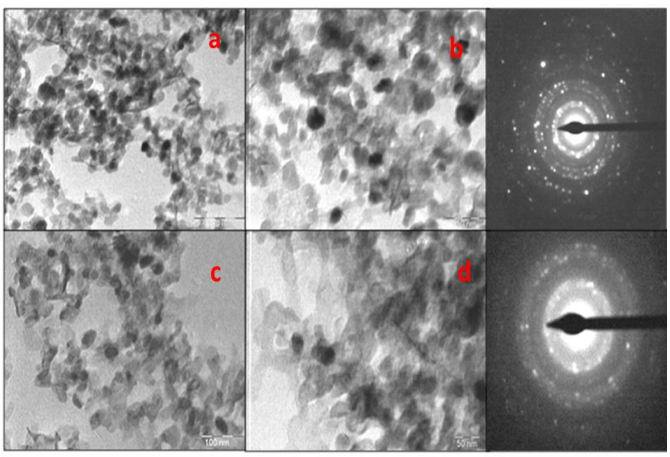


**Figure 2c**. ZnO particles synthesized with RTILs (a) PAA (b) PAF (c) 3 HPAA (d) 3 HPAF at 0.5 ml

This synthesis method provides control over the surface area. These microscopic results suggest that RTIL's can be used as a template for the fabrication of metal oxide hollow spheres as compared to other alternative methods. The selected-area electron diffraction (SAED) patterns taken from the TEM images for all the samples showed a similar pattern. As can be seen, the observed SAED patterns show distinct spots indexed to (100), (002), (101), (102) and (110) corresponding to wurtzite ZnO structure, which is consistent with the XRD results.

**Particle analyzer**

Using Nano Particle Analyzer (SZ100) the size of the as-synthesized nanopowders is measured for the RTIL PAA at 0.1ml. The average particle size of the sample is shown in the histogram in Figure 5. As can be seen from the profile, the size of the particles is in good agreement with XRD and TEM observations with an average particle size of 21.6 nm

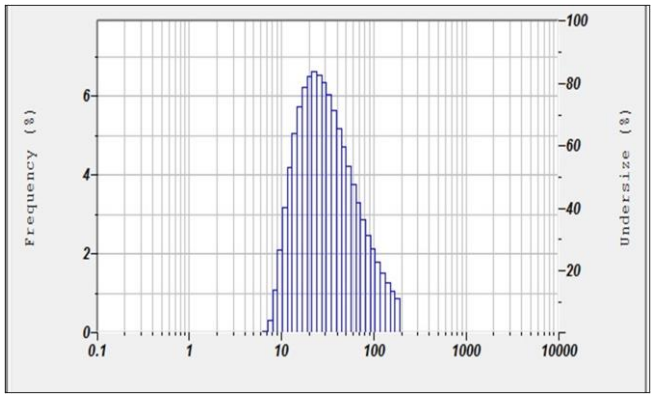


**Figure 5.** Particle analyzer histograms of ZnO powders.

**UV-Vis-DRS spectra**

To examine the optical properties, synthesized ZnO nanostructures were examined by ultraviolet-visible-diffused reflectance spectroscopy (UV-Vis-DRS), and results are presented in fig 3. As displayed in figure 3, a strong absorption at about 401, 401, 391, 392, with 0.1 ml and 393, 395, 390, 385 nm with 0.5ml are observed for ZnO nanoparticles. The absorption edge of ZnO nanoparticles shows an obvious blue shift due to the quantum confinement effect. This phenomenon is explained by Burstein–Moss effect.[34-35] The corresponding band gap energies were determined and found to be 3.09, 3.09 3.17, 3.16 with 0.1 ml and 3.15, 3.14, 3.18, 3.22 eV with 0.5 ml (Fig. 3 inset) for synthesized ZnO nanoparticles. The band gap energies are observed slightly lesser than the commercial ZnO (3.37eV). This demonstrates that the synthesized ZnO particles are pure, showing band gap in the range 3.09 eV - 3.22 eV, and has good optical property.

**FT-IR spectra**

Figure 4 represents the typical FT-IR spectra of as-synthesized ZnO with RTIL's in pressure vial method. The broad peak in the higher energy region, 3100 – 3600 $cm^{-1}$ is due to the stretching vibration of -OH and -$NH_2$ groups on the surface of ZnO nanoparticles.

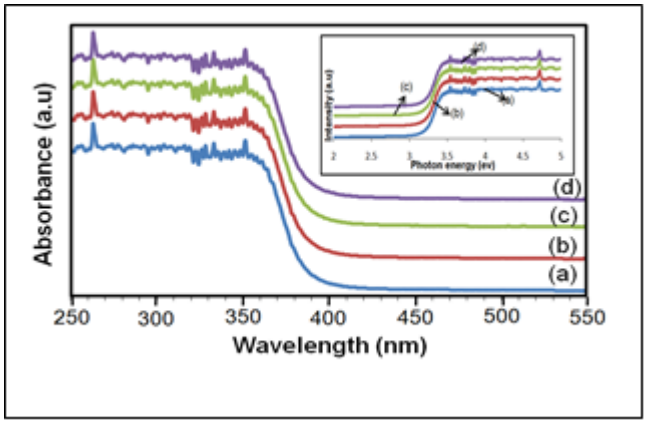


**Figure 3.** Ultraviolet-visible-diffused reflectance spectroscopy of ZnO nanoparticles synthesised in pressure vial with RTILs (a) PAA (b) PAF (c) 3 HPAA (d) 3 HPAF.

The characteristic absorption peak for the bridging coordination modes of acetate group with Zn appears in the range 1500-1650 $cm^{-1}$ resulting from residual acetate used for the synthesis of ZnO nanoparticles. The peaks at 1000 to 1100 $cm^{-1}$ and 2928 $cm^{-1}$ can be assigned to the symmetric methylene stretching. The stabilization of ZnO nanoparticles by using RTIL caused slight changes in the intensities of the absorption band in the range of 600-400 $cm^{-1}$ that is attributed to the Zn-O stretching (characteristic absorption band). These differences in IR spectra can be explained on the basis of constrained growth of the formed nanoparticles.[36]

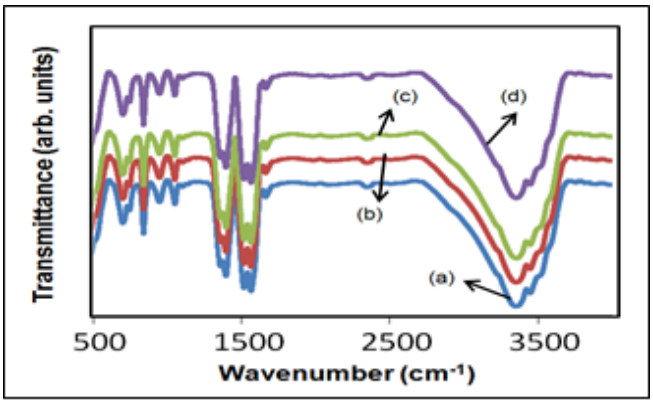


**Figure 4.** FT-IR spectra of ZnO nanoparticles synthesised in pressure vial with RTIL (a) PAA (b) PAF (c) 3 HPAA (d) 3 HPAF.

## Conclusions

In this work, ZnO nanoparticles were synthesized using the direct precipitation method at 80°C by pressure vial reaction. The advantage of this method is that a large quantity of ZnO nanoparticles can be synthesized with high purity and the size of the particles is reduced by applying pressure and also an environmentally friendly route. The role of different concentrations of RTIL's (propylammonium acetate (PAA), propylammonium formate (PAF), 3-hydroxypropylammonium acetate (3-HPAA), 3-hydroxypropylammonium formate(3HPAF) on the particle size was studied. X-ray diffraction results show the formation of a hexagonal wurtzite zinc oxide structure with a high degree of crystallinity. By increasing the concentration ratio of the reactant raw materials from 0.1ml to 0.5ml, the intensity of the reflection peaks increased, and the average size of the as-prepared nanoparticles increased from 10 to 20 nm. Transmission electron microscopy revealed the size distribution of the nanoparticles. The actual average size of nanoparticles obtained by TEM for a concentration ratio of 0.5ml was 20 nm. The ZnO nanoparticles were approximately spherical, confirming the result obtain by TEM. The nanoparticle sizes estimated given XRD and TEM are all in good agreement with each other.

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