Structural Investigation of ZnO Nanocapsule using $ZnCl_2$ as precursor and PEG 2000 as Surfactant by chemical method

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Abstract: Crystalline ZnO nano-capsule was prepared from hydrated zinc chloride ($ZnCl_2.2H_2O$) precursor stabilized by PEG 2000 surfactants and calcined at 400 °C. XRD result indicated the pure wurtzite-structure and crystalline nature, which is well supported to the SAED obtained from pattern HRTEM studies. The synthesized product has been also characterized by FT-IR spectroscopy for analyzing the presence of different bands of the prepared materials. Surface morphological analysis is done by FESEM (Field emission scanning electron microscope) and HRTEM (High resolution transmission electron microscope) of ZnO. The analysis is well indicated the thermo-reaction of prepared materials, which is a formed different types ZnO nanomaterials. FESEM analysis showed the Nano-capsule like structure of as-prepared ZnO materials with surfactant, whereas particle type morphology was observed in absence of surfactants. A capsule-like structure without long-range order of HRTEM images of ZnOwas shown.The obtained particles were indicated thenon-uniform shape distributions at 400 ºC. The average particle size of ZnO without PEG 2000 is found to ~86 nm. EDS data for chemical component analysis showed that the as-prepared ZnO with PEG 2000 were free from impurities i.e., 100% purity.

Keywords: Zinc Oxide, Nano-capsule, HRTEM, Surfactant

I. INTRODUCTION.

ZnO is a widely used and multi-functionality material, leading to technological applications such as optoelectronic devices [1],piezoelectricity [1], gas sensing [1], photocatalysis [2], solar cells[2], etc. The electronic properties of ZnO depend on direct band gap. The direct wide band gap of ZnO (Eg~3.3 eV at 300 K)with a large exciton binding energy (EB ~60meV at 300 K) makesit an excellent material for optoelectronic applications [1,2]. It has been shown that the variation of optical and electrical properties of ZnO can betuned by variation of different parameters such as growth conditions, introducing dopants, and/or reducing the grain dimensions [3]. These properties of ZnO can be further manipulated by forming thin films and nanostructures [4].Well separated nanorods of ZnO have been grown and tested for gassensing due to the increased surface to volume ratio [1]. Nanoparticlecoating of ZnO has found applications in electroluminescence[5].

ZnO nanostructures have also been explored in dye-sensitizedsolar cell (DSSC), which is one of the most promising candidates in photovoltaics [6]. Zhang et al. reported a high energy conversion efficiency of up to 5.4% for polydisperse ZnO aggregates based DSSCs [6]. ZnO nanobullets and nanoflakes have recently beenstudied as active photoanodes in DSSC systems [7]. It has been reported that the light-to-energy conversion efficiency of 3.64% ishigh for the case of ZnO nanoflakes based DSSCs, while it is 1.93% forthe case of nanobullets based DSSCs [7]. From a spintronic application perspective, it is interesting to note that room-temperature ferromagnetism (RTFM) has been reported on undoped and dopedZnO thin films and nanoparticles [8]. In this case, a good control over the size distribution of ZnO nanoparticles is vitally important. Until now, synthesis of ZnO nanoparticles has been accomplished by thermal decomposition [9], co-precipitation[10], combustion [11], and sol–gel techniques [12].In most of these techniques, however, the synthesized nanoparticlesare often not spherical and have a large size distribution. An additional high-temperature processing step is also required in order to obtain crystallinity, which may lead to significant side effects such as the formation of multiple phases [13]. Therefore, development of a new technique for the synthesis of spherical ZnOnanoparticles with a narrow size distribution is of great interest.In this letter, we report on a novel microwave plasma assisted spray (MPAS) technique for the growth of uniform ZnO nanoparticles. This technique has several advantages over conventional methods, including short reaction time, formed spherical particles, narrow size distribution, and high purity. A comparative study of the magnetic and photoluminescence (PL) properties of 400nmand200nm ZnO nanoparticles are presented [14].

In the present work, we have synthesized nanospnidel ZnO from titanium isopropoxide precursor with using PEG 20000 surfactant, which is different from nanoparticles in thermal-chemical process. The surface

morphology, FTIR, UV-Visible, optical band gap, and thermal properties of prepared TiO_2 nanomaterials were performed.

II. EXPERIMENTAL SECTION

2.1. Materials and Method. $ZnCl_2.H_2O$ was purchased from Loba Chemicals (Assay= 97 %), whereas other chemical like ammonium hydroxide (NH_4OH) was bought from Merck India. All the purchased chemicals are research grade. Distilled water was used throughout the synthesis process.

2.2. Synthesis of Nano-capsuleZnO. In a typical synthesis, we are slightly modified the synthetic procedure for the synthesis of ZnO at room temperature [15]. In this route, 0.2 M solution of zinc chloride ($ZnCl_2.2H_2O$) was added to ammonium hydroxide (NH_4OH) with 10 min of stirring to prepare white precipitate **of zinc hydroxide [$Zn(OH)_2$]**. **$Zn(OH)_2$ was** calcined at 400 ºC, to form ZnO. The appearance of calcined ZnO is to be yellowish. The flow chart of synthesised ZnO Nanocapsule is shown in **Figure 1**.

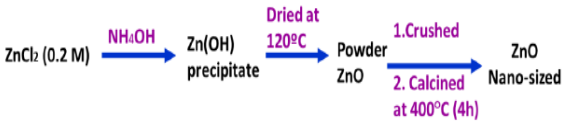


Figure 1: Flow chart of synthesised ZnO nano-sized materials

2.3. Sample Characterizations. High resolution transmission electron microscopy (**HRTEM**) samples were prepared by drop-casting method. ZnO dispersed in ethanolsolutions and put on carboncoated copper grids. The measurements were performed using a JEM-2100 HRTEM, JEOL, and Japan and an accelerating voltage of 200 kV. Surface morphology of as-prepared ZnO nano-capsule was analysed by **FESEM** using Carl Zeiss Supra 40 scanning electron microscope. For this experiment, operating voltage was maintained at 30 kV. EDX was analysed by FESEM. **XRD** experiments were performed using a Phillips PW-1710 advance wide angle X-ray diffractometer, Phillips PW-1729 X-ray generator and Cu Kα radiation (wavelength, λ = 0.154 nm). The generator was operated at 40 kV and 20 mA. **FTIR** spectra were recorded on a Thermo Nicolt Nexus 870 spectrophotometer in the range of 400-4000 cm^{-1}. The instrument settings were kept constant (50 scan at 4 cm^{-1} resolution, absorbance mode). UV-Vis spectra were measured on the powdered samples with a spectrophotometer (Micropack **UV-VIS-NIR**, DH 2000 and 200-800 nm wavelengths). The optical band gap is estimated from UV-Vis spectra data.

2.4. Results and Discussion

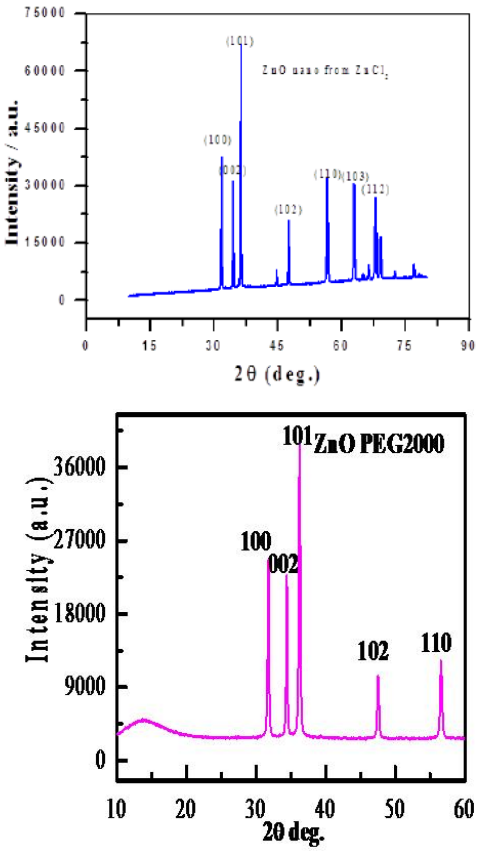


Figure 1XRD pattern of ZnO nanomaterials without (ZnO from ZnCl2) and with(ZnO PEG 2000) surfactant

In order to study the surfactant effect on crystallinity and particle size of as-prepared ZnO nanomaterials were employed. **Fig. 1** shows the XRD patterns of the synthesized ZnO nanomaterials at room temperature and calcined at 400 ^oC. All the diffraction peaks fit well with the wurtzite ZnO crystal structure, proving that ZnO was successfully formedvia this chemical synthesis route [16,17]. The intensity of all diffraction peaks of ZnO assist PEG2000 surfactant was decreased as compare with ZnO nanoparticles, indicating that the crystallinity of ZnOcould be decreased[16,17].

The morphology of the prepared nanoparticles was examined using field emission scanning electron microscopy (FESEM). Figure 5 shows the surface morphology of the particles prepared in our report. The shapes of the particles are nearly spherical and obviously demonstrate aggregation of the particles. The aggregation of particles should have been originated from the large specific surface area and high surface energy of ZnO nanoparticles. The aggregation occurred probably during the process of drying.

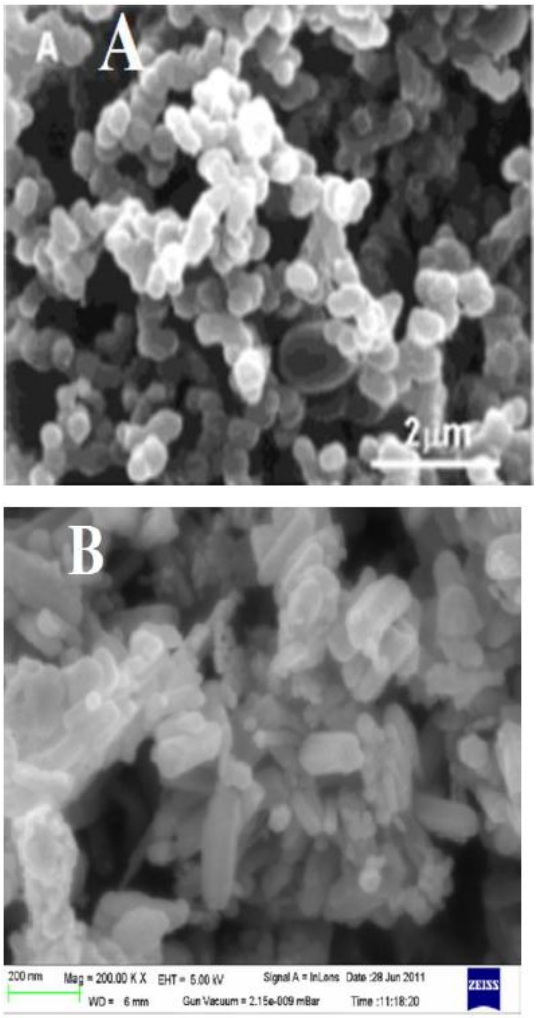


Figure 2FESEM images of ZnO nanoparticles without PEG 2000 (A) and with PEG 2000 (B)

HRTEM images, SAED pattern and lattice pattern of the corresponding ZnO nanoparticles (synthesized using without and with surfactant are shown in **Fig. 3** and **4**. The particle size distribution of ZnO synthesized without using surfactant ranges from 90 to 150 nm, as shown in **Fig. 3**. The particle size is changed to rod-like shaped after using the PEG 2000 surfactant during the synthesis of ZnO. The diameter size of the rod is ranging from 100-150 nm. The SAED pattern is indicated non-homogeneity in crystalline ZnO phase. The lattice fringes of the ZnO nanoparticles were further revealed in an HRTEM image (inset picture of **Fig. 1D**), suggesting that the as-synthesized ZnO nanomaterials with and without PEG2000 surfactant were crystallized nature.

The EDAX Study of the prepared sample contains PEG 2000 surfactant is shown in **Figure 3**. This shows that the sample contains only Zinc and Oxygen and no other elements are present in the sample. Hence, the prepared sample is high purity [18].

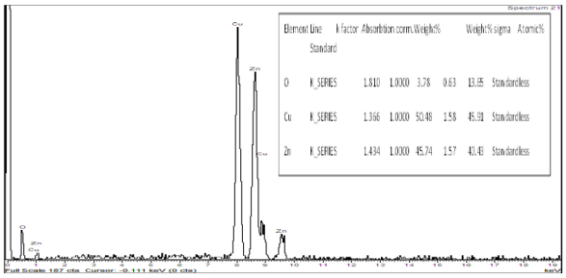
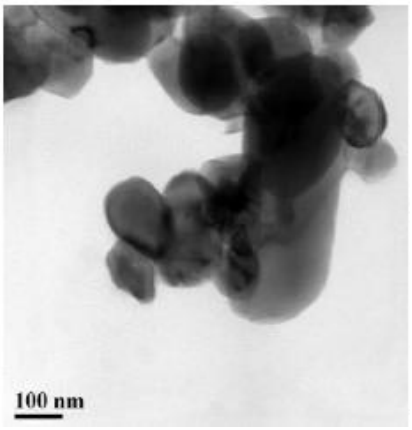
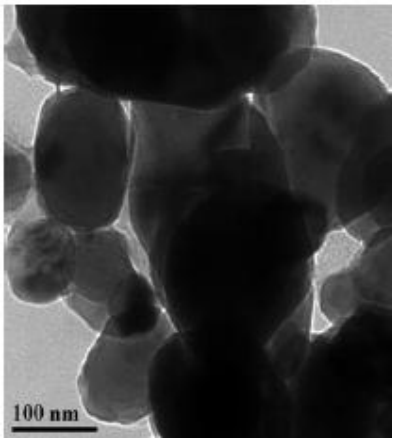
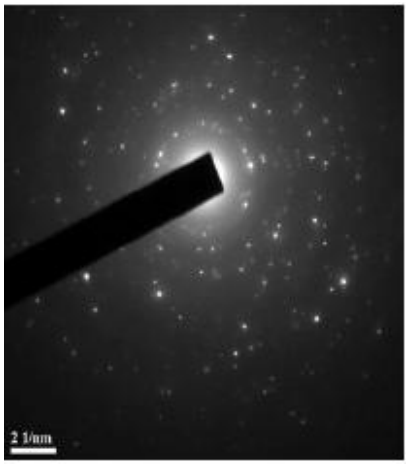


Figure 3 EDX of ZnO with PEG 2000 surfactant







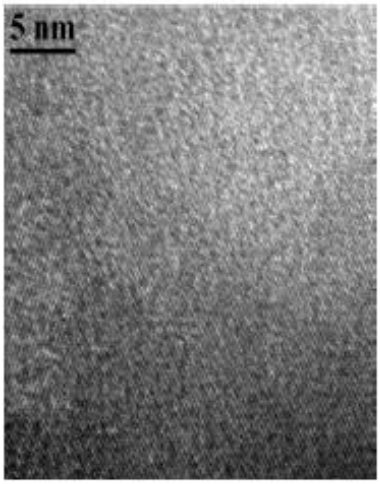
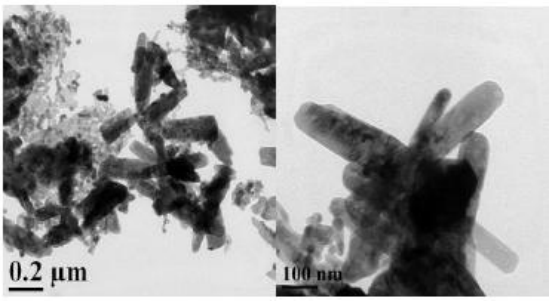


Figure 4HRTEM image and Lattice pattern of ZnO nanoparticles without PEG 2000 surfactant



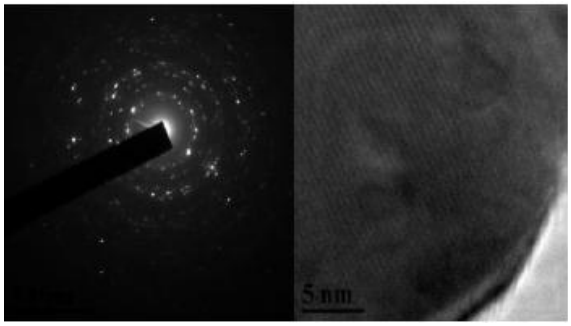


Figure 5HRTEM image, SAD pattern and Lattice pattern of ZnO nanoparticles with PEG 2000

Fig. 6 shows the FTIR spectra of different samples within the region 4000 -1000 cm^{-1}. The as-prepared ZnO nanoparticle without PEG2000 surfactant exhibits small absorption bandat 3491 cm^{-1} whereas, ZnO Nanocapsule with PEG2000 surfactant shows broaden peaks at 3453 cm^{-1}. This is indicating the presence of OH bond in PEG2000 and adsorbs a small amount of moister [19,20]. The triplet band of the C-O stretching vibrations with maxima at 1109 cm^{-1}, and the split band of CH_2 wagging mode with maxima at **1412** cm^{-1} is evidence for the presence of a crystalline PEG2000 phase [19,20]. They are observed clearly in the FTIR spectrum of the PEG2000 (Fig.6). Zn-O stretching band of ZnO nanoparticles and ZnO Nanocapsule is found to be 576 and 428 cm^{-1}respectively.

The wurtzite structure of ZnO was further confirmed using UV–visible optical spectroscopy measured in the range 300–800 nm. **Fig.7** shows the room temperature optical absorption spectra of ZnO Nanocapsuleis a function of wave length. The UV-Visible absorption spectroscopy of ZnO nanoparticles in ethanol solvent shows an excitonic absorption peak at at 369 nm.It is due to aggregation and agglomeration of Nanocapsule. The nanomaterials size increases and material settled down on the bottom of container causing decrease in the absorbance. This behavior is typical for many semiconductors due to internal electric fields within the crystal and inelastic scattering of charge carriers by phonons [17,21].

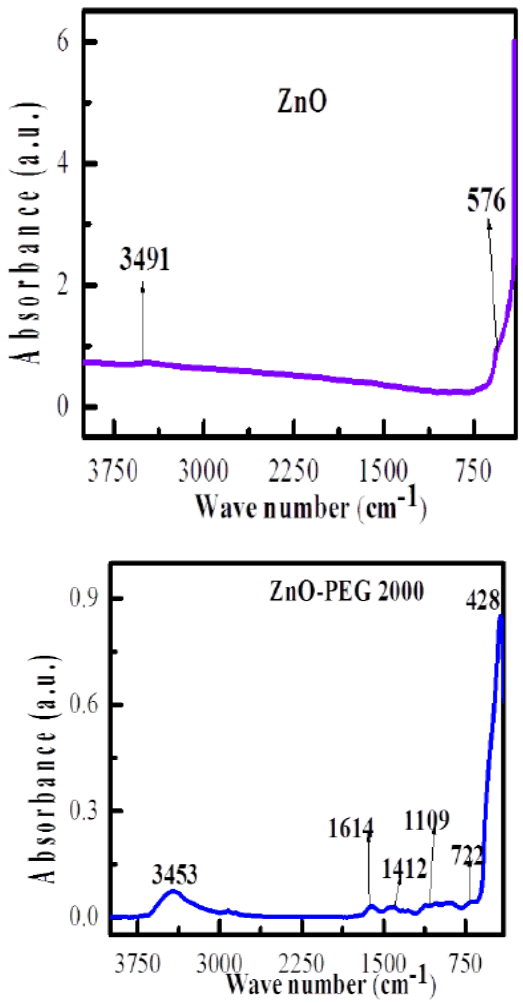


Figure 6 FTIR spectra of ZnO nanomaterials without and with PEG 2000 surfactant

It may be noted that the band gap of pure ZnO is in the range of 2.5- 4.0 eV [22]. The absorption coefficient and the energy band gap can be described by the following equation [22]; $\alpha h\upsilon = B(h\upsilon - E_g)^{1/2}$. Where$h\upsilon$ is the photon energy, α is the absorption coefficient, and B is a constant.A plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ is made to determine bandgap $E_g$using the linear fit process. The extrapolated absorption threshold of the ZnO nano-capsule with PEG 2000 surfactant is shown in **Fig.7.** The estimated band gap is 3.09 eV. This is called wide band gap semiconductor [23].

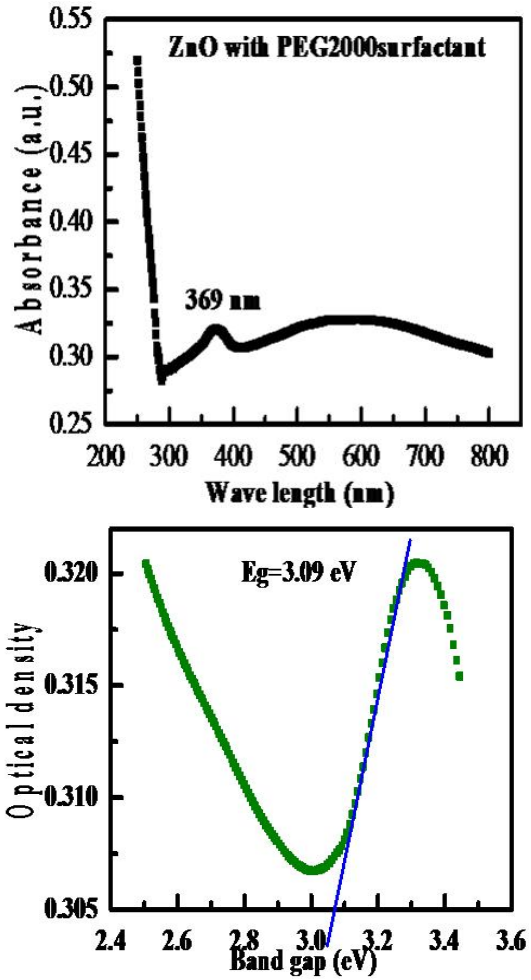


Figure 7 UV-Visible spectra and optical band gap of as-prepared PEG 2000 surfactant based ZnO nanomaterials

III. CONCLUSIONS

In this paper, we have reported the synthesis of ZnO nano materials by chemical method. The obtained ZnO nanomaterials were characterized using XRD, FT-IR, FESEM, HRTEM, and UV Visible analysis. XRD analysis showed that synthesized ZnO nano powder has the pure wurtzite structure with hexagonal phase. From EDS data, the atomic percentage of Zn and oxygen was obtained to be 100% which revealed that sample has high purity. SEM picture showed that particles were arranged on one another. Due to quantum confinement effects, the band gap of the ZnO Nanocapsule (with surfactant) is found to be 3.09 eV.

IV. ACKNOWLEDGEMENT

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