Microwave assisted additive free synthesis of nanocrystalline zinc oxide

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Abstracts: An additive free synthesis of nanocrystalline zinc oxide using microwave technique is reported. Current methodology is faster, cleaner and cost effective compared with conventional method for the synthesis of zinc oxide nanocrystalline materials. The structure and morphology of nanocrystalline zinc oxide was investigated by TEM, XRD, EDAX, UV-Vis spectroscopy. The results demonstrate that microwave heating can produce polygonal zinc oxide within a short span of time.

Keywords- Nanocrystalline, ZnO, microwave, 1,4-butanediol.

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1. Introduction

In recent years the synthesis of nanocyrstalline metal oxides is an important subject due to their unique properties such as high surface area, unresidual free energies and their applications in various fields. Among the different metal oxides, nanocrystalline zinc oxide has wide applications e.g. it is an important semiconductor with a band gap of 3.37 eV, and large exciton-binding energy of 60 meV. It is also used in field emission displays, dyes sensitized solar cell, gas sensors, optical probe, catalysis, pharmaceuticals and cosmetics industries [1-6]. The preparation of nanocrystalline zinc oxide was reported using several methodologies like solid state reaction [7], chemical vapour phase oxidation of Zn powder [8], solvothermal process [9] and sol gel process [10]. However, most of these methodologies are limited due to use of high temperature, high pressure, toxic reagents, and long reaction time. Efforts were made to replace these methods using polyol process but still they require external additives during the reaction.

Hence there is sufficient scope for the development of facile, rapid, convenient and additive free synthesis of nanocrystalline zinc oxide which can provide both qualitative and quantitative support for its commercial applications vivid areas. Recently, microwave (MW) technique is extensively used for the synthesis of materials. Since microwave heating is an in situ mode of energy conversion they are fundamentally different from conventional heating processes. Heat will be generated internally within the material, instead of originating from external sources. The major advantages of microwave application in industrial processes are rapid heat transfer, volumetric and selective heating, compactness of equipment, speed of switching on -off mode and pollution-free environment as there are no products of combustion. In microwave heating dipolar molecules try to align themselves with alternating electric field of the microwaves [11]. The advantage of microwave-mediated synthesis over the conventional heating is the improved kinetics of the reaction by one or two order of magnitude, due to rapid initial heating and the generation of localized high-temperature zones at reaction sites [11].

These molecular movements generate heat and it is then dispersed as the rotating molecules hit other molecules and put them into motion. The microwave power dissipation in per unit volume in solvent is represented as follows:

$$P = c\, E^2\, f\, \varepsilon'' \quad \text{----(1)}$$

where c, E, f and ε'' are radiation velocity, an electric field in the material, radiation frequency and dielectric loss constants, respectively. ε'' is most critical parameter that determines the ability of the material to heat in the (MW) field. 1, 4-butanediol has a high value of ε'' and a high boiling point of 235°C. Hence, it may serve as an ideal solvent for the microwave heating. 1, 4-butanediol also has good reducing power and sometimes it is used in polyol process.

Herein we repot a facile, additive free microwave assisted protocol for the synthesis of nanocrystalline ZnO using only 1,4-butanediol and zinc acetate [Zn $(CH_3COO)_2$]. To the best of our knowledge, this is first report on additive free microwave assisted synthesis of nanocrystalline ZnO using 1,4-butanediol as solvent and fuel for synthesis of nanocrystalline material. This procedure is simple, rapid and works without complicated apparatus. The catalytic activity of prepared nanocrystalline ZnO for the synthesis propargylamine using benzaldehyde, piperidine and phenylacetylene was also studied.

2. Experimental.

The chemicals such as $Zn(CH_3COO)_2$ (A. R. grade) and 1,4-butanediol were purchased from S. D. Fine chemicals Pvt. Ltd. India and used without further purification. The synthesis of nanocrystalline ZnO was carried out in domestic microwave, which was operated at 100 % power of 800 W and a frequency of 2.45 GHz. In a typical procedure 0.420 g of $Zn(CH_3COO)_2$ was dissolved in 10 mL of 1,4-butanediol. The mixture was put in a 25 mL closed conical flask and placed in microwave. The synthetic reaction was carried out at 200 W for 2 min with on-off mode with a time interval of 30 s. Initial colorless solution of the butanediol became milky white indicating formation of ZnO. The reaction mixture was centrifuged at 8000 rpm to separate the product. The mother liquor was then subjected to GC-MS (Shimadzu QP 2010) analysis in order to reveal the mechanistic pathway.

The separated product was several times washed with deionized water and absolute alcohol and dried under vacuum at 60°C for 4h. The yield of obtained product

was ~70%. The morphology and particle size analysis of prepared sample was carried out using transmission electron microscope (Philips model CM 200, operating voltage 200 kV) with maximum resolution 0.23 Å. The particle size histogram was obtained using dynamic light scattering technique (Beckman coulter Delsa C–instrument). The X-ray crystallographic pattern was obtained by XRD miniflex Rigaku model using Cu Kα =1.54 Å with a scanning rate of 2° per min from 0° to 60°. UV-Vis spectroscopy measurement was done using Shimadzu UV 1650-PC with a quartz cuvette path length of 1 cm. The sample composition was examined by EDAX analysis with JEOL-JFC 1600 with Pt coating.

3. Results and discussion

The morphology of prepared sample was determined by TEM. **Fig. 1** shows that the product formed is in the nano region with uniform polygonal shape and the particles are well monodispersed. **Fig.2** shows the particle size histogram, indicating an average size of 59 nm with a standard deviation of 16 nm. Phase identification was done using X-ray diffraction technique and results were shown in **Fig.3** indicates planes (100), (002), (101), (102), (110) which can be indexed to the hexagonal close packed ZnO. Using Scherrer's equation: $D=0.9\lambda/\beta\cos\theta$ (where D is the average crystalline size, λ is the wavelength of Cu Kα, β is the full width at half maximum of the diffraction peaks, and θ is the Bragg's angle) the average particle size of ZnO is calculated to be around 40 nm. **Fig. 4** shows UV-Vis spectrum of the ZnO particles dispersed in absolute alcohol. The spectrum is recorded from 500 nm to 200 nm, giving an absorption peak at 368 nm. As reported in the literature [12] & [13] this absorption peak indicates that the prepared particles are in nanoregion with an average particle diameter of 48 nm and with band gap energy of 3.37 eV using effective mass method equation as given below:

$$E(R) = E_g + \frac{\hbar^2 \pi^2}{2 \mu R^2} - \frac{1.786\, e^2}{\xi R} - 0.248\, E_{RY} \qquad \text{---- (2)}$$

where *E(R)* is the cluster radius and *Eg* is the band gap of bulk ZnO. EDAX analysis shown in **Fig 5** confirms that the prepared nanocrystalline ZnO is composed of zinc and oxygen elements only.

A brief consideration of the mechanisms of the formation of the ZnO nanoparticles is given. Under the influence of microwave heating, hydroxyl groups of 1, 4-butanediol react with acetate groups of zinc acetate to form zinc hydroxide and butyl ester, followed by dehydration to form nanocrystalline zinc oxide, as illustrated in **Fig. 6**. The presence of butyl ester was confirmed by GC-MS analysis of the mother solvent (**Fig. 7.**)

4. Evaluation of catalytic activity of prepared nanocrystalline ZnO.

In nanosize metal oxide the number of surface atoms is a large fraction of the total. Therefore, catalytic activity of nanocrystalline metal oxide greatly enhances than that of bulk counterpart. It is well known that surface of zinc oxides exhibit both Lewis acid and Lewis base character and surface atoms make a massive participation to its catalyst activity [14]. Herein, we have studied the catalytic activity of prepared nanocrystalline ZnO for the synthesis of propargylamines (Fig.8.) To check the catalyst activity of zinc oxide the reaction was carried out in the absence of catalyst. Even after prolong time products were not observed. See (Table1.Entries 1-2) While in the presence of catalyst it gives good yields of product (Table 1.Entries 3-5) In propargylamine synthesis benzaldehyde and piperidine reacts to form imine. ZnO coordinates with phenylacetylene by C-H bond activation to generate acetylide intermediate which then reacts with iminium ion to form corresponding propargylamines (Fig.9.) [15-17]. Nanocrystalline ZnO posses higher surface area than bulk ZnO hence have higher active sites, which ultimately results in the higher yields and selectivity of products (See Table 1, entries 4 vs 5). The products are well known, reported and were confirmed by comparison of their Gas Chromatographic data (Perkin Elmer-355) and Mass spectral data (GC-MS, Shimadzu QP 2010) with those of authentic samples.

5. Conclusion

Nanocrystalline ZnO materials are synthesized using single-step, microwave-assisted method with zinc acetate as a precursor and 1,4-butanediol as a solvent and promoter under mild conditions. As prepared nanocrystalline ZnO has strong catalytic

activity for synthesis of propargylamines. This simple method would also be applicable to the synthesis of other functional metal oxide materials.

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Table 1. Table showing catalytic activity of ZnO for propargylamine synthesis.

Entry	R_1	R_2,R_3	R_4	Catalyst	Time (h)	Conversion(%)[b]	Selectivity[b]	%yield[b]
1	Ph	Piperidine	Ph	none	12	-	-	-
2	Ph	Morpholine	Ph	none	12	-	-	-
3	Ph	Piperidine	Ph	ZnO bulk	7	100	65/35	61
4	Ph	Piperidine	Ph	Nano ZnO	5	100	100	95
5	Ph	Morpholine	Ph	Nano ZnO	5	100	100	94

[b] The conversion, yield, selectivity is based on GC-analysis & GC-MS analysis. Reaction condition –aldehyde 1 mmol, amine 1.2 mol, alkyene 1.5mmol. Toluene-(3-5mL), catalyst 10 mol%, Reflux.

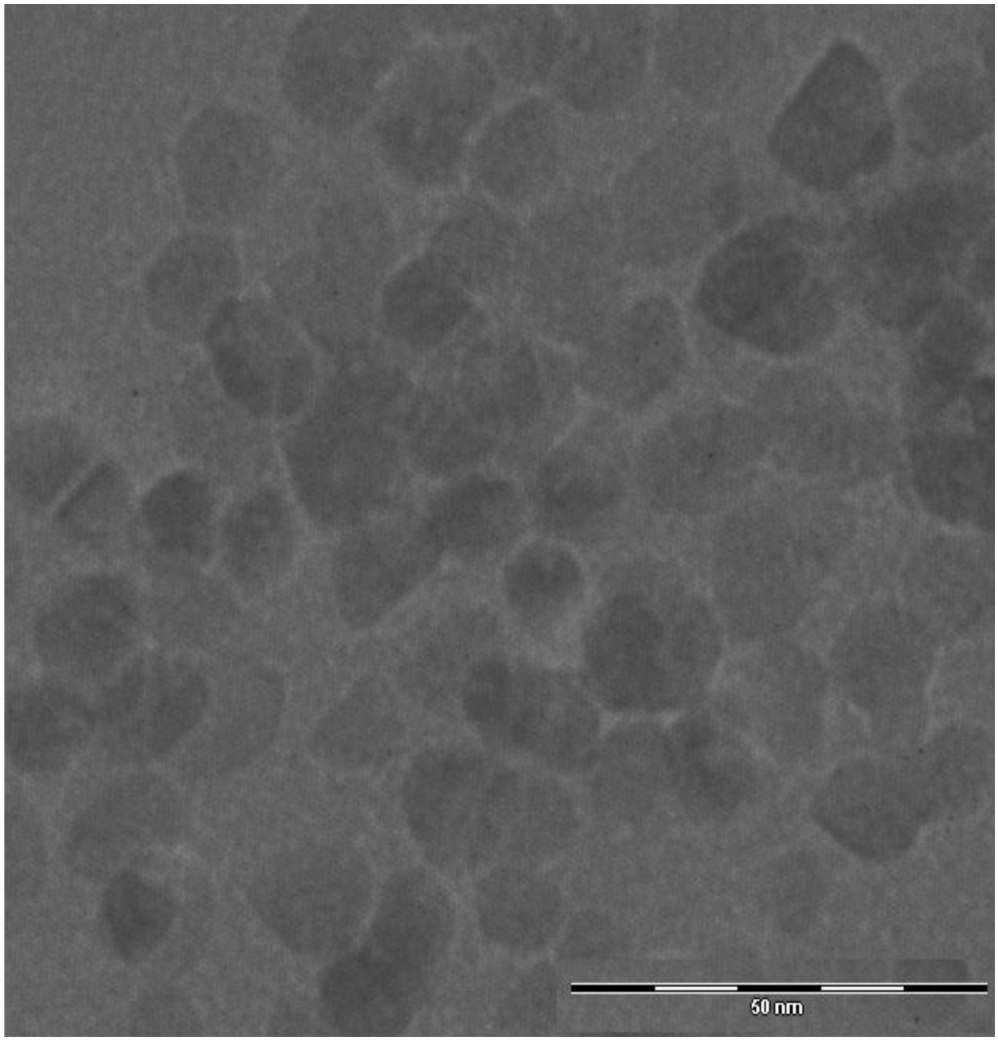


Fig1. TEM image of as prepared nano crystalline zinc oxide.

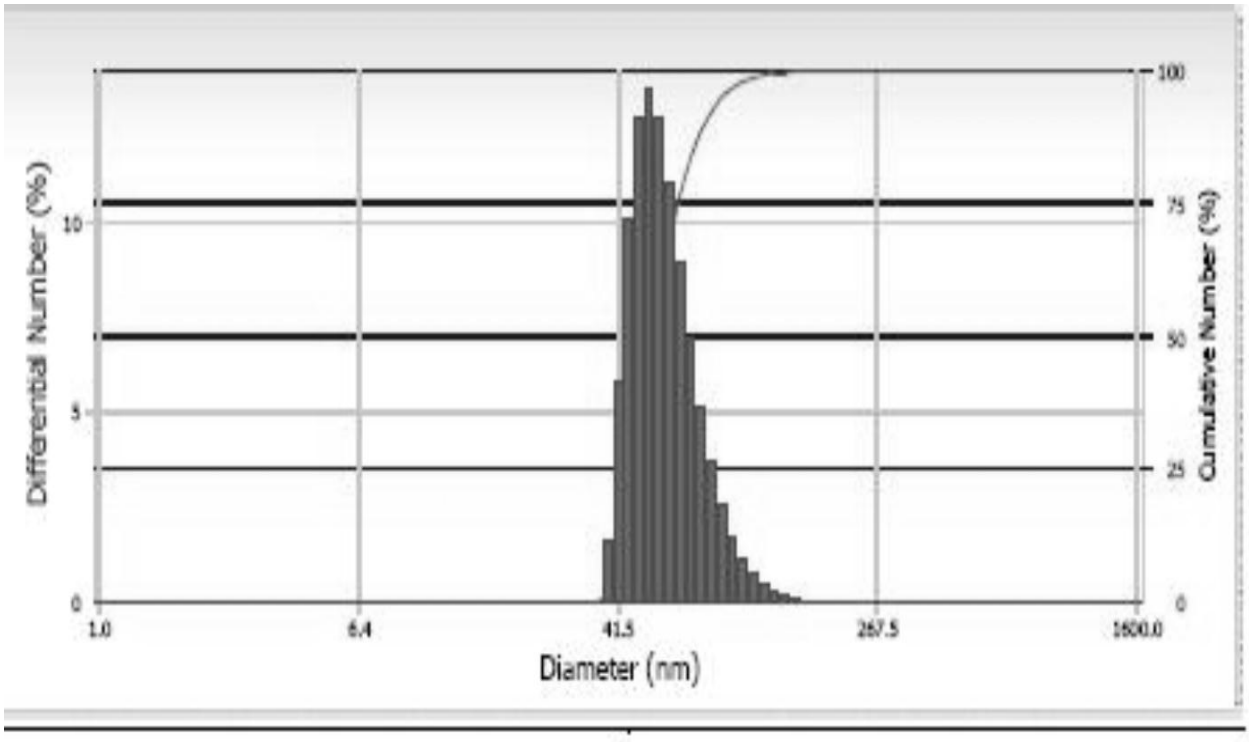


Fig 2. Histogram of as prepaed nanocrystalline ZnO.

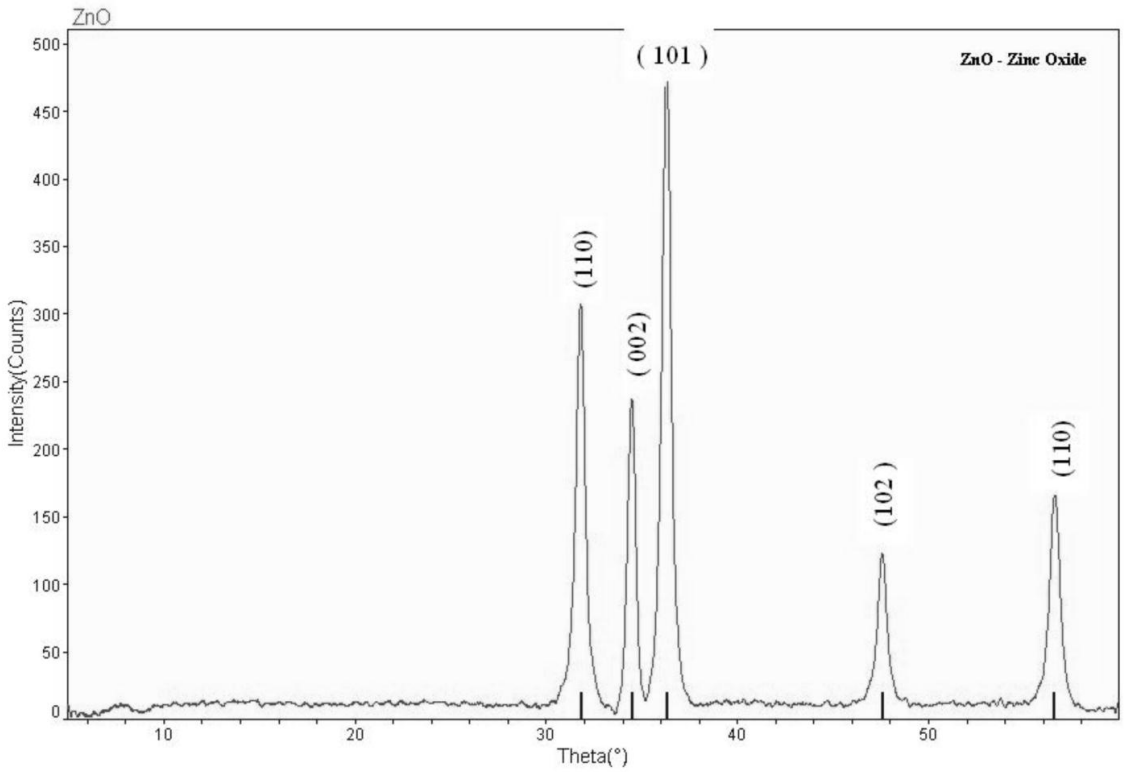


Fig3. XRD pattern for nanocrystalline ZnO.

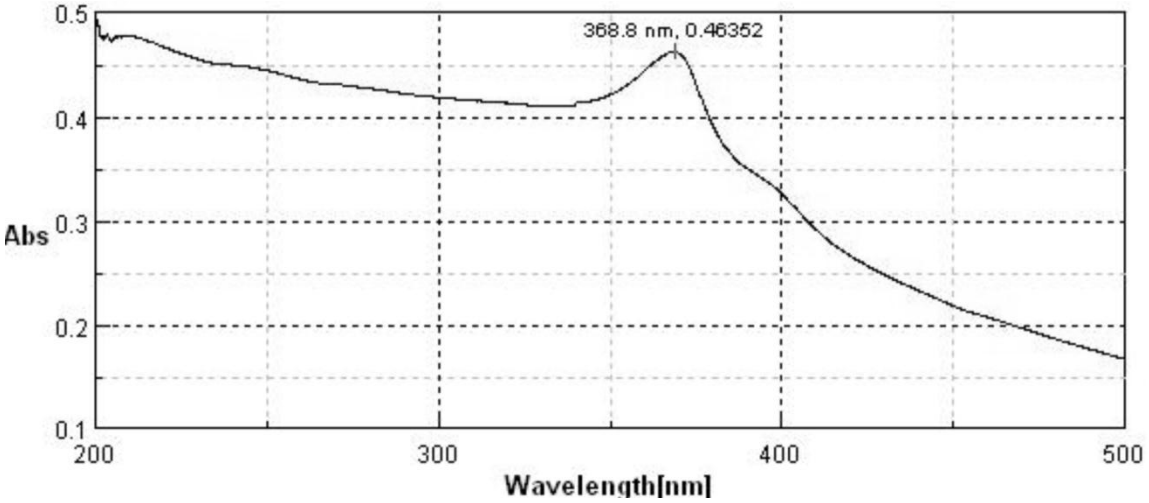


Fig4. UV –Vis spectrum of as prepared nanocrystalline ZnO.

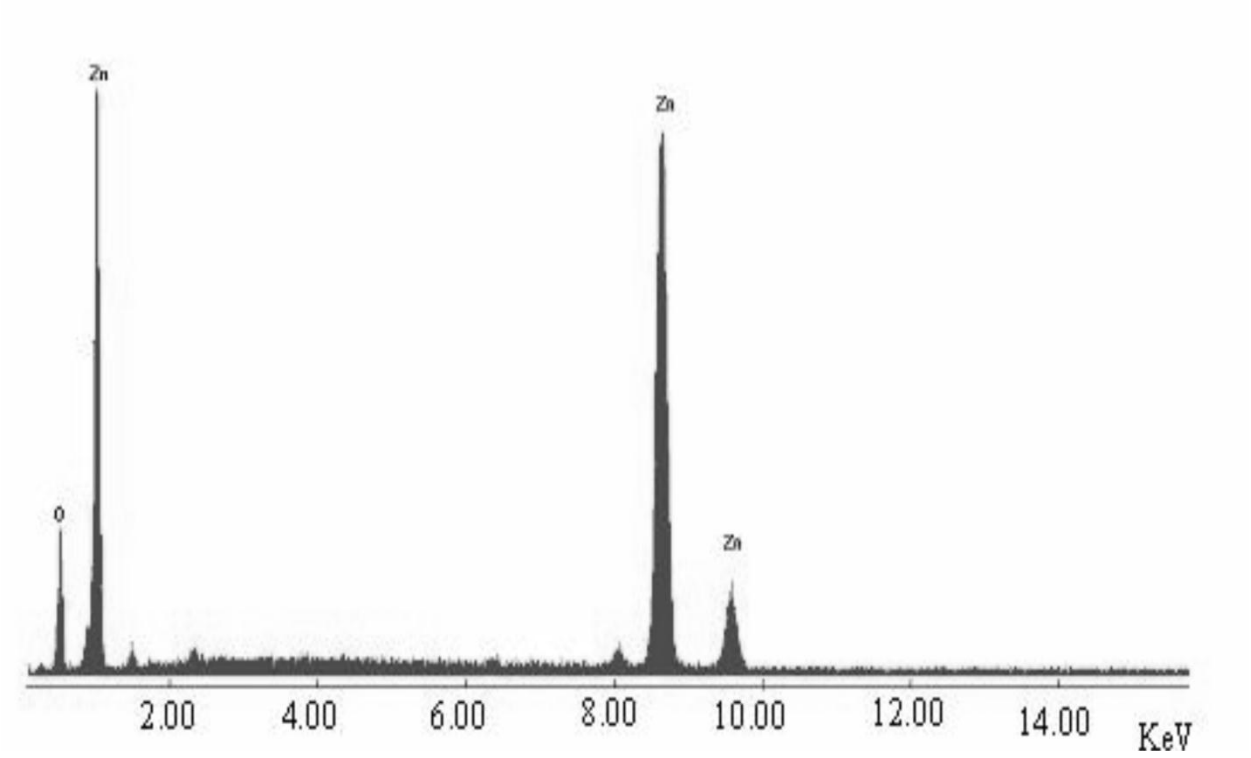


Fig5. EDAX spectrum of the as prepared zinc oxide.

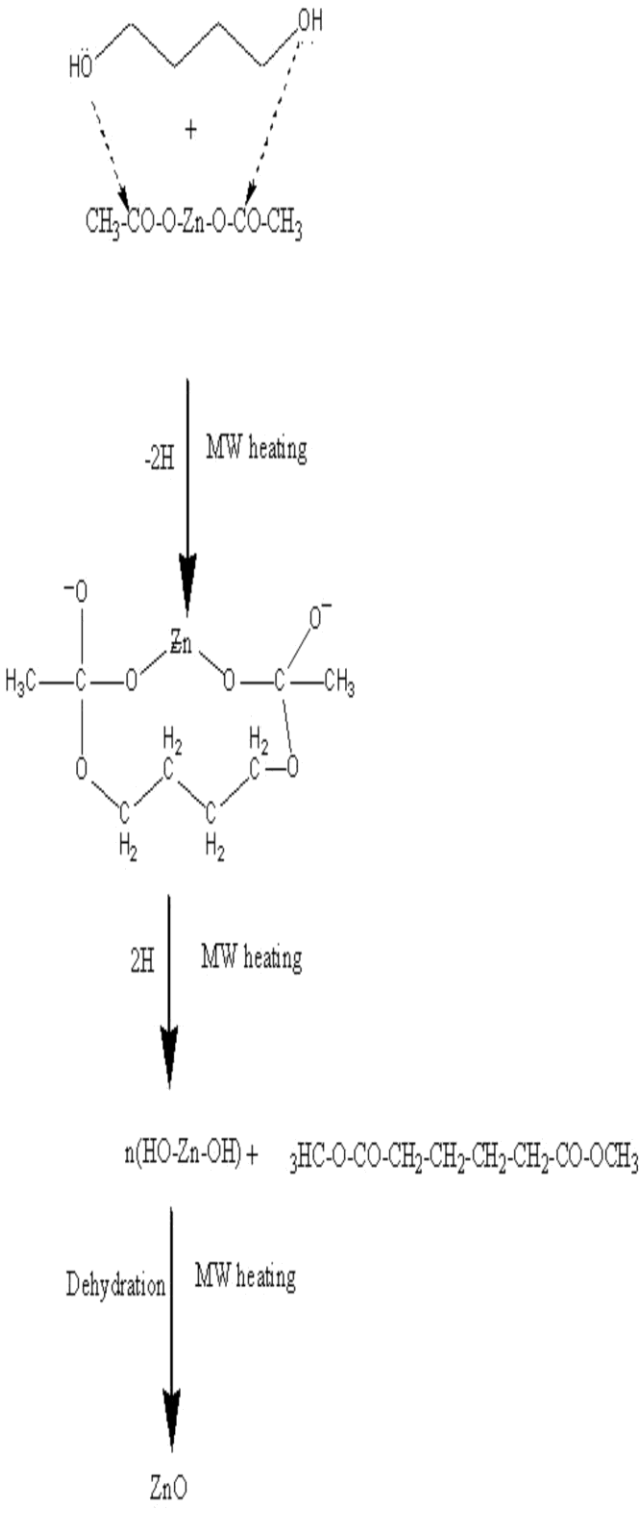


Fig 6. Scheme for synthesis of nanocrystalline ZnO.

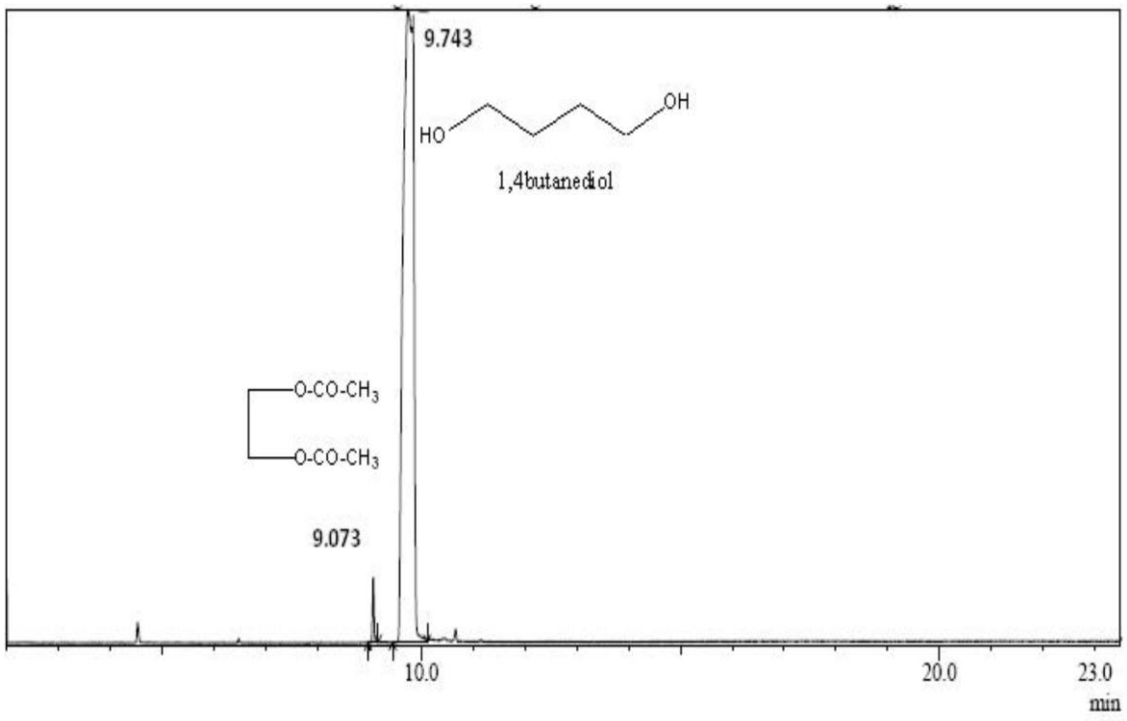
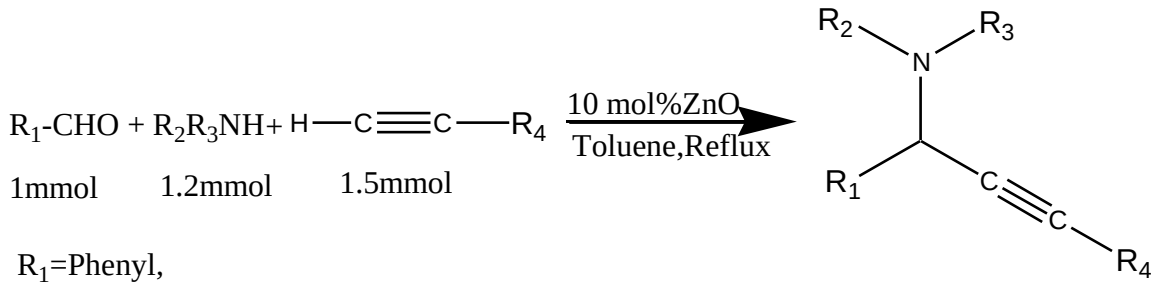


Fig 7. GC-Ms of mother solvent showing butyl ester at R.T.(9.743) unit and 1,4 butanediol at R.T. (9.073) unit



R_1-CHO + R_2R_3NH+ H—C≡C—R_4

1mmol 1.2mmol 1.5mmol

R_1=Phenyl,

R_2,R_3=Morpholine,Piperidene

R_4= Phenyl

Fig .8. Scheme1.