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Novel Assisted Combustion Synthesis of ZnO Nano particles and its Optical Characterizations

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Abstract: ***In an attempt to a novel CMC-assisted combustion method, ZnO has been prepared at low temperature. Interestingly, properties such as phase purity, particle size and structure desirable for better optical band gab are observed with the sample synthesized at 400°C. The study demonstrates the possibility and superiority of synthesizing good optical band gab active ZnO with preferred surface morphology. The as-synthesized nanoparticles has been characterized by XRD, SEM,FTIR, particle size analyzer and Uv visible spectroscopy.***

Keywords: Combustion method, carboxymethyl cellulose (CMC), surface morphology, bandgap**.**

1. Introduction

A development in the field of nanomaterial has prompted scientists and researchers to explore the new possibilities of existing materials with reduced dimensions in the order of nanometers. Unavoidable and important semiconductor of Zinc Oxide (ZnO) is widely studied, II – VI compound semiconductor material owing to its versatile applications in fields including rubber industry, solar cells,sensors, food additives, coatings etc in the past few decades [1-2]. It has several attractive properties like high electron mobility (2000 cm2/(V•s) at 80 K, direct band gap (3.3 eV) and exhibits strong room-temperature luminescence, large binding energy (60 meV) and wide band gap (3.37 eV). [3-4]. In the recent past, synthesis of zinc oxide nanoparticles has been attempted several research groups in different method such as solgel, hydrothermal, Microwave heating [5-7]. Combustion technique is simple, time saving and inexpensive method for preparation of oxide nano particles. The combustion synthesis is an exothermic reaction between fuel and metal nitrate, which gives reduced particle size up to 10nm [8]. As a result, synthesis of ZnO at low temperatures in the range 400 °C has been attempted in the present study using a novel CMC combustion method. The literature is replete with reports on the synthesis of ZnO on that requires 1000°C [9] and 1100oC [10] respectively for pulsed laser deposition and solid state reactions.On the other hand, the current adopted CMC assisted combustion synthesis requires a temperature as low as 400°C, thus leading to the identification of an energy saving synthesis approach to prepare phase pure ZnO. Further, the currently deployed 400°C is found to be lower than the temperature reported in the literature (1000 and 1200 °C) for a combustion method [11] to prepare optical band gab active ZnO compound, which is the highlight of the present study and thus assumes importance and this study is to understand the physical properties such as phase purity, structure and surface morphology and related optical band gab properties of synthesized ZnO as a function of synthesis with a special reference to CMC assisted combustion method.

2. Experimental Section

2.1 Synthesis

In the CMC-assisted combustion method, a mixture consisting of stoichiometric amounts of Zinc nitrate {Zn $(NO_3)_2$•$6H_2O$, Merck} was dissolved in hot water while stirring to get a homogenous solution. To the solution, 3g of CMC was added and the process of stirring and heating was continued to get a dried, foamy mass. The same was furnace heated to 250°C for about 1h followed by an intermittent grinding and subjected to further calcination at temperatures such as 400^{o}C for about 1h in air using alumina crucibles. The ultrafine ZnO powders obtained after grinding were collected and subjected to systematic characterization studies.

2.2 Physical and optical Characterizations

Phase characterization was done by powder X-ray diffraction technique on a Philips 1830 X-ray diffractometer using Ni-filtered Cu Kα radiation (λ=1.54Å) in the 10-90° range at a scan rate of 0.02°/s. The surface morphology of synthesized samples was examined by scanning electron microscopy (TESCAN-VEGA3) and particle size analysis was carried out on a Malvern particle size analyzer. Fourier transform infrared spectroscopy (FTIR) was performed on a Perkin-Elmer Paragon-500 FTIR spectrophotometer using a pellet containing a mixture of KBr and the response of active material in the region 400-1200 cm^{-1} has been noted. Optical absorption spectrum obtained from (Agilent Cary 60 UV-visible-spectrophotometry) UV-visible spectrophotometer.

3. Results and Discussion

3.1 XRD and Particles Analysis

Figure1.shows the XRD patterns of the synthesized ZnO nanoparticles using the CMC assisted combustion method. It

is confirmed from XRD study, hexagonal ZnO compounds match perfectly with the hexagonal structure possessing C46V (P63mc) space group [12] (JCPDS File no: 36-1451) [13]. The striking similarity of Bragg peaks with the standard pattern confirms ZnO compound synthesized at 400^{o}C temperature for combustion methods are possessing desired phase purity and crystalline. A high intensity prominent peak at 37.2 degrees, which is the characteristic peak that belongs to (101) plane. The (100) plane and (002) planes lying beneath the prominent peak, which conclude the formation of hexagonal wurtzite phase in the synthesized powder. From the XRD data approximated crystallite size was measured using Scherer formula L= 0.9ʎ/βcosθ [14] The average particle size is 27nm with confirmed wurtzite hexagonal, the lattice constants 'a'= 3.221 and 'c'= 5.212 values are measured by using the the formula [15] 1/d2= [4/3][(h2+hk+k2)/a2]+ [l2/c2].
Where'd' corresponds to the interplaner distance, 'a' and 'c' are the lattice parameter of the unit cell. Lattice parameter values are evidence for the formation of single crystal structure (wurtzite) of ZnO nano particles.

The particle size analysis of ZnO synthesized clearly evidences the presence of nano crystalline particles with 66nm particle size for 400°C temperature. It corresponds with the crystallite size calculated from the XRD pattern.

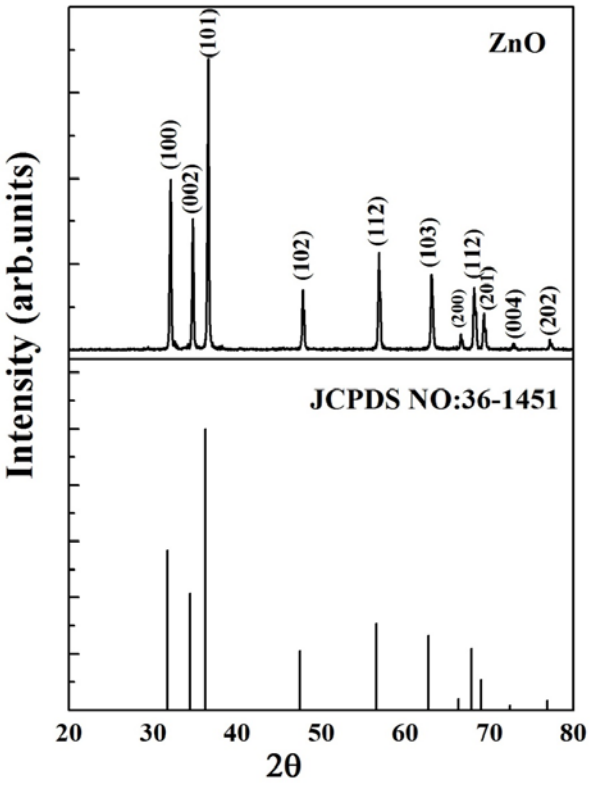

Figure 1: XRD Patterns of ZnO synthesized by CMC-assisted combustion method using 400^{o}C temperatures.

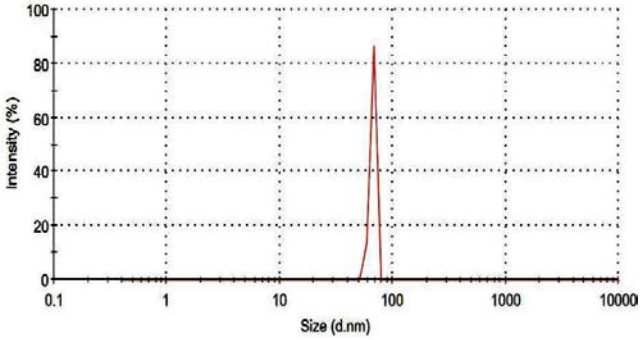

Figure 2: Particles size distributions of ZnO synthesized by CMC-assisted combustion method using 400^{o}C temperature

3.2 Surface Morphology

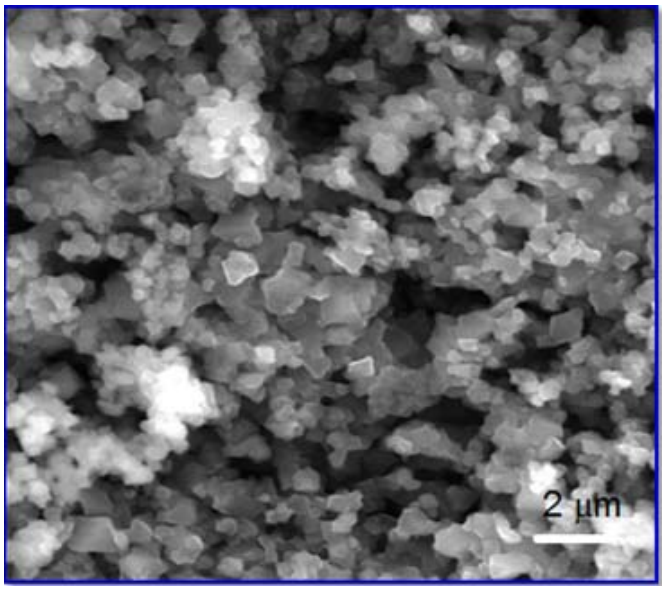

Figure 3: Surface Morphology of ZnO synthesized by CMC-assisted combustion method using 400^{o}C temperatures

Figure3.shows the Presence of perfectly formed hexagonal particles with definite grain boundaries and preferred surface morphology is observed in ZnO synthesized at 400 °C, formation of reduced grain size is understood from the SEM images and slightly particles seems aggregate.The particles size was approximately1-2µm.The CMC assisted combustion process in controlling the growth and wider distribution of particles via. Multistep and controlled rate of heating (2oC/min.) along with the process of intermittent grinding.

3.3 FTIR

Figure 4.shows the vibrational frequency of the functional groups of CMC assisted combustion synthesized ZnO were analyzed by recording FTIR spectrum in the range 4000-500cm^{-1}.Characteristic vibrational peaks at v=556.7cm^{-1} corresponding to the stretching Zn-O bonds and v=3379 absorbed peak indicate the presence of OH- residue. On the other hand Significant shift in FT-IR frequencies of Zn-O bonds observed with ZnO prepared at low 400°C indicates the presence of hexagonal structure instead of the preferred ZnO.

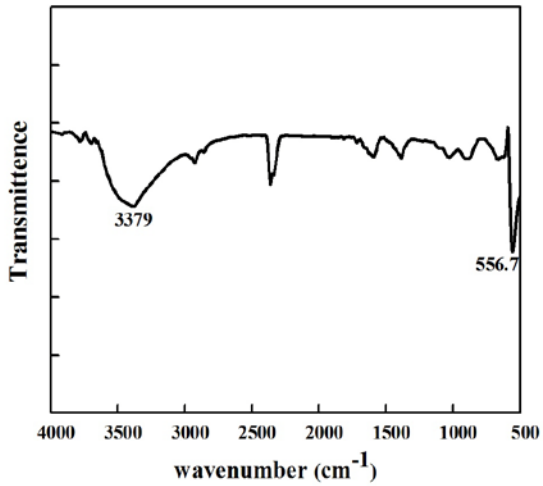

Figure 4: FTIR spectra of CMC-assisted combustion synthesized ZnO

3.4 Optical studies

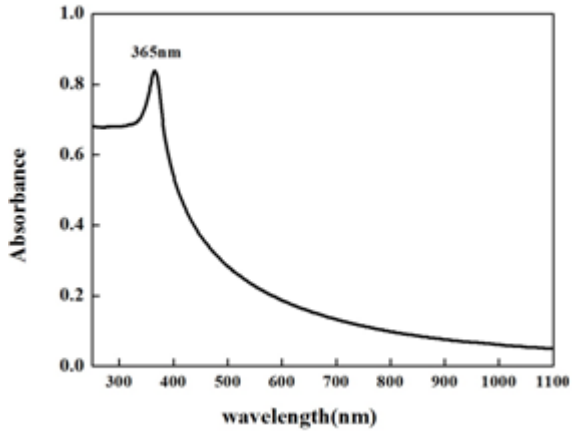

Figure 5: UV-vis absorption spectrum of CMC assisted Combustion synthesized ZnO.

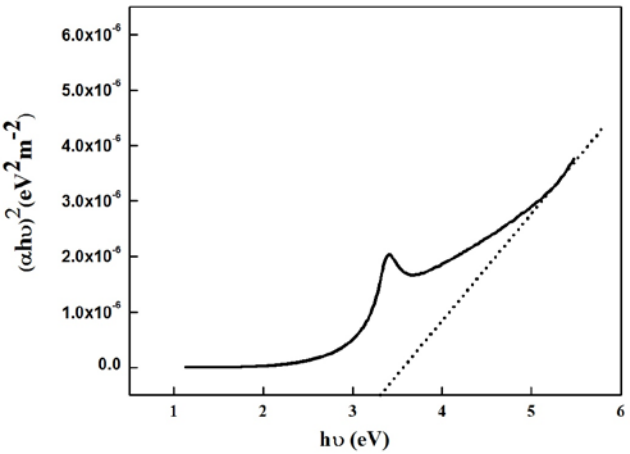

Figure 6: Optical band gap values of CMC-assisted combustion synthesized of ZnO

Figure 5. Shows the absorption spectrum of CMC assisted combustion synthesized ZnO nanoparticles at low temperature. UV–visible spectrums were recorded in the range of 200nm and 1200nm. Strong exciton absorption at 365nm is observed in the absorption spectrum region. The direct band gap energy (Eg) for the ZnO nanoparticles is determined by fitting the reflection data to the direct transition equation [16]

$(\alpha h\nu)^2 = A\,(Eg - h\nu)$

Eg is the optical band gap of the CMC assisted combustion synthesized ZnO, A is a constant, α is the optical absorption coefficient and hν is the photon energy, the variations of $(\alpha h\nu)^2$ versus hν in the fundamental adsorption region are plotted.The optical band gap is found to be 3.3eV which is confirmed from the figure 6. As a consequence of wide band gap, this ZnO can be a suitable material for the optoelectronic devices like LED and laser diodes(17).

4. Conclusion

By adopting a novel CMC-assisted combustion method, ZnO has been prepared at low temperature range 400°C.Interestingly, a phase temperature as low as 400°C is found to be sufficient to prepare phase pure and hexagonal ZnO, which is lower than the temperatures reported in the literature on the same topic. Presence of hexagonal particles with definite grain boundaries, possessing an average particle size of ~100nm is obtained at 400°C.The study demonstrates the feasibility of deploying a novel and low temperature, CMC-assisted combustion method to prepare phase pure and better performing ZnO besides evidencing the variation of powder properties such as phase purity, surface morphology, particle size and band gap as a function of temperature involved in the synthesis approach

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