MICROWAVE ASSISTED pH CONTROLLED ZnO MORPHOLOGY

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The effect of time and pH on ZnO nanoparticles were observed as prepared via microwave-assisted approach. Zinc acetate dihydrate Zn $(CH_3COO)_2.2H_2O$ used as precursor and 2 Propanol as solvent, NaOH was used as pH controller. ZnO nanoparticles (band gap 3.91 ev) of size within the range 50 nm to 80 nm were obtained by controlling the pH (6-8). Characterization techniques of synthesized samples were investigated by X-ray diffraction (XRD), UV Visible spectroscopy, Raman spectroscopy, scanning electron microscope (SEM). Porous structure of ZnO nanoparticles was clearly observed with agglomeration. Above-mentioned variables, influenced the shape and size of prepared nanoparticles prominently. Briefly, the microwave irradiation technique with pH control was highlighted as quick, cheap and single step approach to control the morphology of semiconductor nanoparticles in present work.

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1. Introduction

The intra-atomic spacing of a particle changes with the decrease of particle size and increase of surface area and surface free energy, so the structural properties of a material exhibit different behavior at nanoscale, such as high surface area to volume ratio, unique electrochemical, optical and electronic properties, increased catalytic activity in comparison with bulk materials[1-3].ZnO is one of the most significant nanomaterials that have been extensively studied due to wide usage in many materials and products like plastics, paints and ceramics etc [4].

II-VI group semiconductors exhibit several unique properties like wide bandgap (ZnO, Eg=3.370 eV and refractive index 2.008), intense luminescence at room temperature, high electron mobility [5].

In the last few decades, among many techniques like hydrothermal[6-8], precipitation [9,10.], spray pyrolysis[11, 12], sol-gel[13, 14] and microemuslion [15], the microwave assisted radiation based method was found to be promising for synthesis of II-VI semiconductors.

The word ‘microwaves’ refers for those energies having wavelengths approximately from 1m to 0.1 cm and their frequency ranges between 300 MHz to 300 GHz. In 1946 Dr Percy Spencer revealed the heating property of microwave. As compare to conventional heating the heat transmission produced by microwave is extensively shortened and homogeneous to save time as well as energy. The conversion of electromagnetic radiations (microwaves) into heat energy is combination of two steps, the dipolar rotation and ionic conduction.

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2. Materials and Methods

First of all, precursor Zinc acetate dehydrate $Zn(CH_3COO)_2.2H_2O$, propanol 2 as solvent and Sodium Hydroxide NaOH (pH Controller) were taken in particular amounts. Microwave irradiation was used to synthesize ZnO nanoparticles, Variety of samples were prepared on different pH by adding NaOH drop wise.

Amount of precursor was measured by digital balance, 21.95gm of zinc acetate dihydrate was taken in flask and 100mL distilled water was added and magnetic stirring was done for the preparation of 1M solution of zinc acetate.10mL of the above solution was dissolved into 40mL propanol 2 for the preparation of transparent 0.2M $Zn(CH_3COO)_2$solution. After that 4gm NaOH was dissolved into 100ml distilled water and mixed well with propanol 2 as pH controller. Finally, this solution was added drop wise to 0.2M. $Zn(CH_3COO)_2$ to obtain different ZnO samples at different pH. A milky color solution was obtained. The solutions with different pH values were placed in the microwave oven for different time intervals. Series of samples were prepared within pH range for 6-8 at heating time 5 to 15 seconds. A domestic microwave oven was used for the assistance of microwave radiations on samples. The microwave oven has following specifications. Model no is HPK-2070M, its input frequency is 230V-50Hz and output is 2450MHz, it has related power input 1080 W and related microwave output is 700W, the volume is about 201. After assisting microwave radiations, the white precipitates were obtained. For the characterization of samples, it was necessary to dry it and convert it into fine powder; first the precipitates of Zinc oxide were separated by centrifuge at 3000rpm for 30 min. In order to dry the samples, oven of model wise ven fuzzy control system at the temperature 80^OC for 24 hours was used. After drying the solution fine white powder was attained.

3. Characterization and Analysis

ZnO nanoparticles were synthesized by assisting microwave radiations at different pH. Characterization of all samples was done by using UV visible spectroscopy, Raman spectroscopy, X-ray diffraction technique (XRD) and scanning electron microscopy (SEM).

3.1. UV-Visbile Analysis

Comparative UV-Vis spectrum of samples were observed with the two varying parameters, pH and time.

UV-visible spectrum of ZnO nanoparticles at pH 6-8 and time 5 sec, 10 sec and 15 sec displayed prominent exciton absorption at 371nm and 372nm due to exciton transition [16,17]. UV-visible spectra for ZnO nanoparticles at pH= 7.0 for 15 sec shoed in Fig 1.The spectrum was taken in the range of 300-400 nm. This absorption peaks lies in the visible band of wavelength.

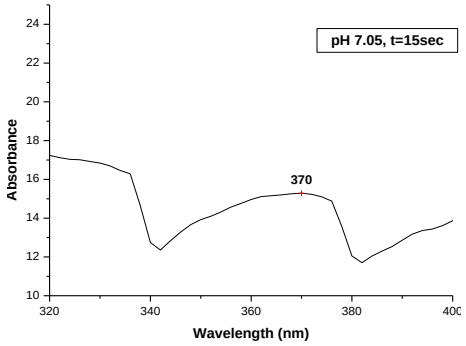

Fig. 1. UV-Visible absorption spectrum for microwave assisted ZnO nanoparticles at pH 7.0 for 15 sec.

For such transition $(\alpha h\nu)^2=A(h\nu-Eg)^n$ where α is absorption coefficient, Eg is optical band gap, hν is photon energy, n is 1 for direct transition & A is a constant. The band gap energy is

acquired by deducing the straight line portion of the plot to zero absorption coefficient. The optical band gap (Eg) of the ZnO nanoparticles was calculated from Tauc plot (Fig. 2).

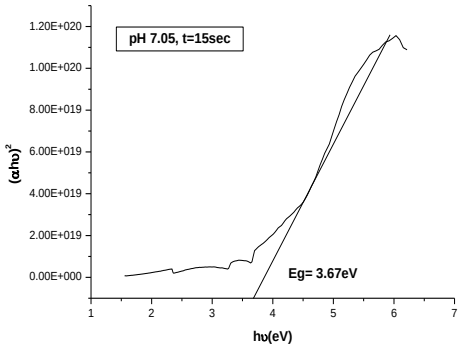

Fig. 2. Bndgap of CuS nanoparticles at pH 7.0 Assisted by Microwave Radiations for 15sec.

Table 1. Average values of Band gap of ZnO nanoparticles at pH 6,7 and 8.01 Assisted by Microwave Radiations for 5sec, 10sec and 15sec

pH values	Microwave Time	Band gap
6.0	5 Sec	3.70eV
7.0	10 Sec	3.69eV
8.0	15 Sec	3.67eV

By comparing the average band gap values of ZnO nanoparticles synthesized by microwave radiations were found to be 3.70eV, 3.69eV and 3.67eV for time 5sec, 10sec and 15sec respectively which is larger than the bulk ZnO (3.37 eV) [18]. It can be concluded that the band gap decreases by increasing the time.

3.2. XRD Analysis

Crystal phases and purity of samples were observed by using X-Ray Diffraction at different pH 6.18, 6.5 and 8 for different time by assisting microwave radiations (Fig. 3). The diffraction peaks equivalent with the standard peaks of ZnO JCPDS card no 36-1451, 75-0576 and 74-0543. ZnO showedhexagonal wurzite structure. Intense and sharp intensity peaks revealed the good crystallinity of synthesized ZnO nanoparticles.

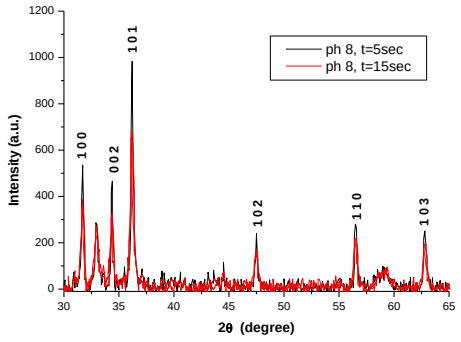

Fig. 3. XRD Pattern of Sample with pH 8 by Assisted Microwave Radiations for time 5sec and 15sec.

For the calculation of mean crystallite size of crystal, the Sherrer's equation was used:

$$Dp = \frac{k\lambda}{\beta \cos\theta}$$

Where: k = Sherrer's constant, λ = Wavelength of X-ray, β = Full width half maxima (FWHM), Dp = Crystallite size, Θ = Diffraction angle

The average crystallite size at pH 6 is 55.14nm and for 8 is 82.06nm, which means that crystallite size increases with increases in pH. For finding the dislocation line density following formula was used:

$$\sigma = \frac{1}{Dp}$$

Where:
σ = Dislocation line density, Dp = Crystallite size

The dislocation line density for samples having pH 6 is 0.0003289nm and for pH 8 is 0.00014850nm.

3.3. Raman Analysis

Purity of ZnO nanoparticles were confirmed by Raman spectroscopy. The observed Raman shifts inthe typical Raman-active modes allocated to ZnO. According to Group theory, there are eight groups of zone center optical phonons, where A1 and E1 modes are polar which divided into transverse optical A1(TO) and E1(TO) and longitudinal-optical A1(LO) and E1(LO) phonons, while the E2 mode contains twomodes of low and high-frequency phonons which are Raman-active [19]. The following figures shows phonon modeswith (Nd:YAG) laser of wavelength 532 nm as an excitation source.

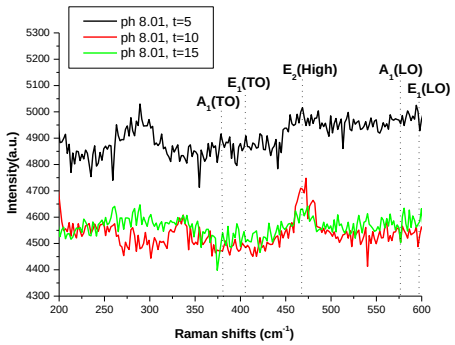

Fig. 4. Raman Spectra of ZnO Nanoparticles prepared by Assisted Microwave Irradiations at pH 8.

The peak E_2 (High) demonstrate blue shift for all nanoparticles in contrast with the theoretical and experimental bulk. The main peaks categorized as E_2(High) at 386.8, 438.8 and 467.3 cm^{-1} for samples having pH 7.05, 6.5 and 8.01 respectively and known as Raman active phonon mode, which is the representative of wurtzite hexagonal phase of ZnO. The relatively higher sharp peak of E2 mode at 437 cm^{-1} associated with the experimental peaks, demonstrated that the as-grown ZnO structures are of wurtzite hexagonal phase with good crystallinity. The optical phonon confinement by nanostructures shows blue shift in E_2 (High) [20,21]. Raman peaks compare with the theoretical results of ZnO nanostructure were given in Table 2 below.

Table 2. Raman active modes of the ZnO nanoparticles compared with the theoretical values

Symmetry	*Theoretical* (cm^{-1})	*Sample with pH 6 (cm^{-1})*	*Sample with pH 7 (cm^{-1})*	*Sample with pH 8 ($cm^{=1}$)*
A1(TO)	380	382.5	318.0	380.9
E1(TO)	407	415.5	349.5	405.9
E2(High)	437	438.8	386.8	467.3
A1(LO)	574	575.5	575.4	576.3
E1(LO)	583	595.7	591.0	597.0

3.4. Morphological study by Scanning Electron microscopy SEM

Morphological studies of ZnO nanoparticles prepared by microwave radiations were investigated by SEM. Nanoparticles exhibited a porous structure (Fig. 5). By increasing pH and time the particle size also increases, the surface is still porous and somewhere agglomerated with uniform distribution. Morphology of samples by varying the pH also changes from porous to whisker like. Particle size was found to be 20 -30 nm as measured by Image J software.

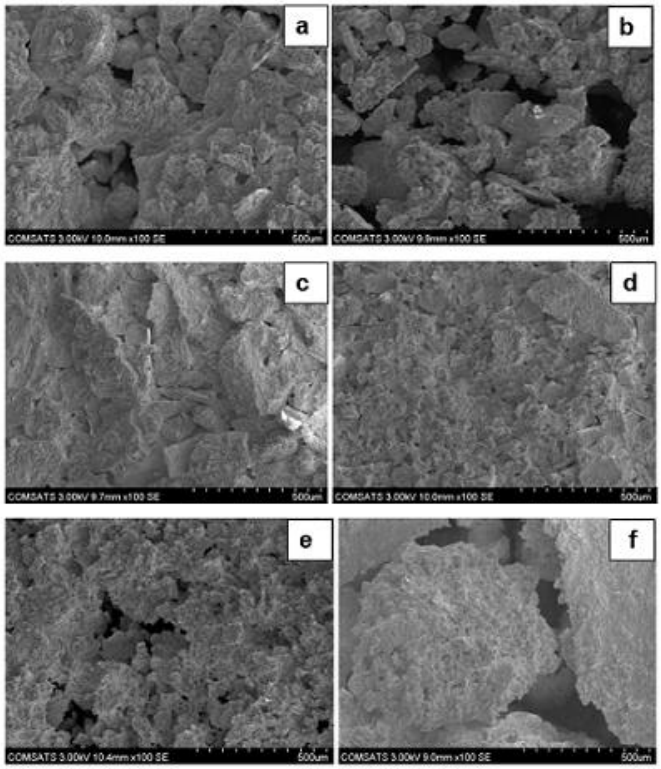

Fig. 5. SEM Images of ZnO Nanoparticles at pH 6.0 Assisted by Microwave Radiations for (a) 5sec and (b) 15 sec, at pH 7.0 (c) 5 sec and (d) 15 sec. at pH 8.0 (e) 5 sec and (f) 15 sec.

4. Conclusions

Zinc Oxide ZnO nanoparticles were successfully synthesized by assisting microwave radiations at different pH and time. Precursor Zinc acetate dihydrate, propanol 2 as solvent and Sodium Hydroxide. X-ray diffraction confirmed wurtzite hexagonal structure of ZnO porous structure. The crystallite size at pH 6 was 55.14nm and for 8 is 82.06nm, which means that crystallite size increases with increases in pH, was found to be within range from 20 to 30 nm. The measured dislocation line density is 0.0003289nm and 0.00014850nm respectively. UV visible

spectrum showed the absorbance of ZnO nanoparticles within wavelength of ~ 370 371 nm. By comparing the band gap of samples it can be concluded that increasing the time of assisting microwave radiations the band gap of nanoparticles decreases from 3.91eV to 3.38eV.

Raman spectroscopy used to confirm the purity of samples prepared by assisting microwave radiations at different pH. It can be noticed that Raman shifts for these ZnO nanostructures in the typical Raman-active modes assigned to ZnO. The main sharp peaks categorized as E_2(High) at 386.8, 438.8 and 467.3 cm^{-1} for samples having pH 7.05, 6.5 and 8.01 respectively observed and is known as Raman active optical phonon mode, which is the characteristic of wurtzite hexagonal phase ZnO. Morphological studies demonstrated that nanoparticles exhibited a porous and agglomerated structure. By increasing pH and time the particle size also increases, the surface is still porous and somewhere agglomerated and shifted to whisker like.

Briefly, the microwave technique is one step, simple, cost effective and environment friendly approach to prepare metal nanoparticles with controlled morphology.

5. Future work

Other metal oxide can also be prepared by simple and facile microwave approach. By changing frequency of microwave radiations nanomaterial with different sizes and morphology can also be synthesized. To make thin films these synthesized nanoparticles can be fabricated on different substrates.

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