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Synthesis and characterization of ZnO nanoparticles via aqueous solution, sol-gel and hydrothermal methods

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Abstract: *ZnO nanoparticles were synthesized by aqueous solution method, sol-gel method and hydrothermal method.The synthesized particles were characterized by XRD ,SEM ,EDX and UV .The X-ray diffraction studies reveals that the synthesized ZnO nanoparticles have wurtzite structure and the particle size varies from 13 to 18 nm. Scanning Electron Microscopic investigation reveals that the surface morphology of ZnO nanoparticle is spherical in hydrothermal process and varies to flower like arrangement in aqueous solution and sol-gel process. The UV-Visible spectrum of the nanoparticles shows a blue shift compared to that of the bulk sample.*
Keywords: *Nanoparticles, Zinc oxide, X-ray diffraction, hydrothermal , sol-gel.*

I. Introduction

Zinc oxide is the one of the most important n-type semiconductor materials with a 3.37 eV band gap at room temperature and 60 meV excitation binding energy that is in the UV region and makes this nanoparticle as an efficient UV absorber [1]. Semiconductor nanomaterials have been received great attentions. Among these various semiconductor nanomaterials zinc oxide is a versatile material because of its physic-chemical properties such as mechanical, electrical, optical, magnetic and chemical sensing properties [2]. Zinc oxide a chemical compound found naturally in the mineral called zincite has attracted much attention in recent times due to its low cost and because it can be obtained by simple techniques [3]. Chemical synthesis is one of the most important techniques which can be performed by using a range of precursors and different conditions like temperature, time, concentration of reactants, and so forth. Variation of these parameters leads to morphological differences in size and geometries of resulting nanoparticles. . Among the nanoscale metal oxides, zinc oxide is a common host material that has been widely used due to its excellent chemical and thermal stability, low cost and environmental-friendliness [4]. The high exciton binding energy of ZnO would allow for excitonic transitions even at room temperature, which could mean high radiative recombination efficiency for spontaneous emission as well as a lower threshold voltage for laser emission. The lack of a centre of symmetry in wurtzite, combined with a large electromechanical coupling, results in strong piezoelectric and pyroelectric properties and hence the use of ZnO in mechanical actuators and piezoelectric sensors [5, 6].

In the second part of the contribution we try to list some very important new areas of research ZnO. These are in particular the core–shell nanorods for the photovoltaic dye-sensitized solar cells, transparent conducting oxide thin films, thin film transistors, removal of the hydrogen sulfide from natural gas streams,coal gas and chemical feedstocks, chemical gas sensors, diluted magnetic semiconductors, photocatalysis and toxicity. ZnO nanocrystals or quantum dots (QDs) have superior optical properties of the bulk crystals owing to quantum confinement effects [7]. The high exciton binding energy of ZnO (~60 meV) would allow for excitonic transitions even at room temperature, which could mean high radiative recombination efficiency for spontaneous emission as well as a lower threshold voltage for laser emission [8]. Studies have been carried out to fine-tune the properties of ZnO to adopt it for different applications; for example, the band gap of ZnO is modified to use as UV detectors and emitters. ZnO nanoparticles are widely employed in fundamental research and potential applications, such as hydrogen-storage, field emitters, ultraviolet lasers and diodes, piezoelectric devices and photo catalysts [9]fluorescence labels in medicine and biology, controlling units as UV photo detectors and as high-flame detectors in cosmetic industry and as a component of sun screens[10].

ZnO nanostructures have a great advantage to apply to a catalytic reaction process due to their large surface area and high catalytic activity. Since zinc oxide shows different physical and chemical properties depending upon the morphology of nanostructures, not only various synthesis methods but also the physical and chemical properties of synthesized zinc oxide are to be investigated in terms its morphology [11]. The demonstration of room temperature ultraviolet lasers, field effect transistors and field emission arrays based on ZnO nanorods have stimulated great interest in developing functional nanodevices. Moreover, the wide range of morphological diversity in the nano-regime has made this material a promising candidate in the field of nanotechnology and opened up new possibilities for the fabrication of high performance devices based on these nanostructures [12]. Application of metal oxides materials have extensively arisen throughout human civilization and the uses of nano-sized particles are even more significant. Among them zinc oxide nanoparticles

are always in the center of attention due to their fascination properties and extensive applications [13]. Most preferentially, among different metal oxide nanoparticles, zinc oxide (ZnO) nanoparticles have their own importance due to their vast area of applications, for example, gas sensor, biosensor, solar cells, varistors and photocatalysts[14]. Semiconductor zinc oxide (ZnO) nanoparticles have attracted much attention because of their interest in fundamental study and also their applied aspects such as in solar energy conversion, luminescence, electrostatic dissipative coating, transparent UV protection films, and chemical sensors [15].

The hydrothermal technique is becoming one of the most important tools for advanced materials processing, particularly owing to its advantages in the processing of nanostructural materials for a wide variety of technological applications such as electronics, optoelectronics, catalysis, ceramics, magnetic data storage, biomedical, bio photonics, etc [16]. ZnO nanoparticles can be synthesized by various approaches including sol-gel processing, chemical precipitation, mechanical milling, organometallic synthesis, microwave method, spray pyrolysis, thermal evaporation and mechanochemical synthesis [17]. The present study focuses on the preparation of ZnO nanoparticles by three different methods and shows the variation of particle size, morphology and elemental composition of the nanoparticles obtained by these methods.

II. Experimental details

1.1 Preparation of ZnO nanoparticles by aqueous solution method

ZnO nanoparticles were synthesized by aqueous solution method using zinc acetate as a precursor. The entire process was carried out with double distilled water. About 2.1 g of zinc acetate was dissolved in 200 ml of double distilled water. After 10 minutes of stirring about 1.5 g of trisodium citrate in 10 ml water and 4.2 ml of 25% ammonia solution were added. Then, 20 ml of 2M NaOH solution was added dropwise with vigorous stirring. The temperature of the contents were raised to 80^0C and kept at this temperature for about 6 hours. The contents were centrifuged and the precipitate was washed five times in distilled water and then dried at 60^0C and thoroughly ground [18].

1.2 Preparation of ZnO nanoparticles by sol-gel method

Zinc oxide nanoparticles were synthesized by sol-gel method using zinc acetate and methanol as precursors. In the preparation, 16 g of zinc acetate was dissolved in 112 ml of methanol. After 10 minutes magnetic stirring at room temperature the resultant solution was subjected to gellation at 80^0 C with constant stirring for 5 hours, from which the zinc oxide nanomaterials in the form of powder was obtained. The resultant powder was annealed at 450^0C for 6 hours [19].

1.3 Preparation of ZnO nanoparticles by hydrothermal method

ZnO nanoparticles were synthesized by hydrothermal method using zinc acetate and methanol as precursors. 0.1 M zinc acetate solution was prepared in 50ml methanol under stirring. To this solution 25ml of NaOH (0.2M) solution was added under continuous stirring. The solution was transferred into teflon lined sealed autoclaves and heated at 100^0C for 6 hours under autogenous pressure. It was then allowed to cool naturally to room temperature. After the reaction was complete, the resulting white solid product was washed with methanol, filtered and then dried in air in a laboratory oven at 60^0 C [20].

1.4 Characterization of synthesized nanoparticles

The structural properties including structure and crystallite size of the samples were determined by x-ray diffractometer .The powder x-ray diffraction (XRD) was performed using automated x-ray diffractometer (X-PERTPRO Philips system) operating CuK_α at wavelength 1.54056 Å. The average crystallite size (D) has been calculated using Scherer's relation $D = K\lambda/\beta\cos\theta$, where the constant K is taken to be 0.94 , λ is the wavelength of x-ray used and β the full width of half maximum (FWHM). The morphology of the zinc oxide samples were characterized by scanning electron microscope (SEM) equipped with an energy dispersive x-ray spectrometer (EDX) to analyse the elemental composition of the synthesized materials. Smart double beam spectrophotometer 2203 was employed to record the UV-visible absorption spectra of the samples.

III. Results and discussion

3.1 XRD Analysis

The XRD pattern of ZnO nanopaticles prepared by aqueous solution method is shown in Fig. 1(a). The diffraction peaks are at 2θ values of 31.6811^0, 34.3596^0, 36.1769^0, 47.4835^0, 56.5269^0, 62.8115^0 and 67.9130^0 were identified to originate from (100), (002), (101), (102), (110), (103) and (112) planes. Based on the Scherrer equation the average crystallite size of the nanoparticles are observed as 13 nm. The main diffraction peak is observed at 2θ value of 36.1769^0. The value of (β) observed for ZnO is 0.70730. This peak is identified to originate from (101) planes of the ZnO. All the peaks are indexed and found to be well matched to wurtzite

structure of ZnO having hexagonal phase, which is in good agreement with the standard JCPDS (Card No. 36-1451).

Fig. 1(b) shows the XRD patterns of ZnO nanoparticles from Sol-gel method. The seven diffraction peaks are at 2θ values of 31.653^0, 33.7903^0, 35.9608^0, 47.3924^0, 58.3000^0, 62.5000^0 and 66.7208^0. The peaks were identified to originate from (100), (002), (101), (102), (110), (103) and (112) planes. Based on the Scherrer equation the average crystallite size of the nanoparticles are observed as 18 nm.

Fig. 1(c) shows XRD patterns of ZnO nanoparticles from hydrothermal method. The diffraction peaks are at 2θ values of 31.9456^0, 34.5903^0, 36.4341^0, 47.6971^0, 56.7894^0, 63.0411^0 and 68.1135^0. The peaks are identified to originate from (100), (002), (101), (102), (110), (103) and (112) planes. Based on the Scherrer equation the average crystallite size of the nanoparticles are observed as 14 nm.

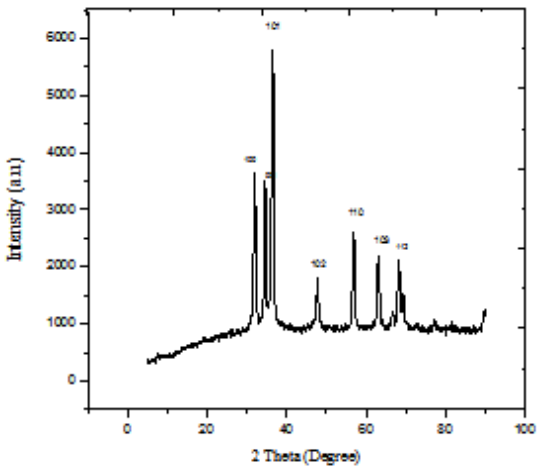

Fig. 1(a) XRD patterns of ZnO nanoparticles (aqueous solution method)

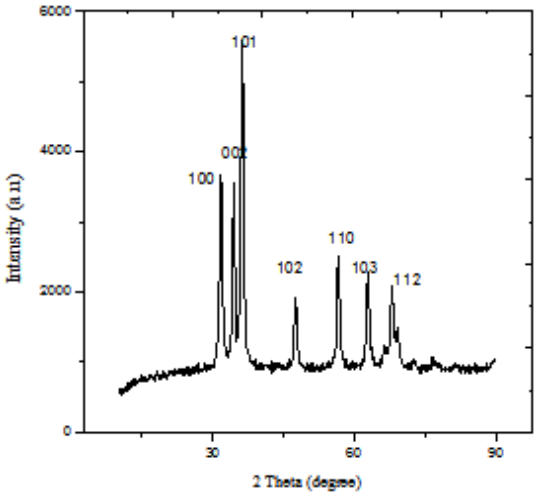

Fig. 1(b) XRD patterns ZnO nanoparticles (sol-gel method)

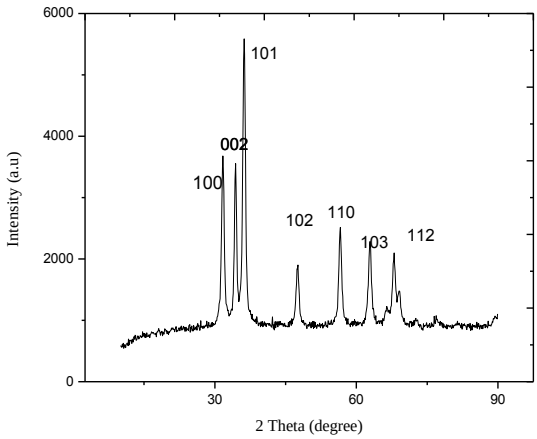

Fig.1(c) XRD patterns of zinc oxide nanoparticles (hydrothermal method)

3.2 Structural studies

Fig. 2(a) shows that the SEM images of zinc oxide nanoparticles obtained by aqueous solution method.. The image shows spherical and flower like structure. Fig.2(b) shows SEM images of the ZnO nano powders prepared by sol-gel method. The ZnO nanoparticles have flower- like shape. The same results observed in structural and optical characterization of Ni and Ni, Al co-doped ZnO nanopowders synthesized via the sol-gel process (Amor Sayari and Lassaad EI Mir, 2015) [19]. Fig. 2(c) shows the SEM image of ZnO nanoparticles prepared by hydrothermal method. The zinc oxide particles prepared are spherical shape. It also shows that a network formation of the zinc oxide nanoparticle has taken place which clearly indicates that agglomeration has taken place.

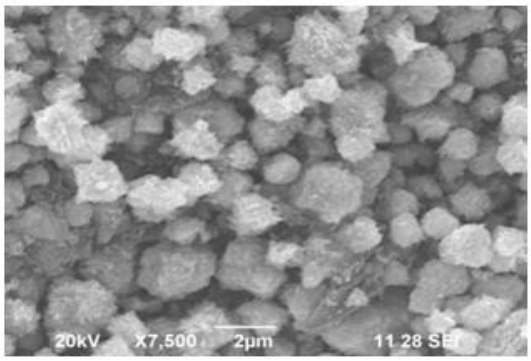

Fig. 2(a) SEM image of ZnO nanoparticles (Aqueous solution method)

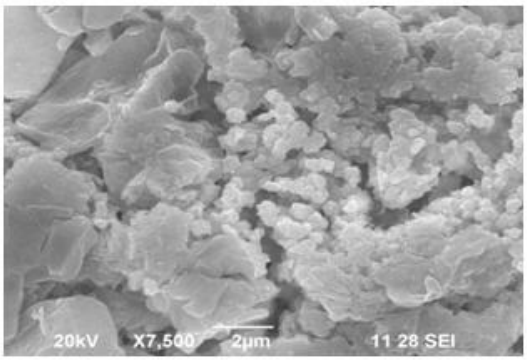

Fig. 2(b) SEM image of ZnO nanoparticles (sol-gel method)

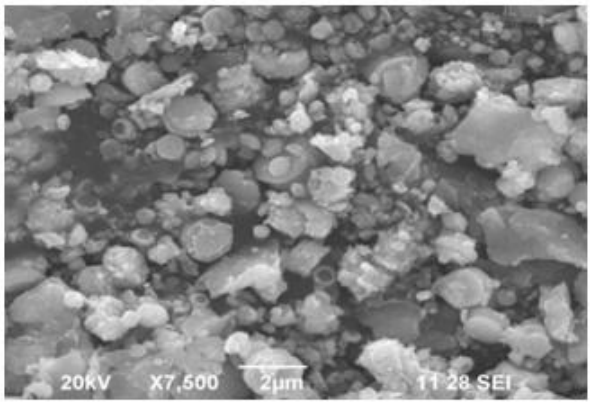

Fig. 2(c) SEM image of zinc oxide nanoparticles (hydrothermal method)

3.3 Energy dispersive x-ray diffraction spectroscop (EDX)

Fig. 3(a) shows the EDX spectrum of ZnO nanoparticles prepared by aqueous solution method. The strong peaks observed in the spectrum related to Zinc and oxygen. The elemental constitution of ZnO nanoparticles with two major peaks was found to have weight percentage of 73.87 of Zinc and 26.13 of oxygen. The prepared ZnO nanoparticles have atomic percentage of 40.90 of Zinc and 59.10 of oxygen. Fig. 3(b) shows the EDX spectrum of ZnO nanoparticles synthesized by sol-gel method. The elemental constitution of ZnO nanoparticles with two major peaks was found to have weight percentage of 61.08 of Zinc and 38.92 of oxygen. The prepared ZnO nanoparticles have atomic percentage of 27.75 of Zinc and 72.25 of oxygen. Fig. 3(c) shows the EDX spectrum of ZnO nanoparticles prepared by hydrothermal method. The elemental constitution of ZnO nanoparticles with two major peaks was found to have weight percentage at 67.97 of Zn and 32.03 of oxygen. The prepared ZnO nanoparticles have atomic percentage at 34.19 of Zn and 65.81 of oxygen. This confirmed the formation of ZnO nanoparticles in all the three process.

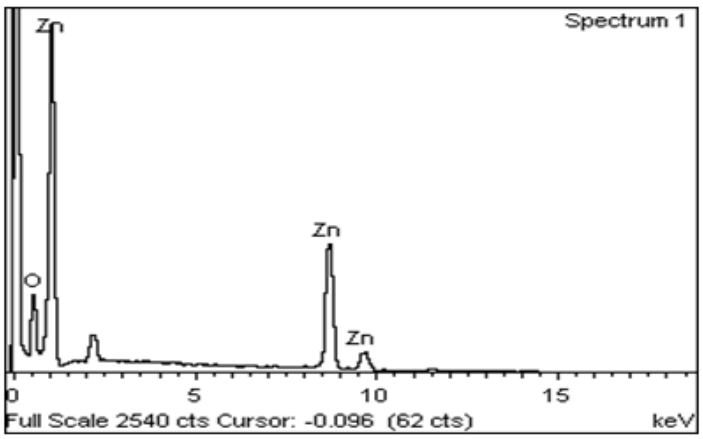

Fig. 3(a) EDX spectrum of ZnO nanoparticles (aqueous solution method)

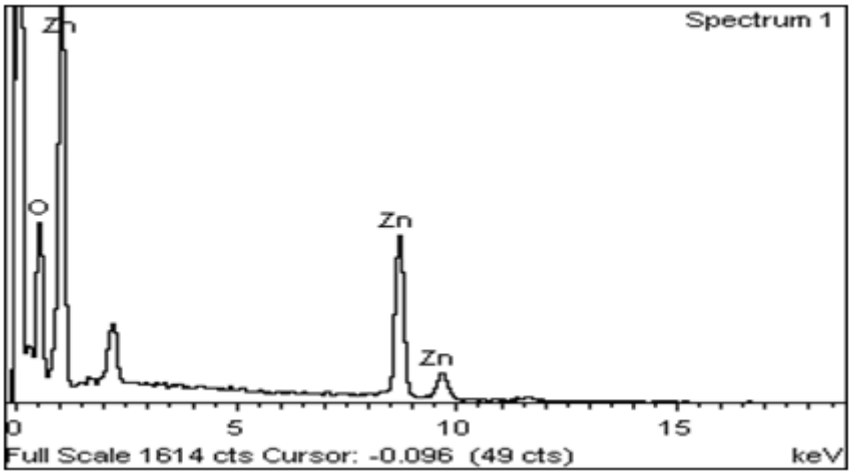

Fig. 3(b) EDX spectrum of ZnO nanoparticles (sol-gel method)

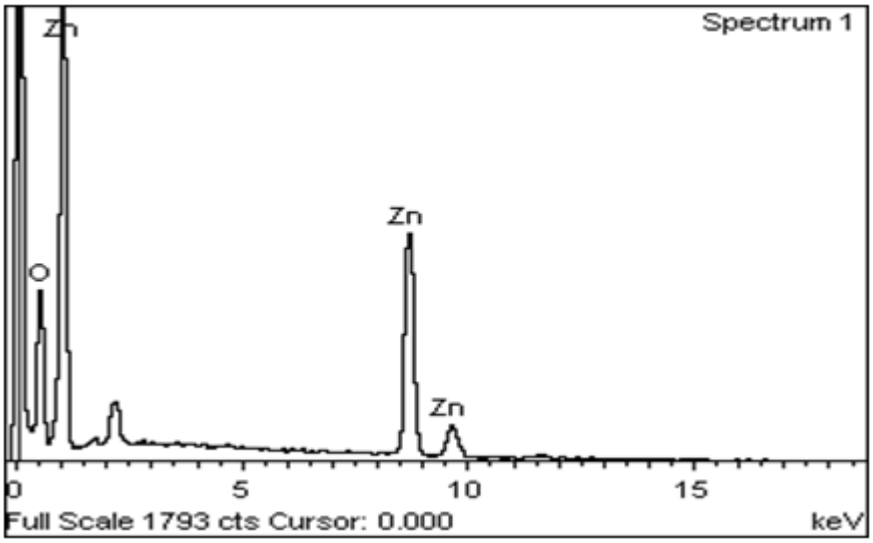

Fig. 3(c) EDX spectrum of ZnO nanoparticles (hydrothermal method)

Table. 1 The atomic content of the nanoparticles obtained from the EDX measurements

Type of nanoparticles	**EDX results**	
	Oxygen (at%)	**Zinc (at%)**
ZnO(aqueous solution method)	59.10	40.90
ZnO (sol-gel method)	72.25	27.75
ZnO (hydrothermal method)	65.81	34.19

3.4 UV-Visible spectroscopy

The UV-visible absorption spectrum of zinc oxide nanoparticle obtained from various methods was shown in Fig. 4(a), 4(b) and 4(c). The absorption edge takes the value around 300 nm for zinc oxide nanoparticles prepared by aqueous solution method, 328 nm for zinc oxide nanoparticles prepared by sol-gel method and 328 nm for zinc oxide nanoparticles prepared by hydrothermal method. This indicates a blue shift in the spectrum. The excitonic absorption peak observed due to zinc oxide nano particles lies much below the band gap wavelength of bulk zinc oxide (388nm) and indicates monodispersion of nanoparticles .

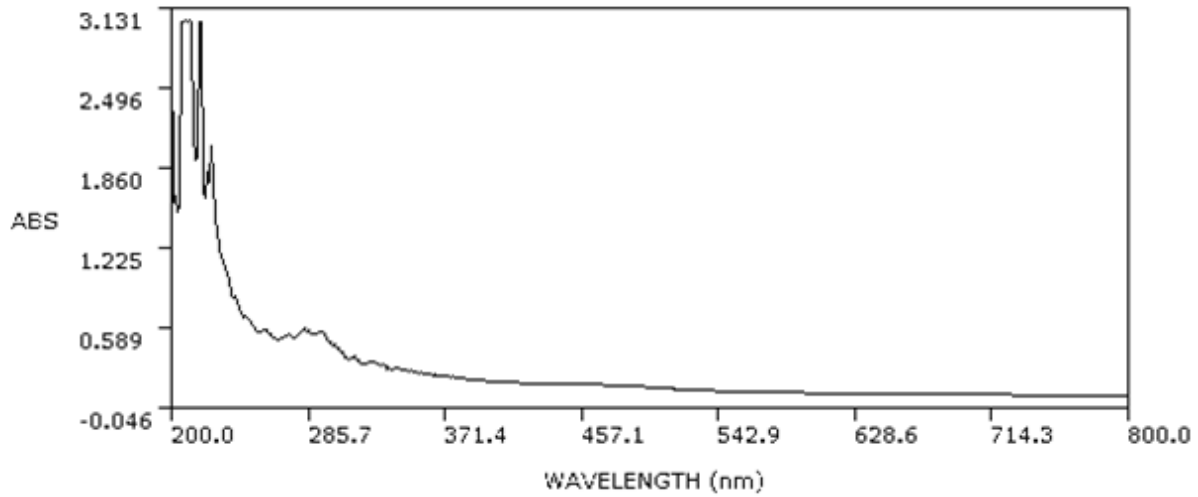

Fig. 4(a) UV spectrum of ZnO nanoparticles (aqueous solution method)

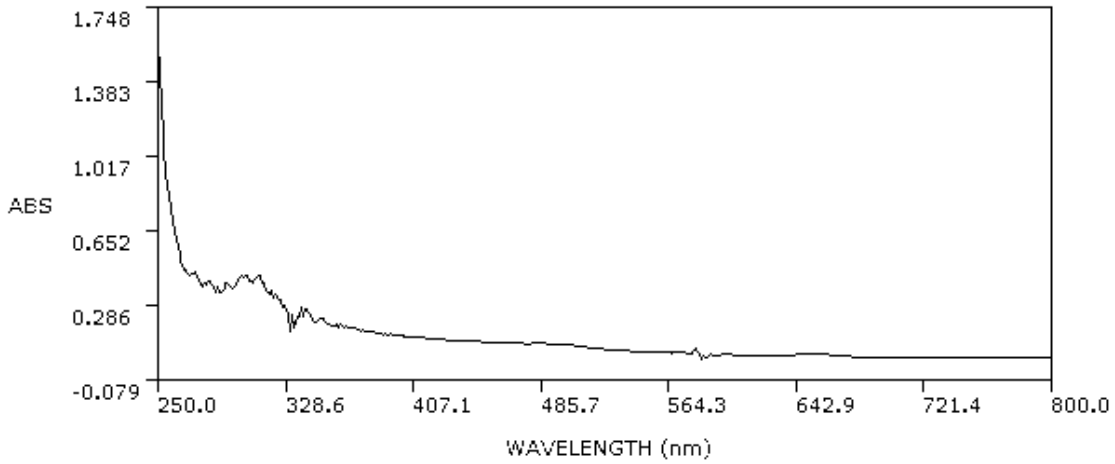

Fig. 4(b) UV spectrum of ZnO nanoparticles (sol-gel method)

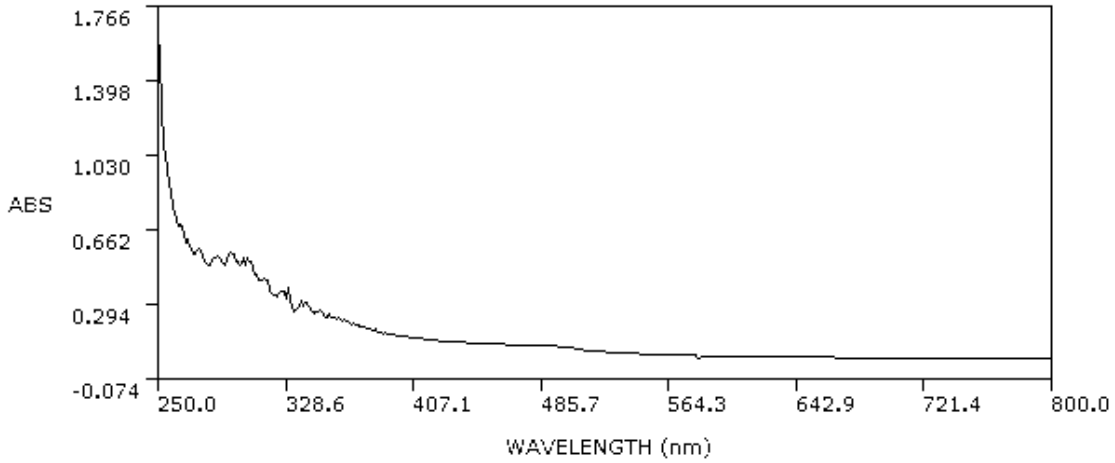

Fig. 4(c) UV spectrum of ZnO nanoparticles (hydrothermal method)

IV. Conclusion

Zinc oxide nanoparticles were prepared by different methods such as aqueous solution, sol-gel and hydrothermal methods and the prepared nanoparticles were characterized by XRD, SEM, EDX, and UV. The crystallite size of the prepared nanoparticles were determined by Debye-scherrer's equation and it was found to be in the nanometer range 13nm , 14nm and 18nm respectively for the nanoparticles prepared by aqueous solution, sol-gel and hydrothermal methods and show preferred growth orientation along (101) plane. All the prepared nanoparticles showed wurtzite structure. SEM analysis, suggested different morphological structures from flower like arrangement to spherical shape. Chemical purity and stoichiometry of the samples were investigated by EDAX Spectroscopy inorder to confirm the presence of Zinc and Oxygen . UV- Visible spectrum show blue shift in all the synthesized nanoparticles.

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