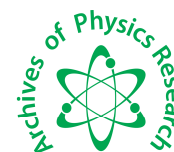




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Synthesis of ZnO nanostructures by solvothermal method

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ABSTRACT

Zinc oxide (ZnO) nanostructures are synthesised by solvothermal method from zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) using water and methanol as solvents. The structures, morphology, and optical properties of the grown ZnO nanostructures are characterized by X-ray Diffraction (XRD), Field-emission Scanning Electron Microscopy (FESEM), Energy dispersive spectroscopy (EDS) in the FESEM, Ultraviolet-visible (UV-vis) spectroscopy, respectively. In case of ZnO nanostructures synthesised using water as solvent, the growth of hexagonal shaped nanocrystals are observed at pH value of 8 and growth of platelet shaped nanostructures are observed at pH value of 12. The ZnO nanostructures synthesised using methanol as solvent, the growth of hexagonal shaped nanorods is observed at pH value of 8 and 9. The above results indicates that the solvents and the pH value of the $Zn(CH_3COO)_2 \cdot 2H_2O$ solution may be playing an important role in the morphology of the ZnO nanostructures in hydrothermal synthesis.

Keywords: Solvothermal growth, nanostructures, ZnO, XRD, SEM.

INTRODUCTION

Zinc oxide (ZnO), a wide band-gap semiconductor with a band-gap of 3.36 eV at room temperature [1, 2], has been investigated intensively for optoelectronic devices, high power devices, spintronics, and transparent conductive layer [2]. ZnO with its high bulk free exciton binding energy (60 meV) [2-4] and excitonic stability even at room temperature has attracted a great deal of attention for blue and ultraviolet optoelectronic devices [2, 5]. The nanostructures of ZnO are widely under investigation by researchers due to their fascinating morphologies, physical properties, and applications in efficient optoelectronic devices operating in blue and ultraviolet region [2]. ZnO nanostructures are promising candidate for ultraviolet laser devices operating at room temperature [6]. The quantum confinement in nanostructures, enhance the exciton oscillator strength and quantum efficiency of optical transitions [2, 6]. Researchers have developed various methods such as chemical vapour deposition (CVD), physical vapour deposition, electrodeposition, thermal evaporation, aqueous synthesis, and solvothermal techniques to prepare ZnO nanostructures [2]. In the present work, we have synthesised ZnO nanostructures by hydrothermal method. The crystal structures, surface morphology and optical properties of the synthesised ZnO nanostructures are studied.

MATERIALS AND METHODS

In the present work ZnO nanostructures are synthesised by solvothermal method from $Zn(CH_3COO)_2 \cdot 2H_2O$ using water and methanol as solvents. The solvothermal synthesis of ZnO nanostructures are carried out using 50 ml capacity teflon lined stainless steel autoclave. The grown nanostructures are characterized by powder XRD using a Rikagu MiniFlex 600 diffractometer with Cu K_α radiation, UV-visible absorption spectroscopy using Shimadzu 1800 spectrophotometer, and FESEM imaging using ULTRA 55, FESEM (Karl Zeiss) equipped with energy-dispersive x-ray spectroscopy (EDS). The FESEM imaging and EDS is carried out at Centre for Nano Science and Engineering (CeNSE), Indian Institute of Science (IISc), Bangalore.

2.1 Synthesis of ZnO nanostructures using water as solvent

In order to synthesize the ZnO nanostructures, 0.1 M solution of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ is prepared in 50 ml of water under continuous stirring. The pH of the prepared $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ solution is adjusted to the required value by adding the NaOH solution prepared in water. In the present work ZnO nanostructures are synthesised using 0.1 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ solution with pH value 8 and 12. 0.1 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ solution with pH values 8 is prepared by adding 25 ml of NaOH (0.2 M) solution prepared in water under continuous stirring to 50 ml of 0.1 M solution of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$. The hydrothermal synthesis of ZnO nanostructures are carried out by transferring the solution into the 50 ml capacity teflon lined stainless steel autoclave. The autoclave is then heated using an oven and maintained at 150°C for 6 hour. 0.1 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ solution with pH value 12 is prepared by adding 15 ml of NaOH (2 M) solution prepared in water under continuous stirring to 50 ml of 0.1 M solution of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$. As in the above case, the synthesis of ZnO nanostructures is carried out by transferring the solution into the autoclave and maintaining the autoclave at 160°C for 8 hour in an oven. In both the cases, after the growth the autoclave is allowed to cool naturally to room temperature and the resulting white powder product is washed with methanol, filtered, and then dried in air in an oven at 100°C . The grown nanostructures are characterized by powder XRD, UV-visible absorption spectroscopy, FESEM imaging and EDS.

2.2 Synthesis of ZnO nanostructures using methanol as solvent

In order to synthesize the ZnO nanostructures, 0.1 M solution of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ is prepared in 50 ml of methanol under continuous stirring. The pH of the prepared $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ solution is adjusted to the required value by adding the NaOH solution prepared in methanol. In the present work ZnO nanostructures are synthesised using 0.1 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ solution with pH value 8 and 9. 0.1 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ solution with pH value 8 is prepared by adding 25 ml of NaOH (0.3 M) solution prepared in methanol under continuous stirring to 50 ml of 0.1 M solution of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$. 0.1 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ solution with pH value 9 is prepared by adding 30 ml of NaOH (0.3 M) solution prepared in methanol under continuous stirring to 50 ml of 0.1 M solution of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$. The solvothermal synthesis of ZnO nanostructures are carried out using 50 ml capacity teflon lined stainless steel autoclave. For the growth of ZnO nanostructures the autoclave with $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ solution is maintained 160°C for 8 hour in an oven. The autoclave is then allowed to cool naturally to room temperature and the resulting white powder is washed with methanol, filtered and then dried in air in an oven at 100°C .

RESULTS AND DISCUSSION

3.1 ZnO nanostructures synthesised using water as solvent

The grown ZnO nanostructures have been characterized by powder XRD, FESEM, EDS, and UV-vis spectroscopy. Fig. 1(a) shows the typical powder XRD pattern of the hydrothermal synthesised ZnO nanostructures from 0.1M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ solution. The XRD pattern indicates hexagonal wurtzite structure (JCPDS card no. 36-1451) of the grown ZnO nanostructures. The strong and narrow diffraction peaks indicate high purity and good crystallinity of the grown nanostructures. The intense (101) diffraction peak indicates that the preferential orientation is along c-axis [7]. The morphology of the nanostructures is examined by FESEM. As shown in Fig. 1(b), the FESEM image of ZnO nanostructures grown from 0.1 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ solution with pH = 8 shows the growth of hexagonal shaped ZnO nanostructures. Fig. 1(c) is the SEM-EDS of the nanostructures, showing zinc L peak and oxygen K peak. The weight/atomic percent of Zn, and O elements obtained from EDS in the ZnO nanostructure is shown in Table 1. EDS did not show the presence of any other impurities. The Zn/O atomic percentage indicates that the synthesized ZnO nanostructure is nearly stoichiometric. The UV-visible absorption spectrum of the nanostructures is shown in Fig. 1(d). It shows a strong exciton absorption peak around 359 nm, exhibiting a blue-shift relative to the bulk exciton absorption due to quantum confinement in nanostructures [2, 8]. The appearance of the sharp excitonic peak indicates the high crystalline quality of the grown nanostructures [9].

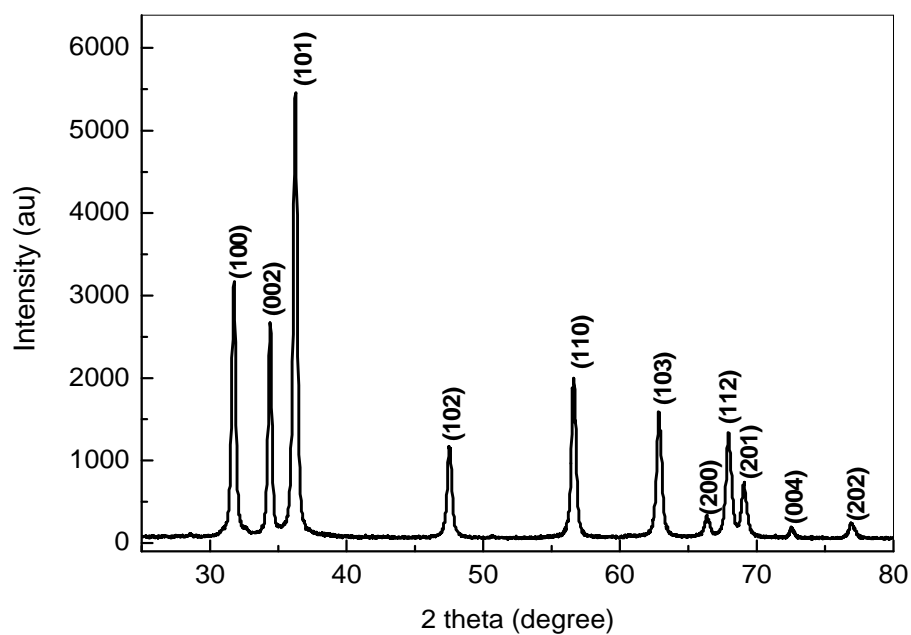


Fig. 1(a). Typical XRD pattern of ZnO nanostructures synthesised from 0.1 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ with water as solvent.

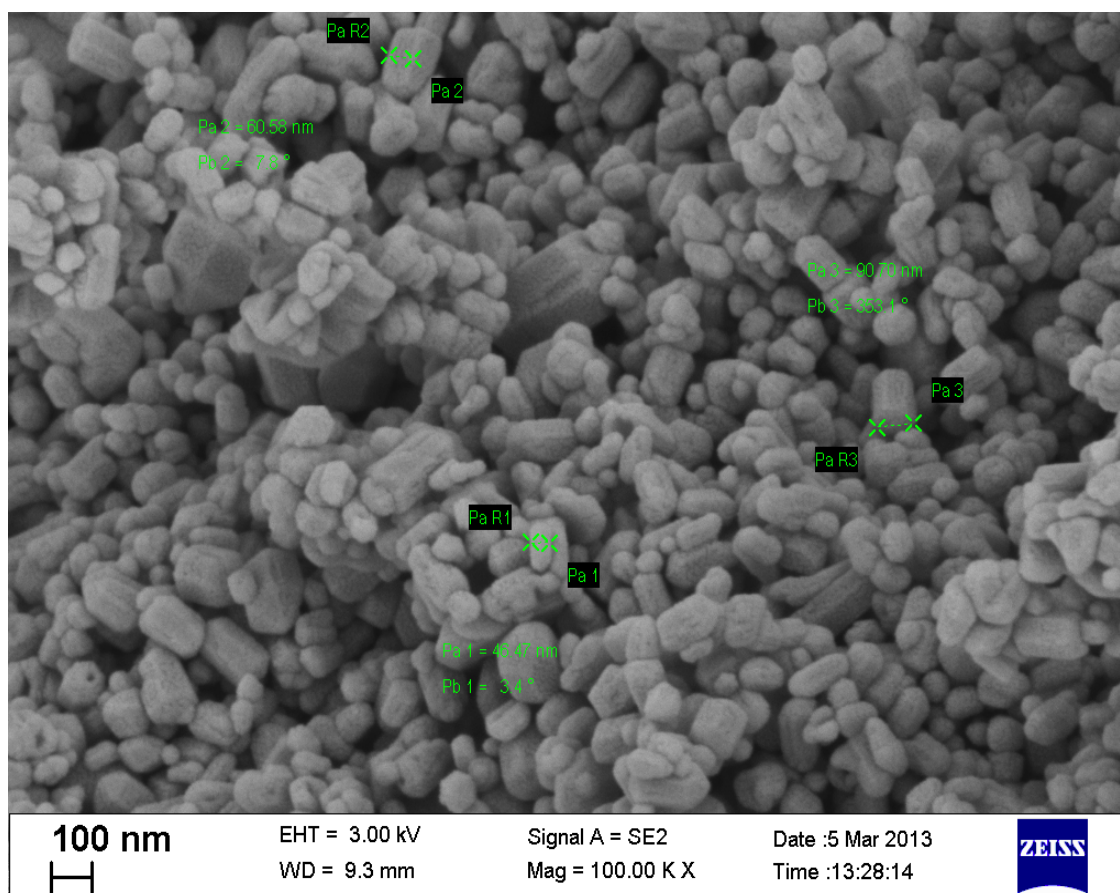


Fig. 1(b). FESEM image of ZnO nanostructures synthesised from 0.1 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in water with pH = 8.

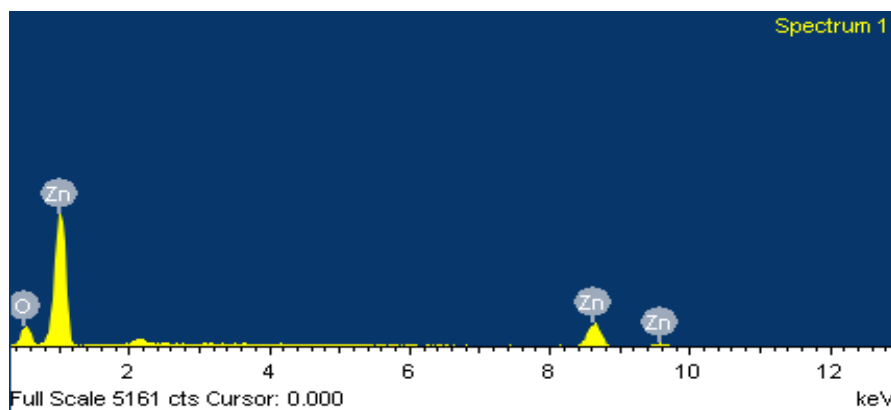


Fig. 1(c). EDS of ZnO nanostructures synthesised from 0.1 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in water with pH = 8.

Table 1. The weight/atomic percent of Zn and O elements obtained from EDS in the ZnO nanostructures synthesised from 0.1 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in water with pH = 8.

Element	Weight%	Atomic%
O K	18.33	47.84
Zn L	81.67	52.16
Totals	100.00	

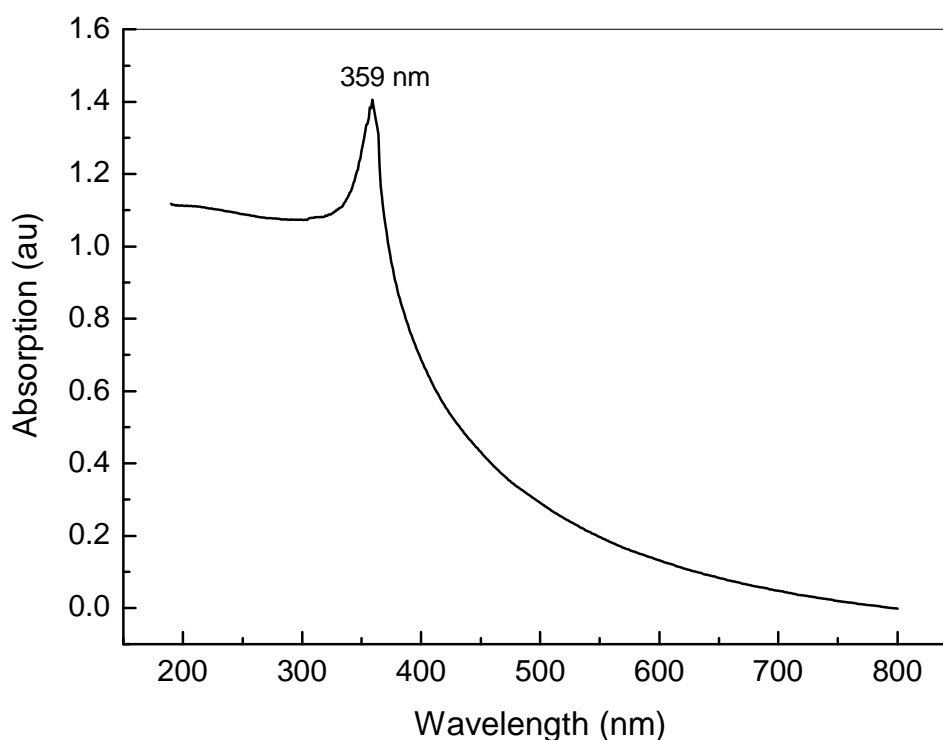


Fig. 1(d). UV-visible absorption spectrum of ZnO nanostructures synthesised from $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in water with pH = 8.

Fig. 2(a) shows the powder XRD pattern of the hydrothermal synthesised ZnO nanostructures from 0.1M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ solution with a pH value of 12. As shown in Fig. 2(b), the FESEM image shows the growth of platelet shaped ZnO nanostructures. The weight/atomic percent of Zn and O elements obtained from EDS are shown in Table 2. EDS did not show the presence of any other impurities. Fig. 2(c) shows the UV-Visible absorption spectra of the nanostructures with a sharp excitonic absorption peak at around 362 nm. The appearance of the sharp excitonic peak indicates the high crystalline quality of the grown nanostructures

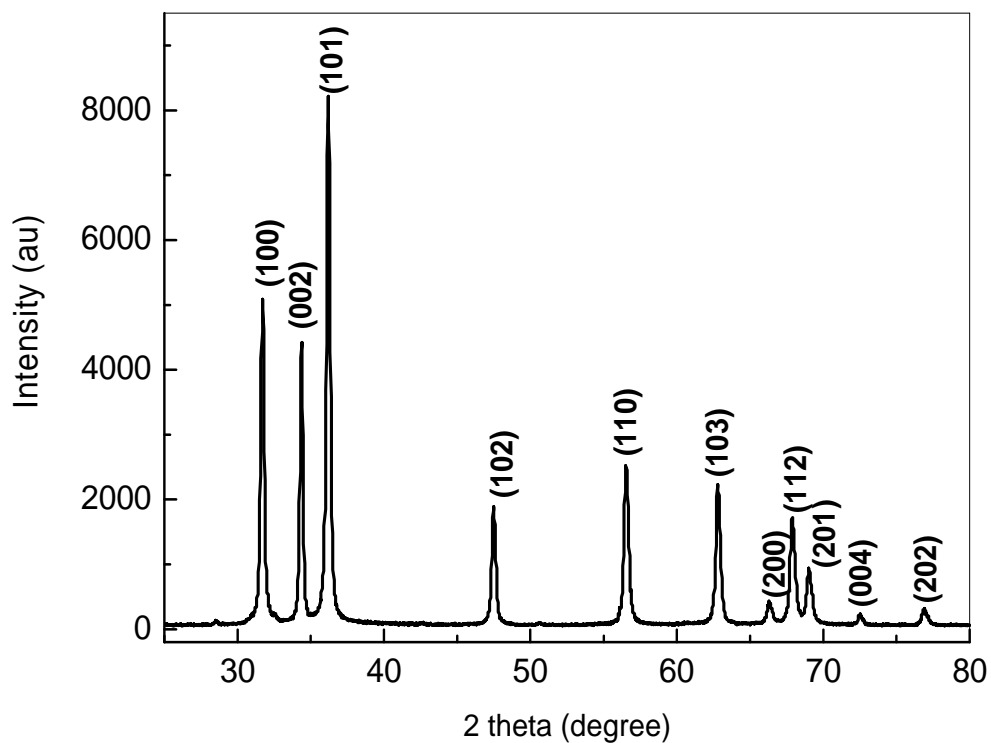


Fig. 2(a). XRD pattern of ZnO nanostructures synthesised from 0.1 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in water with $\text{pH} = 12$.

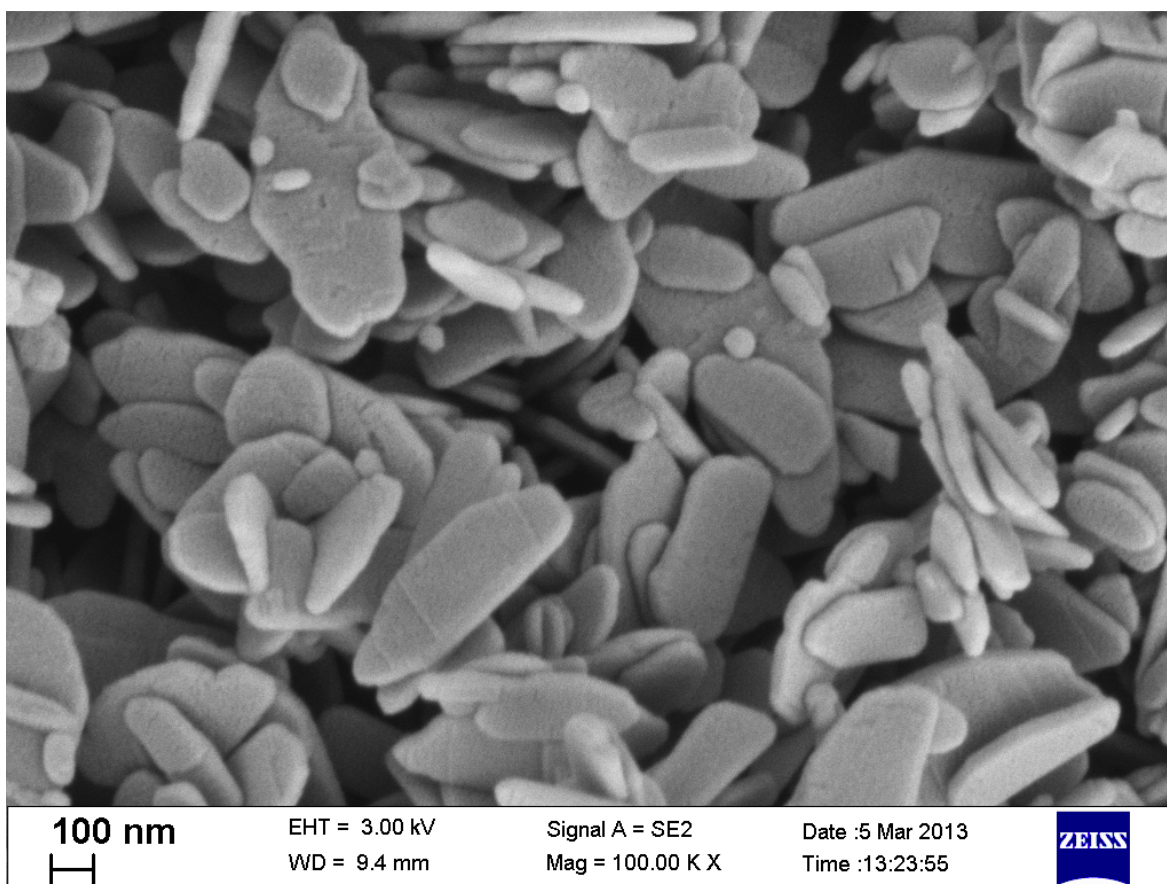


Fig. 2(b). FESEM image of ZnO nanostructures synthesised from $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in water with $\text{pH} = 12$.

Table 2. The weight/atomic percent of Zn and O elements obtained from EDS in the ZnO nanostructures synthesised from 0.1 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in water with pH = 12.

Element	Weight%	Atomic%
O K	22.73	54.59
Zn L	77.27	45.41
Totals	100.00	

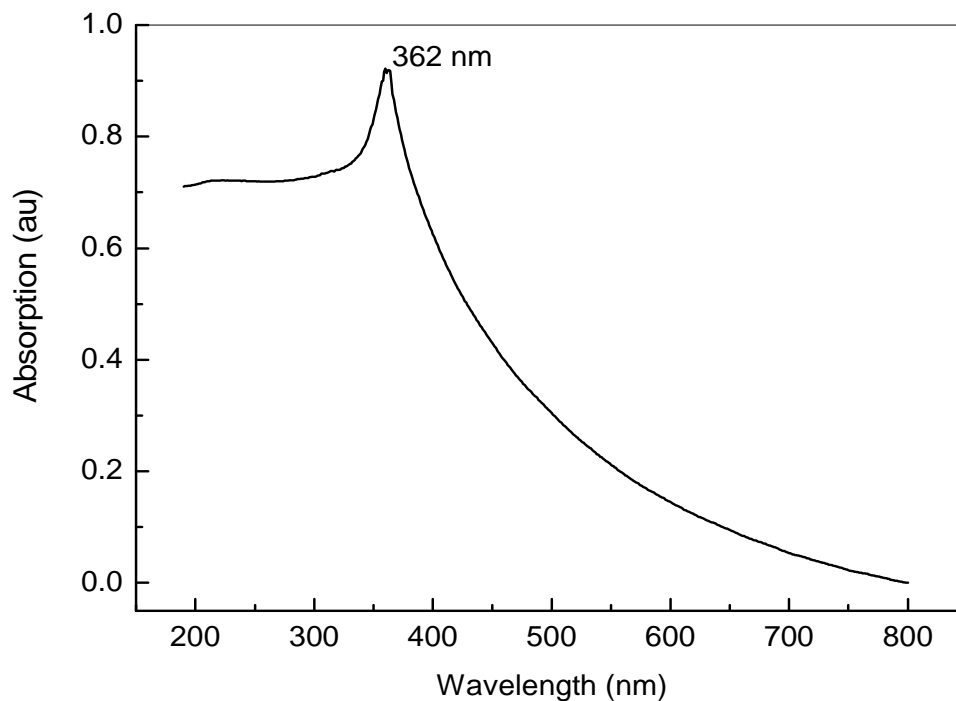


Fig. 2(c). UV-visible absorption spectrum of ZnO nanostructures synthesised from 0.1 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in water with pH = 12.

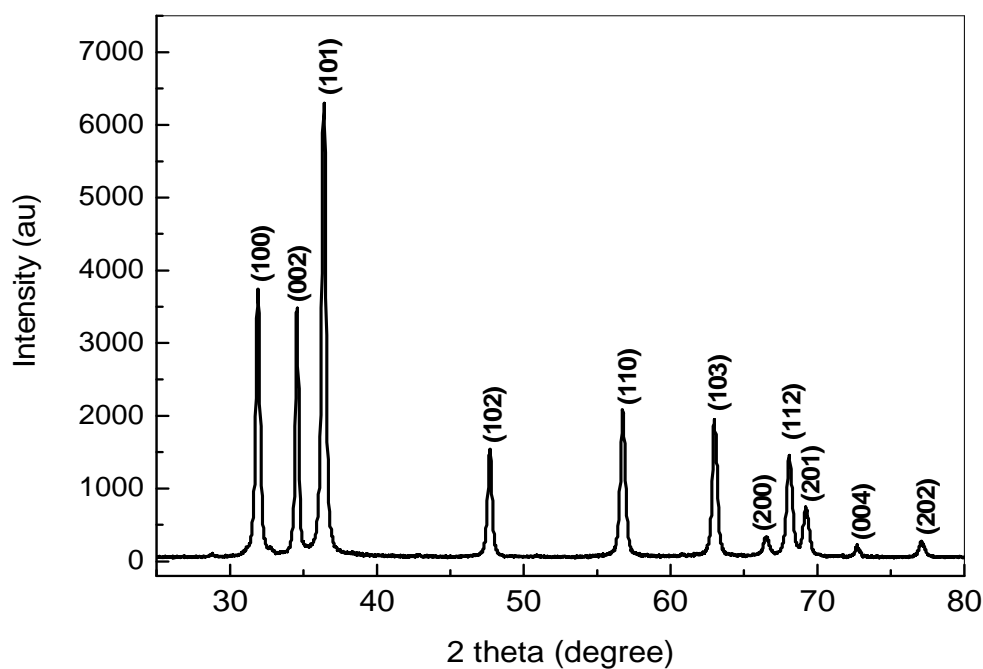


Fig. 3(a). XRD pattern of nanostructures synthesised from 0.1 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in methanol solution with pH = 8.

3.1 ZnO nanostructures using synthesised using water as solvent

Fig. 3(a) shows the powder XRD pattern of the solvothermal synthesised ZnO nanostructures from 0.1M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in methanol solution with a pH value of 8. As shown in Fig. 3(b), the FESEM image shows the growth of hexagonal shaped ZnO nanorods. The weight/atomic percent of Zn and O elements obtained from EDS are shown in Table 3. EDS did not show the presence of any other impurities. Fig. 3(c) shows the UV-Visible absorption spectra of the nanostructures with an excitonic absorption peak at around 356 nm.

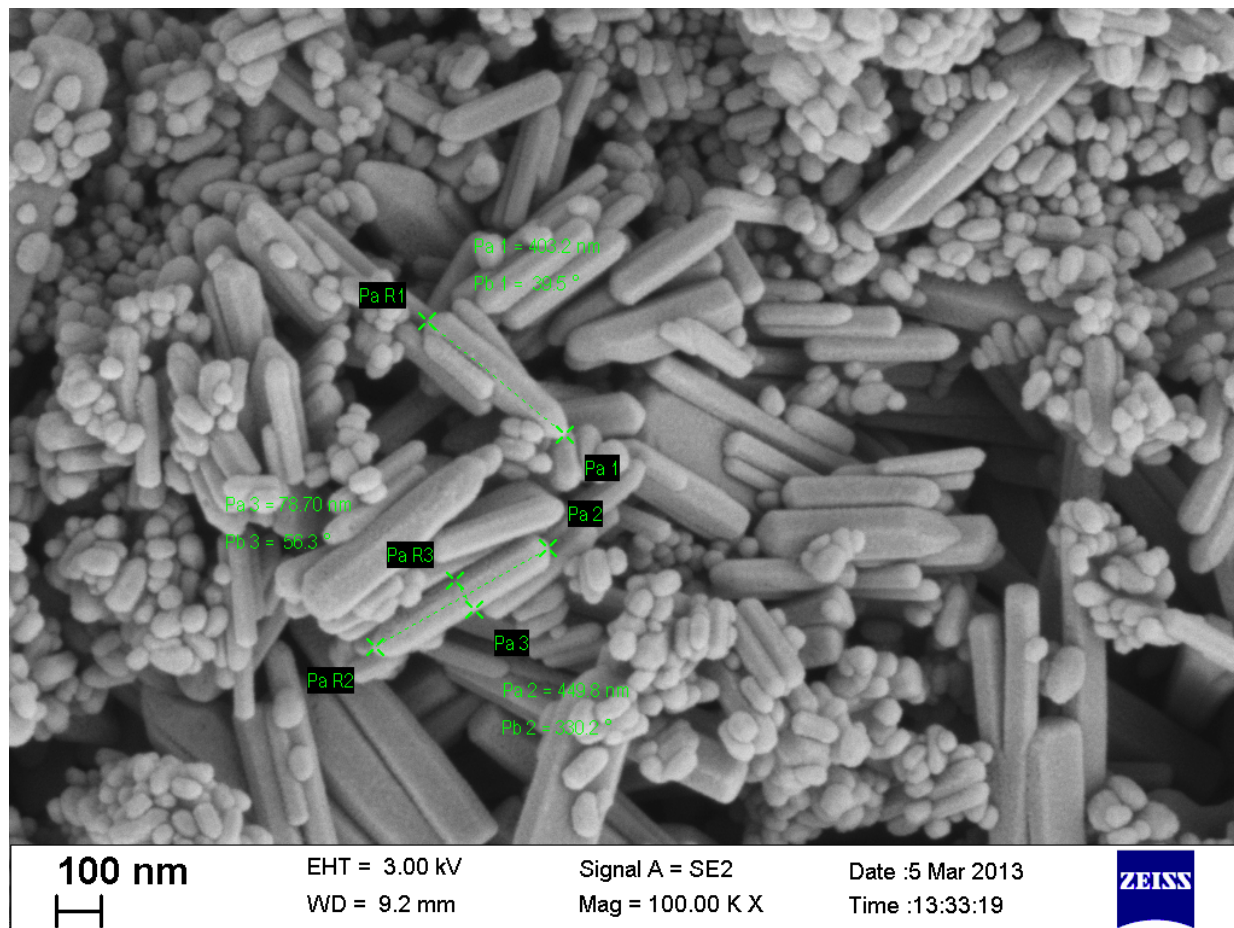


Fig. 3(b). FESEM image of nanostructures synthesised from 0.1 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in methanol solution with pH = 8.

Table 3. The weight/atomic percent of Zn and O elements obtained from EDS in the ZnO nanostructures synthesised from 0.1 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in methanol solution with pH = 8.

Element	Weight%	Atomic%
O K	20.56	51.40
Zn L	79.44	48.60
Totals	100.00	

Fig. 4(a) shows the powder XRD pattern of the solvothermal synthesised ZnO nanostructures from 0.1M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in methanol solution with a pH value of 9. As shown in Fig. 4(b), the FESEM image shows the growth of ZnO particles along with hexagonal shaped nanorods. The weight/atomic percent of Zn and O elements obtained from EDS are shown in Table 4. EDS did not show the presence of any other impurities. Fig. 4(c) shows the UV-vis absorption spectra of the nanostructures with an excitonic absorption peak at around 346 nm.

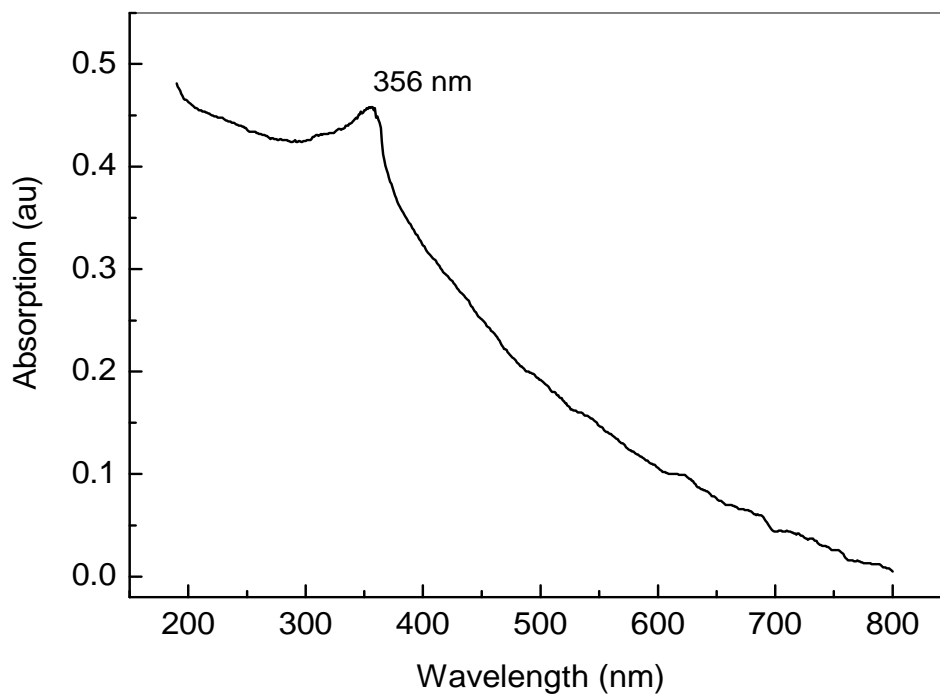


Fig. 3(c). UV-vis absorption spectrum of nanostructures synthesised from 0.1 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in methanol solution with a pH = 8.

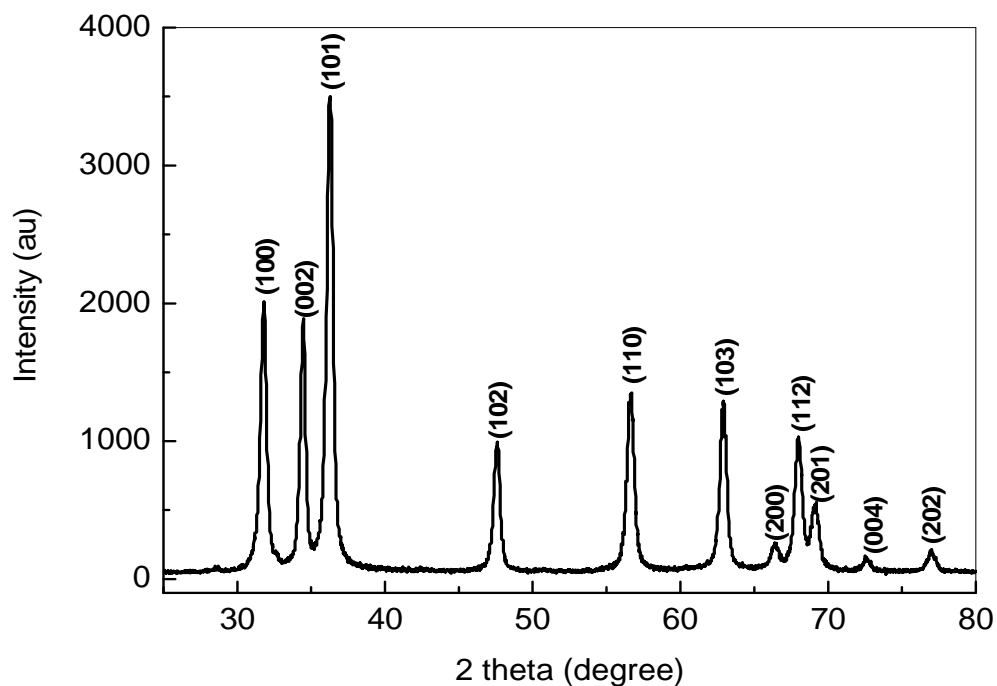


Fig. 4(a). XRD pattern of nanostructures synthesised from 0.1 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in methanol solution with pH = 9.

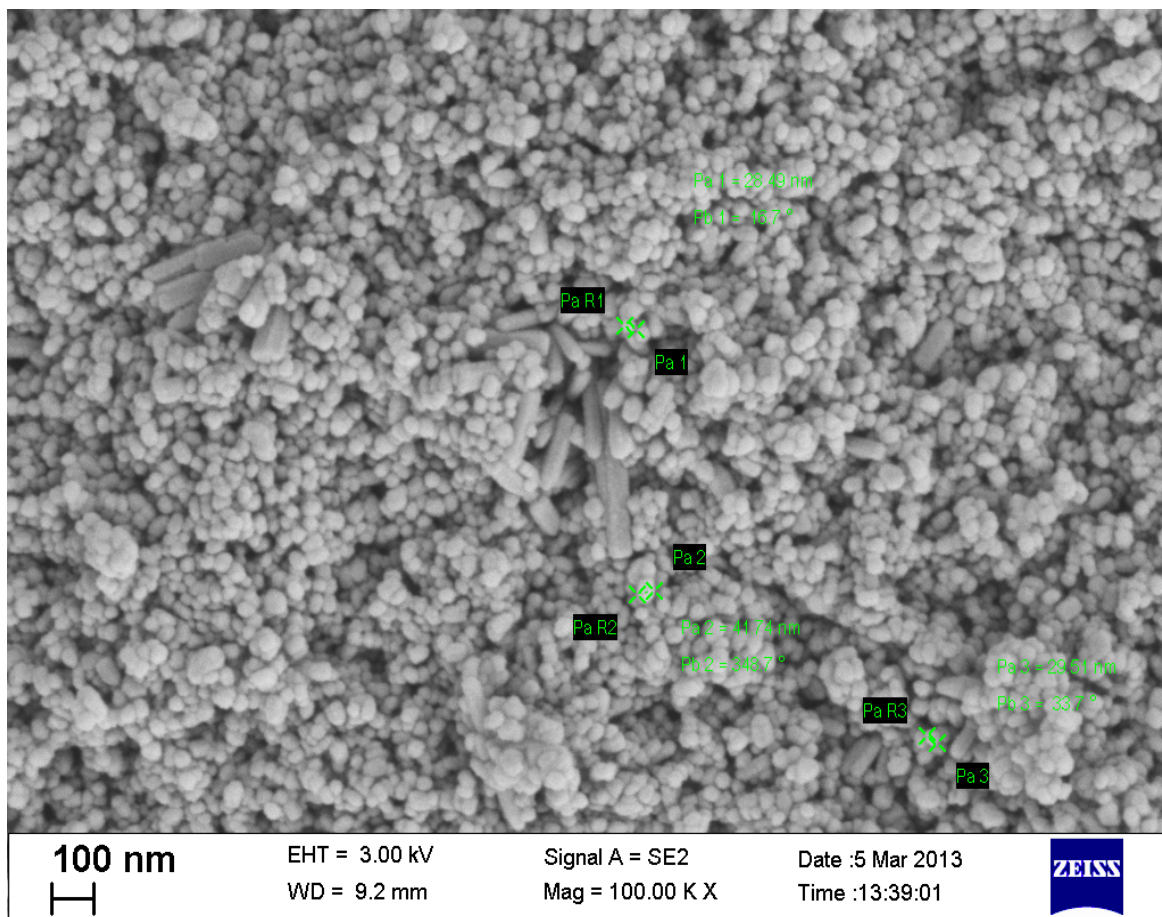


Fig. 4(b). FESEM image of nanostructures synthesised from 0.1 M $Zn(CH_3COO)_2 \cdot 2H_2O$ in methanol solution with pH = 9.

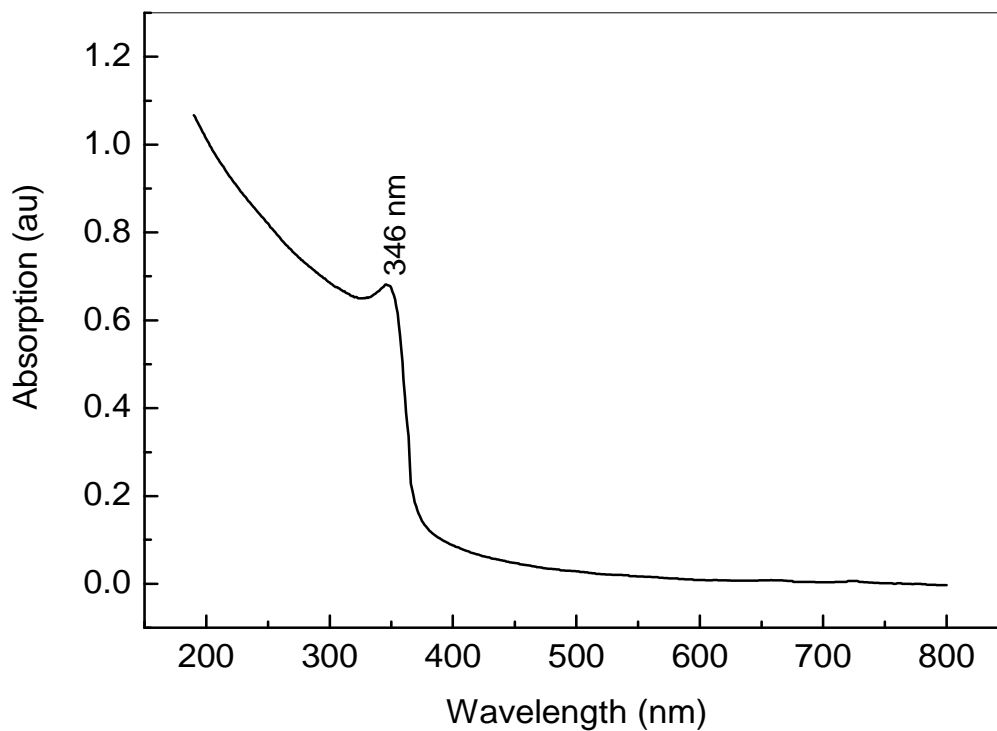


Fig. 4(c). UV-vis absorption spectrum of ZnO of nanostructures synthesised from 0.1 M $Zn(CH_3COO)_2 \cdot 2H_2O$ in methanol solution with pH = 9.

Table 4. The weight/atomic percent of Zn and O elements obtained from EDS in the ZnO nanostructures synthesised from 0.1 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in methanol solution with pH = 9.

Element	Weight%	Atomic%
O K	19.09	49.08
Zn L	80.91	50.92
Totals	100.00	

CONCLUSION

In the present work ZnO nanostructures are synthesised by solvothermal method from $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ using water and methanol as solvents. The grown nanostructures are characterized by powder XRD, UV-visible absorption spectroscopy, FESEM imaging and EDS. The XRD patterns indicate the wurtzite structure of the grown nanostructures and the narrow XRD peaks indicate good crystalline quality of the grown nanostructures. The EDS results indicate that the synthesized ZnO nanostructures are nearly stoichiometric and free of impurities. The UV-visible absorption spectra of the nanostructures show strong exciton absorption peak with blue-shift relative to the bulk exciton absorption in all of the synthesised nanostructures. The appearance of the sharp excitonic peak in all these samples, indicate the high crystalline quality of the grown nanostructures. In case of ZnO nanostructures synthesised using water as solvent, the growth of hexagonal shaped nanocrystals are observed at pH value of 8 and growth of platelet shaped nanostructures are observed at pH value of 12. In the ZnO nanostructures synthesised using methanol as a solvent, the growth of hexagonal shaped nanorods is observed at pH value of 8 and 9. The above results indicate that the solvents as well as the pH values of the $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ solutions may be playing an important role in the morphology of the of ZnO nanostructures in solvothermal synthesis. Further work is in progress to understand the role of solvents and pH values on the morphology of ZnO nanostructures synthesized by solvothermal method.

Acknowledgements

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