Facial hydrothermal approach for the synthesis of Zinc oxide nanosheets

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Abstract

Herein, we synthesis ZnO nanosheets via facial hydrothermal method using sodium hydroxide (NaOH) as a stabilizer. The synthesized ZnO was subjected to various characterizations for analysis of their optical, structural, functional groups, chemical composition, surface morphological and thermal studies, obtained results reveals the following features; UV-Vis spectroscopy analysis shows absorption maximum at 272 nm which confirms the preliminary presence of ZnO material. X-ray diffraction (XRD) analysis reveals the average crystalline grain size is found to be of around 38.10 nm. Fourier transform infrared spectroscopy (FT-IR) analysis reveals the presence of O-H, C-H, C-N and Zn-O bands. Atomic force microscopy (AFM) and scanning electron microscopy analysis (SEM) shows the topological structure of ZnO and it having nanosheets like nature. Energy dispersive X-ray spectroscopy (EDS) analysis confirms the chemical compositions were Zn and O elements. Further, we observed by thermo gravimetric analysis (TGA) that for synthesized ZnO nanosheets weight loss is of 15.574% was occurred at 47.49˚ C to 300˚ C. After 300˚C, none of the materials underwent greater than 1% of weight loss. From DSC analysis, we observed that there are endothermic reactions in between 23˚C to 500˚C. In addition, we proposed to study biological activities of these synthesized ZnO nanosheets.

Keywords: Endothermic, hydrothermal method, nanosheets, thermal decomposition, zinc oxide.

Introduction

There are large numbers of techniques available to synthesis different type of nano materials in the form of collides, clusters, powders, tubes, rods, wires, sheets, thin films etc. There are various physical, chemical, biological and hybrid techniques are available to synthesis nano materials **[1].** Nano crystalline powder with uniform size and shape has interesting properties. Particularly nano crystalline metal oxides have numerous important properties like catalytic, electrical and optical properties **[2].** As we all know any material in its nano form is more demandable than in its bulk form because in nano level the material undergoes a drastic change in its property and has versatile applications. There are spectacular developments in the field of nanotechnology within the recent past years, with various developed methodologies to synthesize nanoparticles with specific form and size which are counted for specific needs **[3].** New applications of nanoparticles and nanomaterials are increasing rapidly; while operating with nanomaterials has allowed a much better understanding of biology. Nanomaterials of metal oxides represent a new class of important materials that are increasingly being developed for use in research and health-related applications. In recent years, zinc oxide (ZnO) being a wide band-gap semiconductor (3.36 eV), has received increased attention regarding potential electronic applications due to its unique optical, electrical and chemical properties. Because of large direct band gap it creates anxiousness in the scientific minds to enhance the research on one dimensional nanostructure especially oxide materials **[4].** Owing to these potential applications of ZnO we have synthesized ZnO material.

ZnO can be synthesized by various approaches including Sol-Gel processing, homogeneous precipitation, mechanical milling, chemical precipitation method, microwave method, spyrolysis, thermal evaporation and mechanochemical synthesis **[5].** Here, we preferred hydrothermal technique because it is most promising alternative synthetic method and of the low reaction temperature makes an attractive one. In growing nanoparticles hydrothermal has many advantages like simple equipment, no need of catalyst, economically low, large area uniform production, eco-friendly and less hazardous **[6].**

In the present work, we synthesized Zinc Oxide nanomaterial using sodium hydroxide as a stabilizer via hydrothermal approach. Further, we characterized the synthesized ZnO by UV-Visible, XRD, FT-IR, AFM, SEM, EDS, TGA and DSC analyses.

Experimental

Materials

For the synthesis of ZnO nanosheets doubly distelled water and high purity AR grade materials zinc sulphate ($ZnSO_47H_2O$) and sodium hydroxide crystal (NaOH) were used.

Synthesis process

To synthesis ZnO nanosheets, 0.57508 gm of zinc sulphate($ZnSO_47H_2O$) crystal of 0.2 M is prepared in 10 ml of distilled water. 0.04 gm of sodium hydroxide (NaOH) crystal of 0.1 M is dissolved in 10 ml of distilled water, and this prepared solution is added to $ZnSO_47H_2O$ solution under continuous stirring. Then mixture is transferred to a Teflon lined stainless steel autoclave and heated at 180˚C for 3 hour in an oven. The autoclave was then allowed to cooldown to room temperature. Later, the mixture is centrifuged several times with distilled water. The resulting white color product is obtained that is dried in an oven at 60˚C and further it is used for various characteristics studies.

Characterizations

1. Absorption spectrum was recorded in the wavelength range of 200-800 nm using UV-Visible spectrophotometer (model: V-670 Jasco at USIC K. U. Dharwad, India).
2. An average grain size of particles was calculated by XRD analysis using CuKα radiations (λ=1.5406Å) (model: Rigaku, SmartLab 3kW at CMST Manasagangotri, Mysore, India).
3. Various functional groups were recorded in the range of 4000 to 400 cm^{-1} at a resolution of 2 cm^{-1} with KBr pellet method by FT-IR analysis (model: Nicolet 6700 at USIC K. U. Dharwad, India).
4. The topological structure of the sample was examined by AFM (model: Nanosurf, AG-easy scan 2 at USIC K. U. Dharwad, India).
5. The nanostructure and surface morphology of the sample were examined by SEM (model: HITACHI, S-3400N at CMST Manasagangotri, Mysore, India).
6. Elemental compositions were analyzed using EDS (model: Thermo Fisher Scientific, NORAN system 7 at CMST Manasagangotri, Mysore, India).
7. Thermal behavior and stability of the synthesized sample were studied by TGA at the temperature range of room temperature-600˚C (model: SDT Q600 at USIC K. U. Dharwad, India) and DSC at the temperature range of room temperature-500˚C (model: Q20 V24.10 Build 122 at USIC K. U. Dharwad, India).

Results and discussion

UV-Visible spectroscopy

In order to confirm the presence of ZnO material UV-Visible spectroscopy is performed. The **Fig. 1** shows the UV-vis absorption spectrum of synthesized ZnO in an ethanol solvent at room temperature. From **Fig. 1** we observed that the absorption maxima (λ_{max}) is at 272 nm **[7].** This reveals that the preliminary confirmation of ZnO material. It is also evident that significant sharp absorption of ZnO indicates the mono dispersed nature of the particle distribution **[8].**

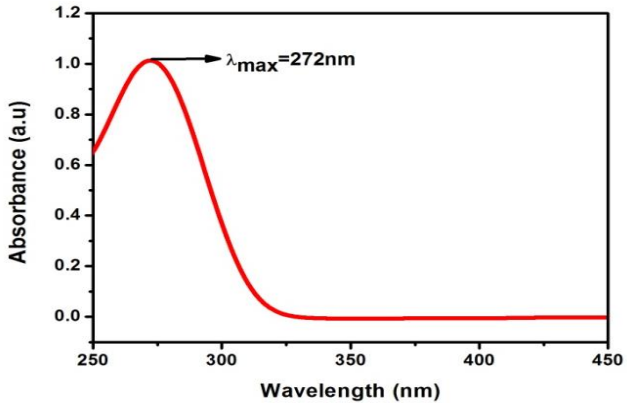

Fig. 1. UV-Visible spectrum of ZnO.

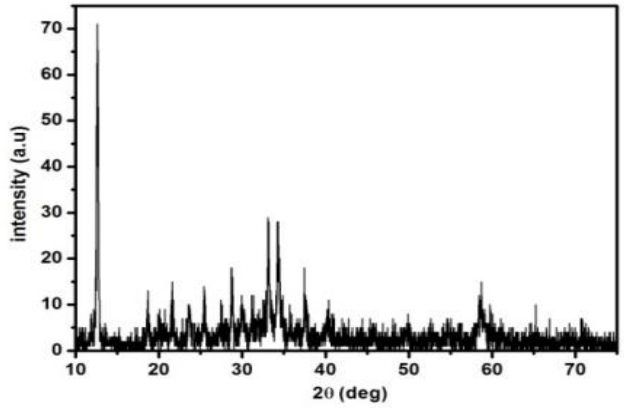

Fig. 2. XRD pattern of ZnO.

X-ray diffraction spectroscopy

The X-ray diffraction spectrum was recorded using CuKα radiation. The intensity data were collected over a 2θ range of 10˚-80˚. The average grain size of the sample was estimated with the help of Scherer's equation using the most intense peak. The **Fig. 2** shows the XRD pattern of synthesized ZnO, which are in good agreement with that of ZnO phase (JCPDS 21-1486), which indicates that sample begin to crystal nature. The diffraction peaks in XRD pattern locating at 33.12˚, 58.61˚ and 69.90˚ are consistent with the literature data JCPDS 21-1486 **[9].** This crystal structure was also studied by Rykl et al **[10]** and Yue Zhao et al **[11].** It is noted that the JCPDS file only gives Bragg angle and relative intensities, but no information is provided about the crystal structure. X-ray diffraction analysis confirmed that synthesized material is ZnO, and no other peaks of impurities are observed, this indicating that purity of obtained ZnO nanoparticles. The average grain size (D) was calculated using Scherrer equation **[12-13]** and it is given by

$$D = \frac{0.89\lambda}{(\beta COS\theta)}$$

Where,

λ : wavelength (CuKα).

β : full width half maxima (FWHM) of the ZnO (most intense peak) peak.

θ : diffraction angle.

The estimated average grain size was found to be 38.10 nm.

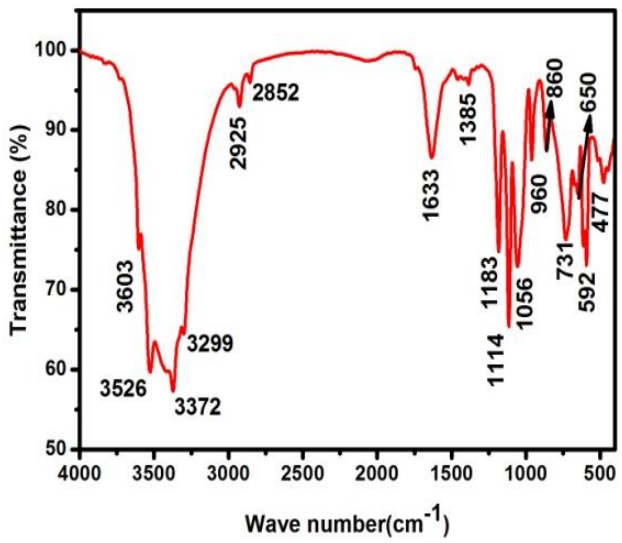

Fig. 3. FT-IR spectrum for ZnO.

FT-IR spectroscopy

Fourier transform infrared spectroscopy study was performed in the region of 4000-400 cm^{-1} using the KBr pellet technique. The FTIR spectrum of the synthesized ZnO is shown in **Fig. 3**. The peaks between 3250 to 3650cm^{-1} are 3603 cm^{-1},3526 cm^{-1},3372 cm^{-1} and 3299 cm^{-1} these peaks represents O-H stretching mode inductive of the presence of hydroxyl ion (OH) in the sample **[7].** Two peaks at 2925 cm^{-1} and 2852 cm^{-1} are attributed to symmetric and asymmetric C-H in sp^2 and $C-H_n$ in sp^3 configuration respectively **[14].** Peak at 1633 cm^{-1} represents H-O-H bending vibration **[15].** The absorption peak at 1385 cm^{-1} is assigned to the bending vibration of C-H stretching **[15].** Peaks at 1183 cm^{-1}, 1114 cm^{-1} and 1056 cm^{-1} are due to C-N bonds vibrations **[16].** Peaks at 731 cm^{-1}, 650 cm^{-1} and 592 cm^{-1} peak are due to vibrations of free water molecules. The peak at 477 cm^{-1} clearly represents the ZnO band arising from bonding between Zn and O **[7].**

AFM and SEM Analysis

Surface and morphological characterizations of ZnO were carried out using the atomic force microscopy method and scanning electron microscopy. AFM is utilized for topological morphology of the synthesized ZnO and to calculate size of the particles. AFM image for synthesized ZnO is shown in **Fig. 4(a).** From **Fig. 4(a)** we observed that image look like nanosheets and size having around 80 to 120 nm sheets. The SEM image for synthesized ZnO nanosheets is shown in **Fig. 4(b).** ZnO can be form in different structures due to the type of precursors that has been used, such; zinc acetate - nanorods like structure, zinc chloride and sulphate - nano-prism structure **[18].** It can be imagined that the pyramid terminated ZnO particles are covered by the dense ZnO nanorods. On each nanorod a few of smaller sized 'nano-tips' distribute on the top flat-plane like nanosheets **[19].**

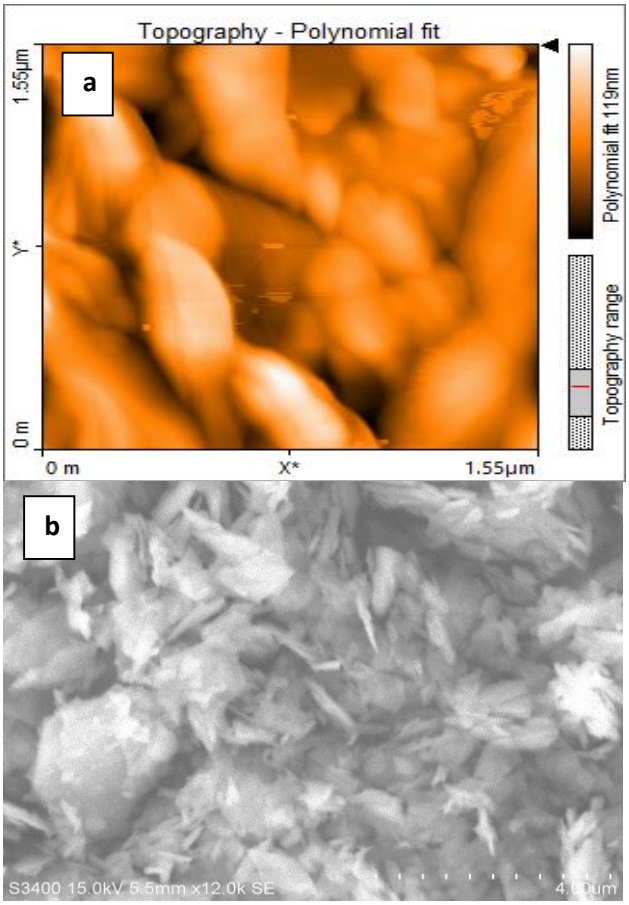

Fig. 4. Surface and morphology study of ZnO (a) AFM image (b) SEM image.

EDS analysis

Energy dispersive X-ray spectrum of synthesized ZnO is shown in **Fig. 5.** Five peaks have been clearly observed from the spectrum, which are related to zinc and oxygen **[17].** Herein, the EDS characterization suggest that the ZnO powder has good purity with zinc content weight of 52.05% and oxide content weight of 47.95%, in which very little impurities can be seen. The obtained sample are in a proper stoichiometry of zinc and oxygen only **[18].**

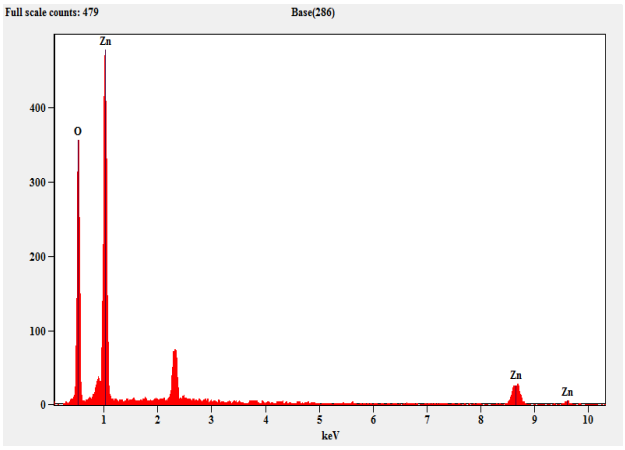

Fig. 5. EDS spectrum for ZnO.

TGA and DSC analyses

Thermo gravimetric analysis (TGA) was carried out to investigate the decomposition of Zinc oxide. TGA curve for synthesized ZnO is shown in **Fig. 6(a).** From **Fig. 6(a)** we observed that material goes under decomposition of 9.871% up to 136˚C due to water and other low molecular weight compounds are volatilized **[20].** In the second stage continuously organic compounds decomposed, continues weight loss occurs up to~ 305 ˚C that is of 7.592%. After the~305 ˚C, there is no more weight loss of material underwent greater than 1**% [21-22].** DSC curve for syntrhesized ZnO was shown in **Fig. 6(b).** From **Fig. 6(b)** it indicates three endothermic peaks in the range of 70˚C - 140˚C, due to the volatilization of water and other low molecular weight compounds. After that due to increase in temperature there is transformation in the sample so anhydrous materials get melts and endothermic peak has been obtained at~302˚C **[23].** Further, there is no great decomposition of synthesized ZnO over the temperature up to 500˚C.

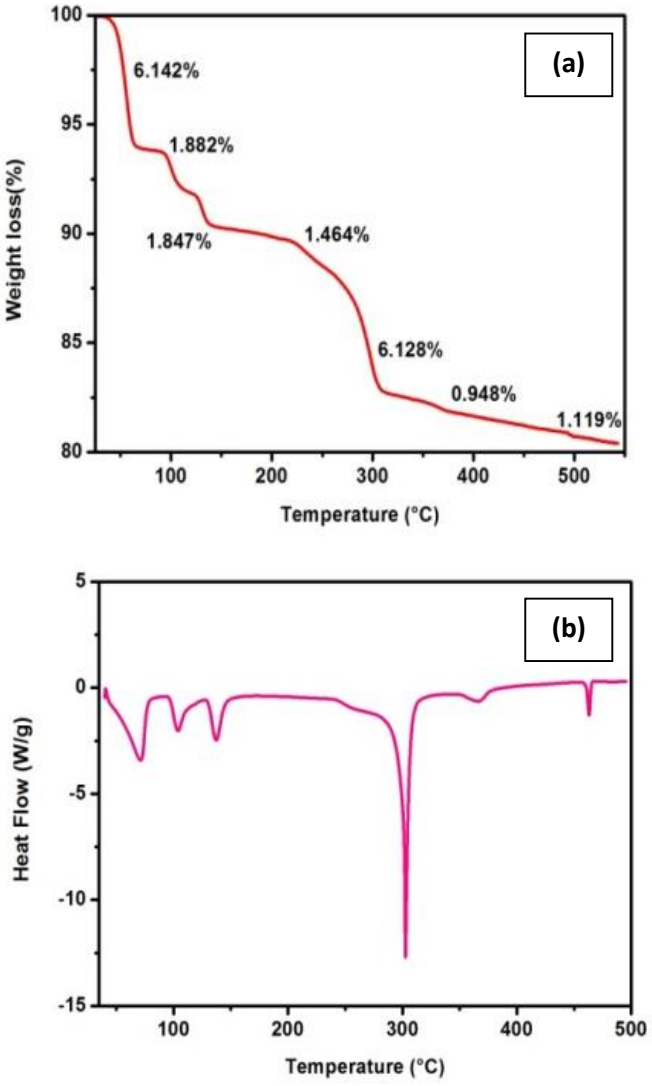

Fig. 6. Thermal behavior and stability of ZnO (a) TGA plot (b) DSC plot.

Conclusion

A simple hydrothermal method used for the synthesis of ZnO nanosheets. Later, it is subjected to various characterizations likes UV-Visible, XRD, FT-IR, AFM, SEM, EDS, TGA and DSC. Herein, we confirmed the presence of ZnO material from UV-Visible spectroscopy. Estimated average grain size is of about 38.10 nm by Scherrer's equation. FT-IR result confirmed the presence of functional groups like O-H, C-H and H-O-H bonds. EDS characterization shows the presence of Zn and O elements. The nanosheets like structure of ZnO was observed using AFM and SEM. Thermal behavior and decomposition of ZnO material were studied by the TGA and DSC analyses. From the obtained results we can signified that these synthesized ZnO can be useful in electronic devices and dye degradation. Further, we proposed to study these synthesized ZnO nanosheets in various biological activities.

Acknowledgments

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