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FULL PAPER

Facile Preparation of Novel Zinc Oxide Nano Sheets and Study of Its Optical Properties

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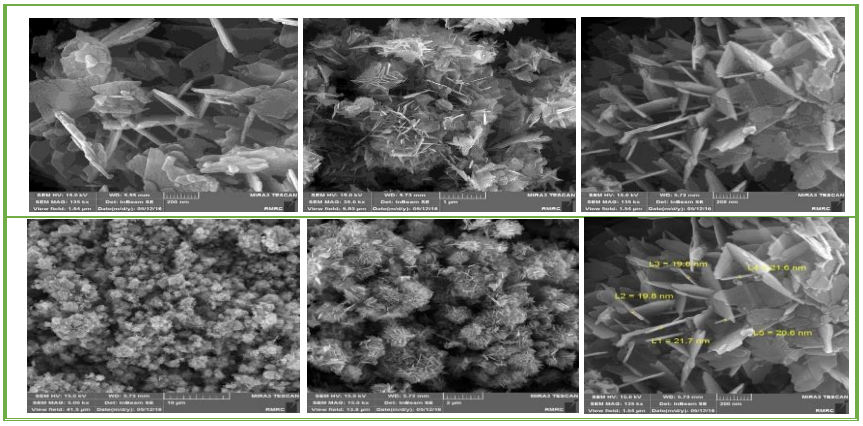
ABSTRACT: The zinc oxide nano sheets were prepared by zinc sulfate and sodium hydroxide via precipitated method and, then, calcinated at 300 ºC. In order to have a reliable characterization of the synthesized ZnO nanosheets, FTIR, XRD, FESEM, XRF, TGA and Raman techniques were applied. The phase and purity of zinc oxide nanosheets were confirmed by XRD and XRF, respectively. FESEM results showed the morphology of zinc oxide and revealed that the size of the prepared powder is in the range of nanometer. TGA analysis revealed that there are two endothermic reactions which have occurred at 35-200 ºC and 300 – 400 ºC temperatures. Optical spectra indicated that the band gap of the prepared nanosheets transmitted a red shift.

KEYWORDS: Zinc Oxide; Synthesis; Optical properties; Nano Sheet.

GRAPHICAL ABSTRACT:



1. Introduction

Recently, researchers have paid much attention to Zinc oxide nanoparticles due to their unique electronic, structural, and thermal properties. The mentioned nanoparticles have a wide variety of applications such as catalysis [1], UV absorber [2], sensors [3-4] etc. ZnO has a wide band gap (3.37 ev) at room temperature [5] and mostly been used as a potential photocatalyst[6]. Different methods are available to synthesis nano zinc oxide, such as sol–gel [7], co-precipitation

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[8], ultrasonic [9], hydrothermal [10], deposition [11, 12], and microwave [13] methods. Precipitation method is mostly applied in large scale productions due to its low cost, facile way and high yields [14-15]. Nano ZnO can be synthesized in a variety of morphologies; including nanowires, nanorods, tetrapods, nanobelts, nanoflowers and nanoparticles [14].The physical and chemical properties of nano zinc oxide is depended on the morphology of zinc oxide [6]. In this sense, in developing nanostructures of zinc oxide, a uniform distribution and controlling the morphology of final particles are very important [16]. As reported, different variables such as pH, rate of mixing, calcination temperature and reactants concentration are controlling the precipitation process [17].

The aim of this research is to synthesize nano ZnO sheet using precipitation method and to characterize its structure and optical properties by FTIR, XRD, FESEM, XRF, TGA, UV-Vis and Raman.

Materials and Methods

Materials

$ZnSO_4.7H_2O$ (M_w=287.58 g/mol) and NaOH (M_w = 40g/mol) were obtained from Merck company and used without further purification. All the solutions were prepared by distillated water.

Synthesis of ZnO nanosheets

89.90 gr of $ZnSO_4.7H_2O$ is dissolved in 250 ml of distillated water. 250 mL of NaOH 2.5 M is prepared and added drop-wise on the $ZnSO_4$.$7H_2O$ solution while vigorously stirring. After the reaction is completed, the solution was stirred on stirrer for further 12h. The obtained precipitate was separated from the solution using Buchner and dried in an oven at 100^oC. Then, it was calcinated in furnace at 300^oC. The gained powder is Zinc oxide nano sheets.

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Characterization

To characterize zinc oxide nano sheets, FTIR (Shimadzu model IRTracer-100), XRD (XRD, X'Pert Pro, Panalytical), XRF(model "ED2000" from "England Oxford"), Field emission scanning electron microscopy (FE-SEM, MIRA3, TESCAN), TGA (model "STA 1500" from "Rheometric Scientific"), UV–Vis spectrophotometer (model UV-2502 from "lab omed inc") and Zeta potential)model zeta sizer Ver 6.01 "Malvern Instruments Ltd") were used.

Results and Discussion

FTIR analysis is used to study the surface properties of synthesized zinc oxide nanosheets in the range of 4000 to 400 cm^{-1} . The results have been illustrated in Figure 1. The observed peaks at 3520 cm^{-1} and 1639 cm^{-1} are related to the stretching vibration of nonchemical bond association hydroxyl groups and H-O-H bonding vibrations, respectively. The adsorption peak at 2391 cm^{-1} is assigned to the presence of carbon dioxide. The peak at 1190 cm^{-1} is attributed to the bending vibration of C-H as the peak at 410 cm^{-1} is for Zn-O [1].

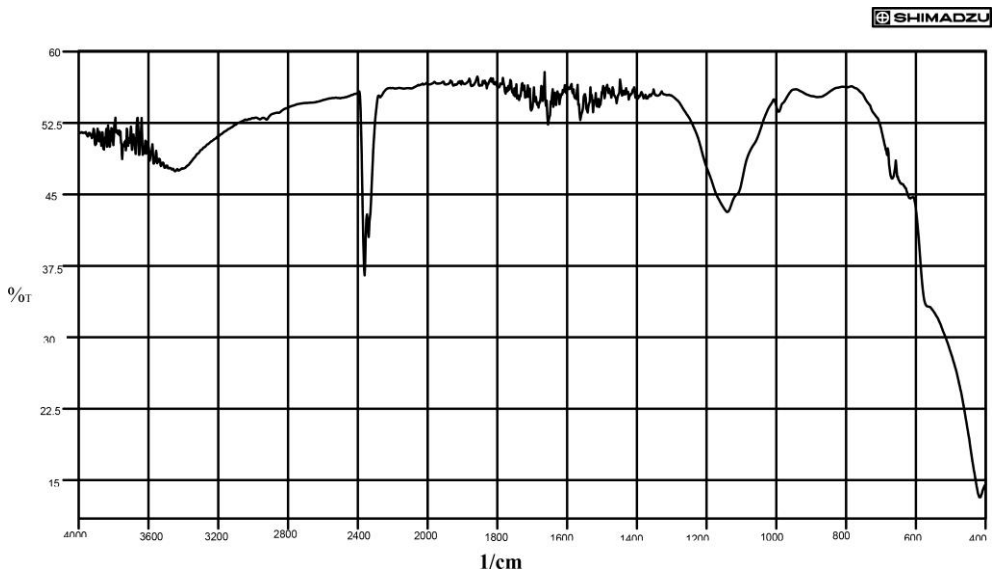

Fig. 1. FTIR spectrum of synthesized ZnO nanosheets

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XRD analysis was performed to identify the crystallinity of the calcinated ZnO nanosheets in 300 ºC . The results have been presented in Figure 2. As shown, the sharp peaks confirmed the high crystallinity of synthesized ZnO and diffraction peaks correspond to the hexagonal wurtzite ZnO[JCPDS 36-1451]. Diffraction peaks show that there are no impurity in the sample, and the synthesized ZnO is pure. The mean size of particles using Debye-scherrer equation (1) is obtained about 30 nm.

$$D = \frac{(0.89\lambda)}{\beta cos\theta} \qquad (1)$$

Where, D is size of the crystal (nm), λ is wavelength of used XRD, β is peak width in half height, and θ is the diffraction angle[18].

Moreover, the X-ray fluorescence assay indicated 96.93% of ZnO in the sample that confirmed the high purity of the synthesized sample.

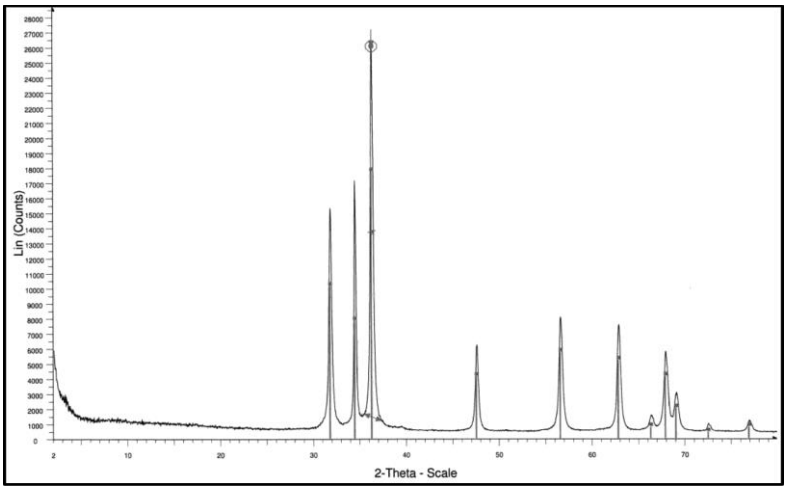

Fig. 2. XRD patteren of synthesized ZnO nanosheets.

In order to study the morphology of Synthesized ZnO nanosheets, some FESEM images were taken revealing the sheet-like shapes in the range of nanometer (Figure 3). As shown, the nano ZnO sheets are uniform as there is no agglomeration.

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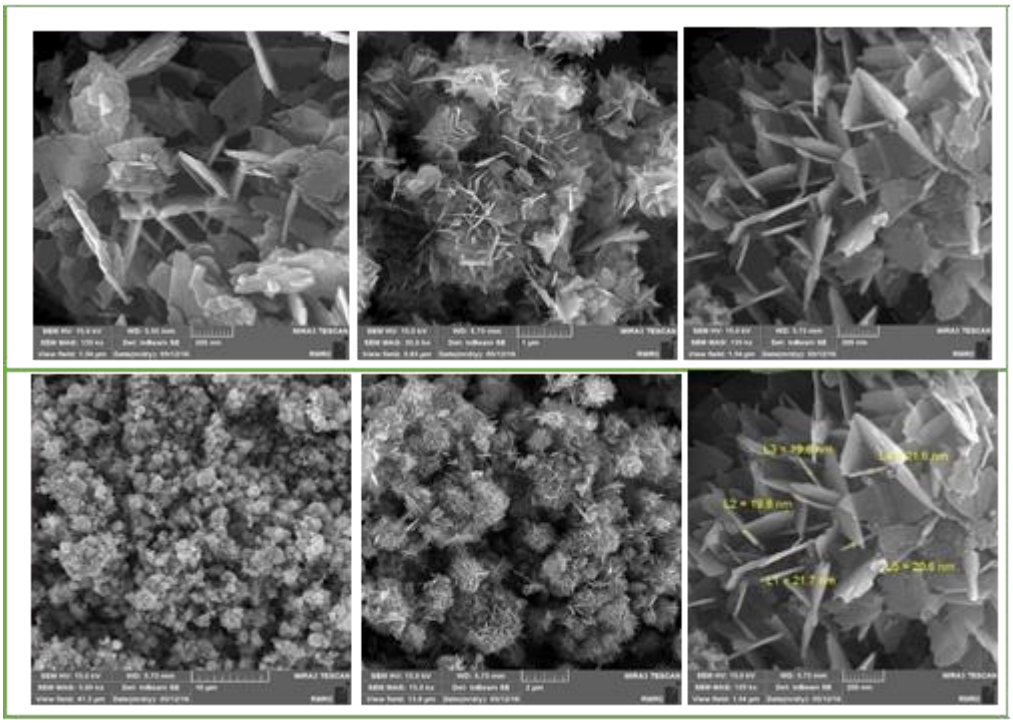

Fig. 3. FESEM images of synthesized ZnO nanosheets.

Thermo gravimetric analysis (TGA) is a test which can be applied to the synthesized materials in order to determine the weight loss at different temperatures. The TGA analysis of the synthesized nano ZnO sheet is shown in Figure 4 .

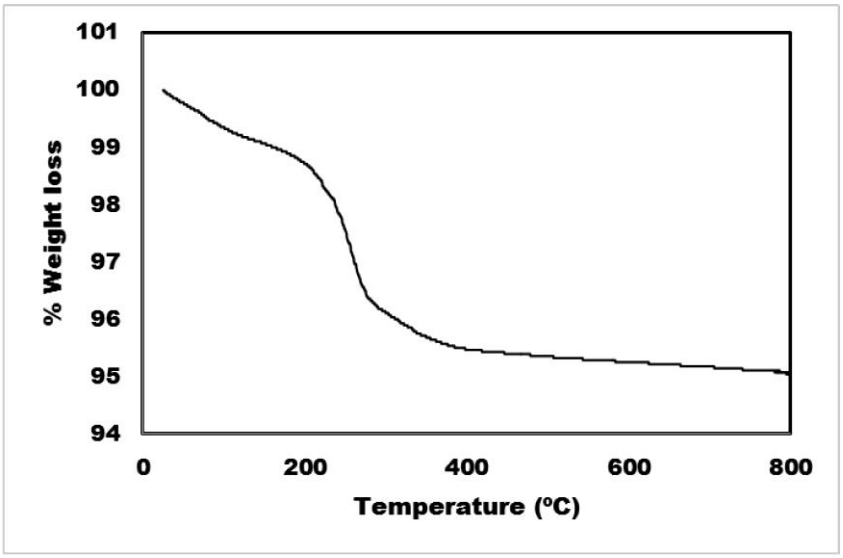

Fig. 4. TGA analysis of synthesized ZnO nanosheets.

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As it is clear, two weight loss regions are visible in 35-200^{o}C and 300-450^{o}C, respectively. The first step of weight loss is generally related to the evaporation of water adsorption and as a result 4% of weight loss is occurred. The next step of weight loss is related to evaporation and combustion of organic compounds which are in the sample in which 0.89% of weight has been lost. After 400^{o}C, there is no signal in the TGA analysis which proves the formation of crystal ZnO and phase-transmission of its phase.

In a colloid system, the potential difference between two stationary ionic and moving layers in ion atmosphere environment, is called zeta potential charge. Zeta potential is used for the determination of surface charge. High zeta potential of colloid particles increases the repulsive force of electrostatic and, therefore, increases the physical stability of the system. The zeta potential was measured using the Zetasizer Nano ZS (Malvern Instruments Ltd., GB) by analyzing 0.1 g the synthesized nano ZnO sheets in 10 mL of water. It is worth mentioning that before the beginning of our analysis the solution was sonicated for 10 min. Zetasizer Nano ZS uses Laser Doppler Velocimetry to determine electrophoretic mobility. The zeta potential was obtained from the electrophoretic mobility by the Smoluchowski equation. As a result, the zeta potential at pH=3.7 was obtained at about + 7.22 mV and diameter size was approximately 23 nm.

Raman spectra of the synthesized zinc oxide nano sheets is presented in Figure 5 with 532 nm laser light as an excitation source. It shows the E2 vibration at 453 cm-1[19], acoustic overtone with A1 symmetry at 628 cm-1[20] and the peaks at 993 and 1155 cm-1 correspond to ethanol [7].

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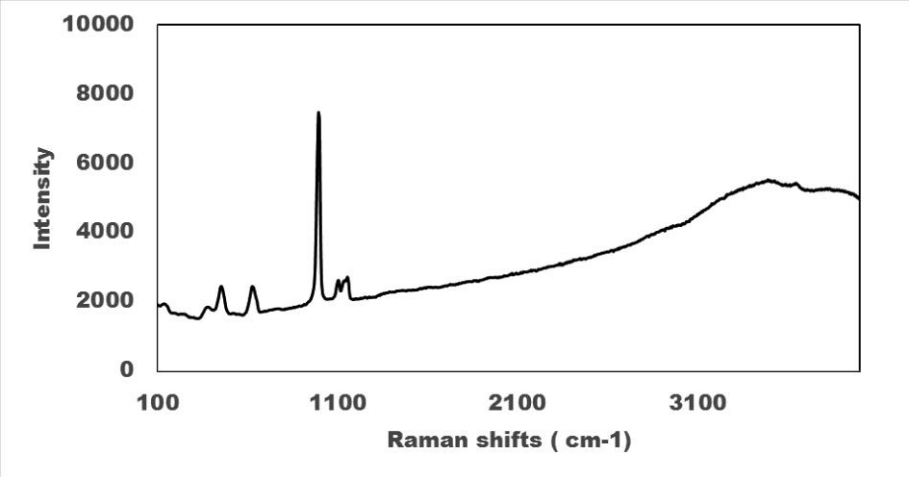

Fig.5. Raman Analysis of synthesized ZnO nanosheets.

Optical properties

The optical properties of the synthesized nano ZnO sheets is studied by UV-vis absorption spectrum (Figure 6a). According to the spectrum, the synthesized sample has a strong peak in lower than 400 nm (375 nm). The optical band gap Eg can be calculated from Eq. (2) and Tauc plot[21].

$$(\alpha h\upsilon)^2 = A\ (h\upsilon - E_g)^n \qquad (2)$$

Here, α is absorption coefficient, hν is photon energy, Eg is optical band gap, n is 1 for direct transition & A is a constant. The band gap energy is obtained by extrapolating the straight line portion of the plot to zero absorption coefficient. A single slope in the plot confirmed the direct and allowed transition. The band gap value of ZnO nanoparticles is found to be 1.67eV. This red shift of the band gap energy may be as a result of nano sheets morphology of synthesized ZnO.

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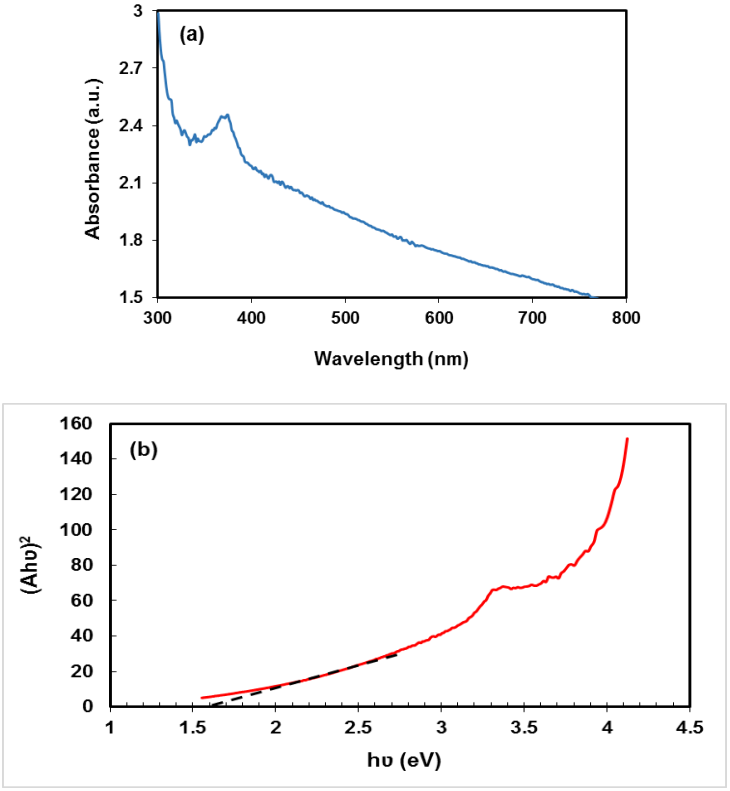

Fig. 6. UV–Vis (a) and DRS (b) spectra of synthesized nano ZnO sheets

Conclusion

ZnO nano sheets was synthesized via the simple precipitation method from NaOH and $ZnSO_4.7H_2O$. XRD, FTIR and TGA analysis indicating that the white obtained power is zinc oxide. The morphology and purity of ZnO nano sheets is confirmed by FESEM and XRF, respectively. Finally, a mean size of nano sheets was obtained at about 20 nm and the study of optical properties indicated the red shift of the band gap energy.

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