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Preparation and Characterization of ZnO Nano-Sheets Prepared by Different Depositing Methods

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Abstract

Hydrothermal technology has many advantages compared to other growth methods such as the availability of their simple equipment,catalyst-free growth,Environmental friendliness, less dangerous environmental, and low costs. Combine spinning method technology with Hydrothermal could improve the structural of ZnO NS by increasing the formation of ZnO NS due to influence of heat annealed treatments on the structure of ZnO NS. ZnONano-Sheets (NS)were prepared to employ hydrothermal process utilizing zinc acetate, that has the chemical composition (Zn $(CH_3CO_2)_{2.}2H_2O$),as a precursor. After preparing the material, it is deposited in two methods, the first being distillation of the material on the glass (S1),while the second method was using the spinning technique (S2).The spinning method showed better results than the other method.The synthesized ZnO NS were analyzed byscanning electron microscopy (SEM),X-ray diffraction (XRD) analysis and their optical properties have been characterized utilizingUV- absorption spectra.

Keywords: Hydrothermal; spinning coater; ZnO; Nanosheets; XRD

تحضير و توصيف صفائح اوكسيد الزنك النانوية المعدة بواسطة طرق مختلفة للترسيب

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الخلاصة

تتمتع تكنولوجيا الحرارية المائية (Hydrothermal) بالعديد من المزايا مقارنة بطرق النمو الأخرى مثل توافر معداتها البسيطة ، والنمو الخالي من المحفزات ، والملائمة البيئية ، والبيئة الأقل خطورة ، والتكاليف المنخفضة. يمكن أن يؤدي الجمع بين تقنية طريقة الغزل مع الحرارية المائية إلى تحسين بنية ZnO NS عن طريق زيادة تكوين ZnO NS بسبب تأثير المعالجات الملدنة بالحرارة على هيكل ZnO NS. تم تحضير

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(ZnONano−Sheets) بتوظيف عملية الحرارية المائية باستخدام أسيتات الزنك التي تحتوي على تركيبة كيميائية (Zn (CH3CO2) 2.2H2O) كمادة اولية ، بعد تحضير المادة تم ترسيبها بطريقتين ، الأولى تقطير المادة على الزجاج ، بينما الطريقة الثانية كانت باستخدام تقنية الغزل ، وأظهرت طريقة الغزل نتائج أفضل من الطريقة الأخرى ، حيث تم تحليل ZnO NS المركب عن طريق استخدام المجهر الإلكتروني (SEM) ، وتحليل حيود الأشعة السينية (XRD) وتم تمييز خصائصها الضوئية باستخدام الأشعة فوق البنفسجية. – أطياف الامتصاص.

I. Introduction

Recently, the application of zinc oxide(ZnO) has increased significantly because of its special properties .ZnO nanoparticles exhibit unique properties such as large surface relative to total volume,biocompatibility,nontoxicity,chemical and photochemicalstability, electrochemical activity, optical transparency, high electron communication features, optical, biologicaland electrical, long-term environmental stability [1-4]. ZnO nanostructure has been widely used in areas as varied as tissue, organic coatingsor antibacterial activity due to the non-toxic nature of zinc oxide and its ability to block ultraviolet rays [6], in addition to its use in other fields. ZnO is considered an n-type semiconductor of hexagonal wurtzite structure that has optical sensitiveness at the range of visible rays [7].

ZnO nanoparticles can be applied in different fields such as thin film transistors, field-emission displays, chemical gas sensors, piezoelectric devices, UV photodiodes, surface acoustic wave (SAW) devices, UV-shielding materials, medical and dental, pigments and coatings and other uses [7,8,11,12]. Among all these forms, the ID nanostructure (nanotubes (NTs) andnanorods (NRs)) of zinc oxide have been studied significantly, due to its ease of manufacturing and multiple applications [10].At room temperature, ZnO has a wide energy gap of a value of 3.37eV[11]. It also has a strong emission in the UV radiation range even at room temperature because its bonding energy is greater than 60 MV that is much larger than other materials [12]. The Zinc oxide with nano-structure has different morphological forms, such as nanoparticles,nanobridges, nanowalls, nanohelixes, mesoporous single-crystal nanowires,nanobelts, nanorods, nanotubes, nanosheets, nanowires and polyhedral cages [13].

Several methods of manufacturing zinc oxide were invented and used such as thermal decomposition [14],vapor transport process [15], hydrothermal synthesis [5,17,16], spray pyrolysis [18] and the processing of sol-gel [19]. But some of these techniques, in order to gain the final structure, usually require multiple steps, high temperature, and advanced equipment.

On the other hand, hydrolysis, hydrothermal process and sedimentation preparation methods are low-cost, easy-to-use and scalable methods and have been applied to prepare various structure of ZnONPs [20, 5]. The Hydrothermal process is a hopeful alternative synthetic method for manufacturing nanomaterials, this is due to the low temperature of the process and the easy way by which to control particle size. Hydrothermal method can be defined as any heterogeneous reaction with solvents or water minerals under high temperature and pressure conditions to dissolve and relatively insoluble materials under normal conditions [5, 21].

In this research,ZnO nanoparticles were prepared using the hydrothermal method. Then ZnO nanoparticles were analyzed by using XRD, SEM and UV-Vis spectroscopy.

II. Experimental

2.1. *Materials*

Zinc acetate (from Beijing Yili Fine Chemical Co., Ltd, China)withthe chemical formula (Zn $(CH_3CO_2)_2.2H_2O$) 6H2O) with a purity of 99.5% was used as the source of Zn^{2+}.Glass slides of 1 mm thickness were used to precipitate the resulting material.

2.2. Procedure of experimental

To prepare ZnOnano-sheets(NS), 0.5 g zinc acetate was mixed with 100 ml distilled water with stirring for 30minutes(without heating) to obtain a homogenous solution. Then the

solution was placed in a special hydrothermal vial and inserted in an oven for three hours at a temperature of 200 ° C (Autoclave). The solution was then pooled by centrifugation, and ZnO NS were examined using ultraviolet (absorption) analysis. After preparing the material by the hydrothermal method, the material was deposited in two ways, the first is by distillation of the material on glass subtrates, and the second method was by spinning technique. Three samples prepared by the hydrothermal method were deposited on glass substrates, dried in an oven at 90 ° C for 15 minutes . The other three samples were deposited by spinning method after being prepared by the hydrothermal process to obtain thin films of ZnO (NS) as listed in Table 1.

Table 1-ZnO NS precipitation by the spinning method

sample	$t_{1\ (sec)}$	sp_1(r/min)	$t_{2\ (sec)}$	sp_2 (r/min)
1	30	2000	60	3000
2	20	1000	30	2000
3	10	1000	20	1000

III. Results and Discussion

3.1 UV-Vis Spectroscopy

ZnO NS samples were examined using UV-Visspectroscopy. The UV-Vis absorption spectrum ofa ZnO NS can describe the absorption edges related to the structure of the semiconductor band. Figure 1 shows a comparison between two samples prepared by the distillation method and by the spinning method.The peaks of the spectra show the change in the structure of the material, the crystal size of the zinc oxide nanoparticles as well as the effect of the sedimentation method on the formation of the resulting material.In addition, energy levels change due to the transformation of a non-crystallinematerial to a nano-sized crystal.

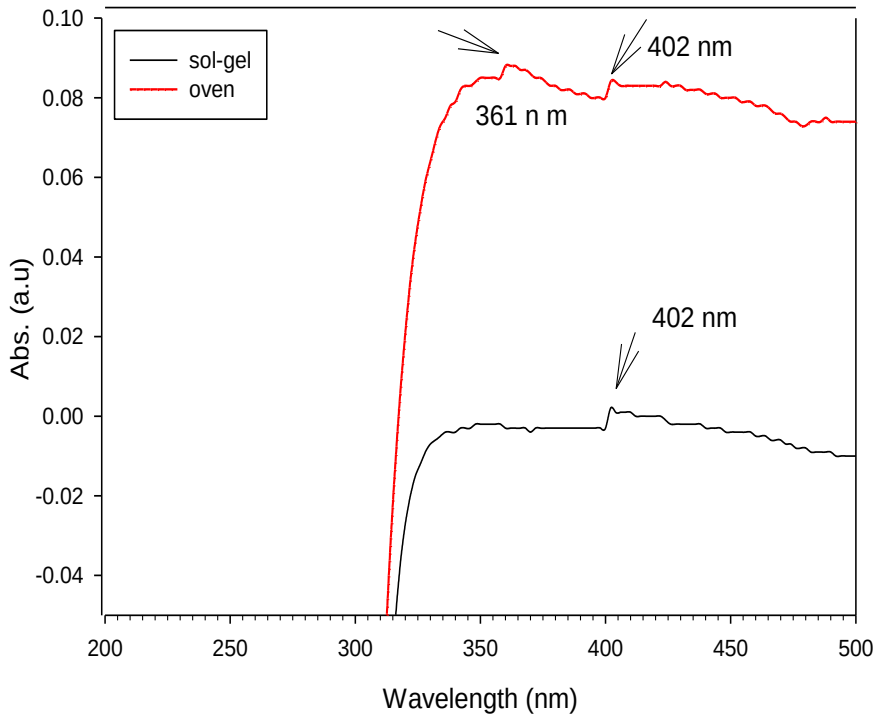

Figure 1-The UV-Vis absorption spectra of ZnO nanoparticles for the two different preparation methods

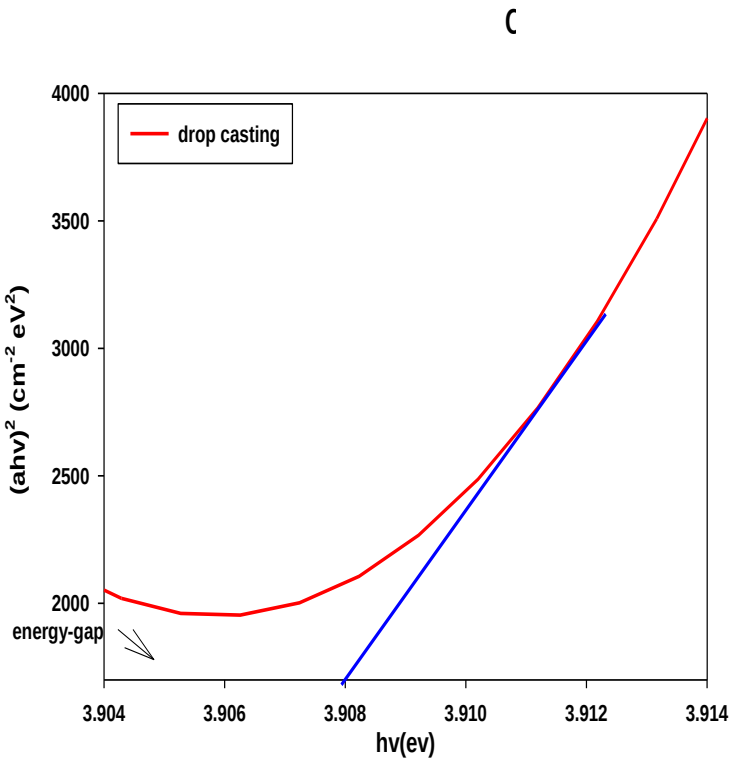

Figure 2-bandgap energy of ZnO nanoparticles for the sample wasdeposited by the drop casting method.

From the UV-Vis reflectance spectrum for ZnO nanoparticles, the bandgap energy was calculated usingTauc relationship. The effect of the UV reflection spectrum on scattering is less than that of the absorption spectrum. This sudden drop in the reflection of radiation at a specific wavelength, corresponding to the optical bandgap, means that the molecules are distributed almost uniformly in the sample. The direct bandgap energy (E_g) for the ZnO nanoparticles is calculated by fitting the reflection data to the direct transition equation $\alpha h\nu = E_D (h\nu - E_g)$ ½, where α is the optical absorption coefficient, $h\nu$ is the photon energy, E_D is a constant and Eg is the direct bandgap. $(\alpha h\nu)^2$was plotted as a function of$h\nu$ for theZnO nanoparticles of the sample processed by the oven (Figure 2).The intercept of the line tangent of the curve with the$h\nu$ axis determines the energy gap. From the figure , the energy gap is observed to be at 3.90 eV. Figure 3 illustrates the plot of $(\alpha h\nu)^2$against $h\nu$ for the samples prepared using spinning technology, from which the bandgap energyvalue is observed to be equal to 3.755 eV.The difference in the values of the energy gap of the two methods used in the deposition of the material is due to the difference in the sizes of the nanoparticles (zinc oxide) from the two methods .

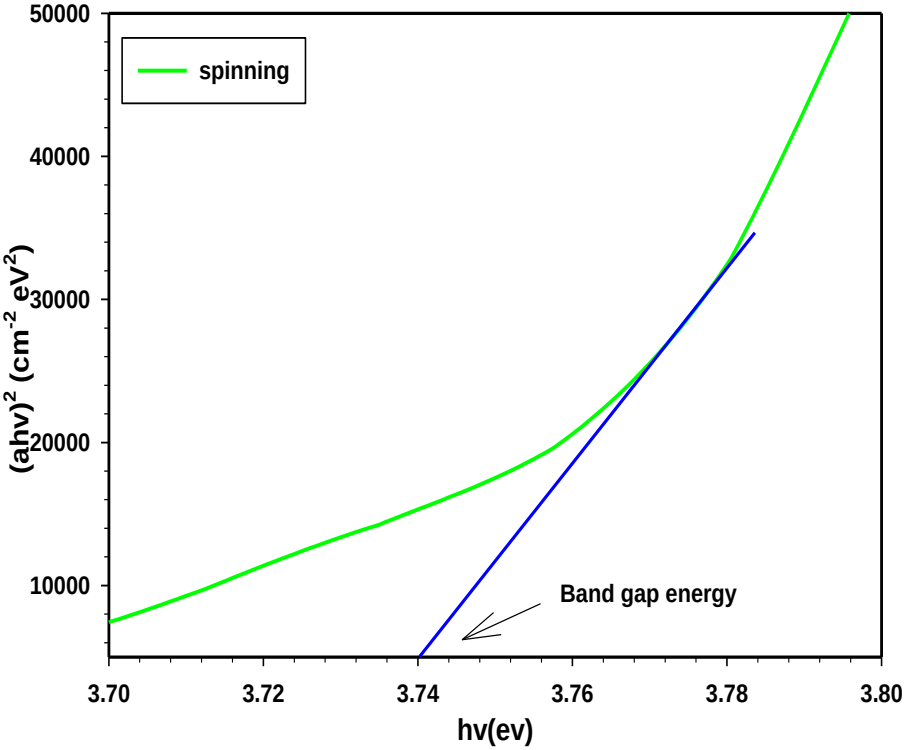

Figure 3-bandgap energy of ZnONS fabricated by spinning technology.

3. 2X-ray diffraction (XRD) analysis

ZnOwas examined using XRD to study its properties and determine particles formation. Using this analysis, it is possible to observe the formation of nanocrystalline zinc oxide and the change of the material from amorphous to crystalline. Figure 4 shows the XRD pattern of the sample which was prepared using the hydrothermal method and then processed using a convection oven, where the prominent peaks clearly indicates the formation of nanoparticles. Figure 5 shows the XRD pattern of the sample processed by the spinning method after preparation with hydrothermal technology. Two broad peaks can be observed referring to the formation of the nanostructure.This pattern shows that the crystal structure is hexagonal. The peaks are wide; it means that particles are smaller in size. The average crystalline size of ZnOnanosheets was determined by Debye-Scherrer equation:

$D = \frac{K\lambda}{\beta \cos\theta}$ ... ... (Debye-Scherrer equation).

Where: D is the crystallite size, K is a dimensionless shape factor, λ is the wavelength of X-ray, β is the width at half maximum(FWHM)of the intense peak and θ is the angle of diffraction. The average crystallite sizes of ZnONS was found to be (22.05, 22.46) nm for S1 and S2, respectively.From this, it appears that the method of precipitation using spinning is better than the method using distillation.

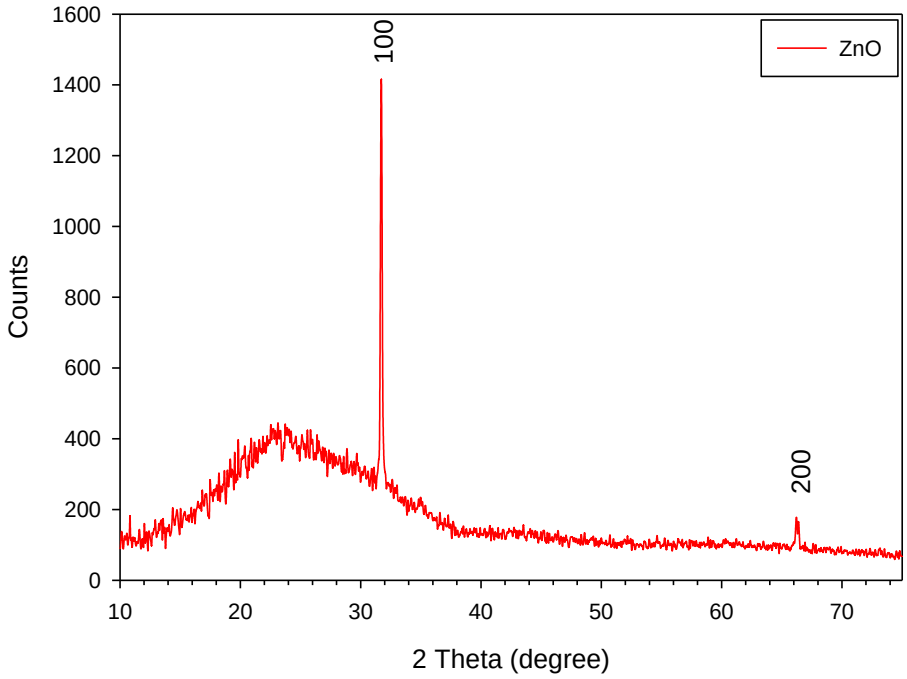

Figure 4-XRD pattern of a sample was prepared using the hydrothermal method and then processed using a convection oven

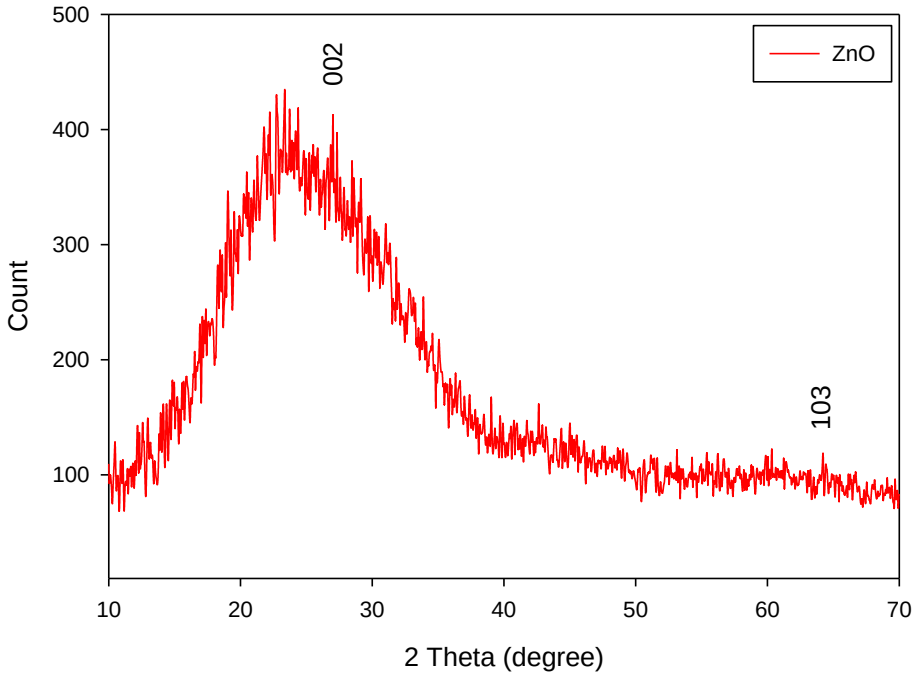

Figure 5-XRD pattern of a sample processed by the spinning method during its preparation.

3.3SEM analysis

Figure 6 represents the SEM images of the sample prepared by the hydrothermal method and annealed by heat treatment(S1). The formation of ZnO can be seen in the form ofnanosheets. The thickness of the nanosheets ranges between (21.70 and 29.34) nm, an average of 26.10

nm. Figure 7 shows the SEM images of the samples prepared using hydrothermal technology processed by the spinning method(S2). The nanosheets can be clearly observed with athickness ranging from 17.10 to 24.51 nm, as shown on the figure, an average of 21.77 nm. The sample thickness (S2) of ZnO NS in the Figure 7 is smaller than that of (S1) in Figure 6

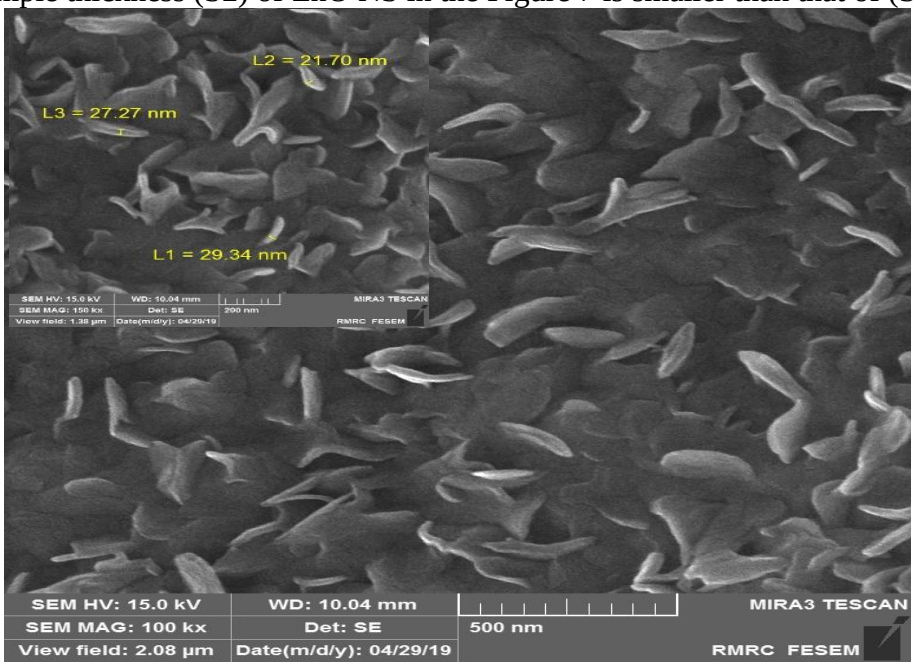

Figure 6-SEM images for the sample prepared by the hydrothermal method and annealed by heat treatment.

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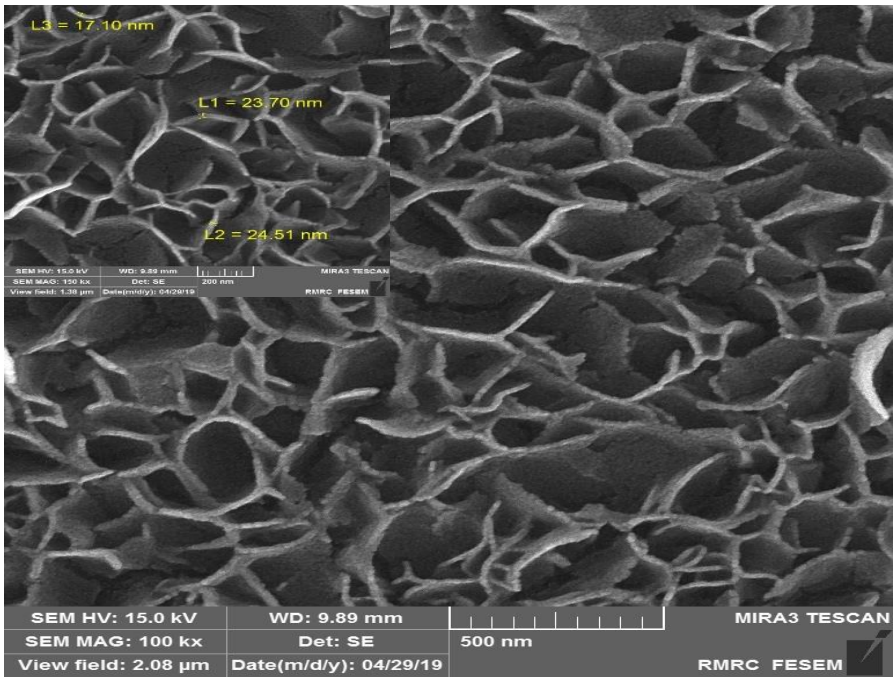

Figure 7-SEM images of the samples prepared using hydrothermal technology processed by the spinning method.

EDX analysis

EDX spectrumof ZnOshown in Figure 8,for the sample prepared using the hydrothermal method and annealed by heat treatment,shows four peaks which were identified as zinc (66%) and oxygen (32%) while ,the EDX spectrum(Figure 9), for the sample of zinc oxide prepared by hydrothermal method and using spinning method, shows four peaks which are identified as zinc (28%) and oxygen (60%). The increase of the formation of ZnO NS is due to the influence of heat annealing onthe structure of ZnO NS.

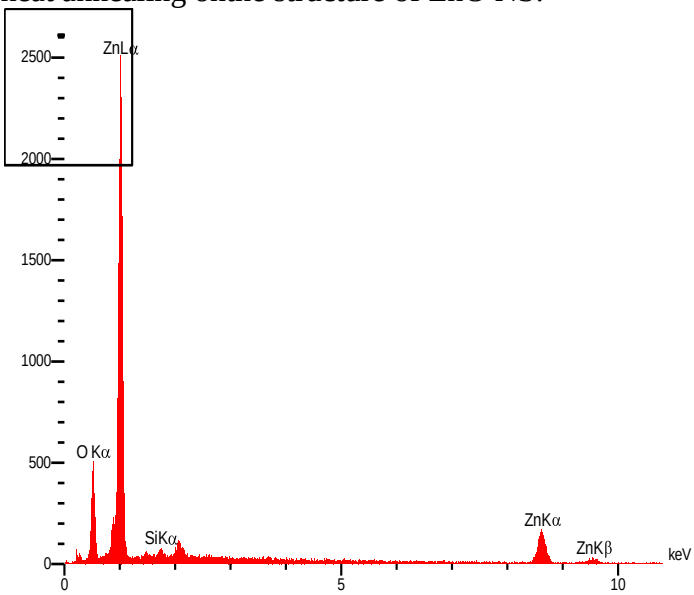

Figure 8- EDX Spectrum of ZnO nanoparticles for a sample of zinc oxideprepared using the hydrothermal method and annealed by heat treatment.

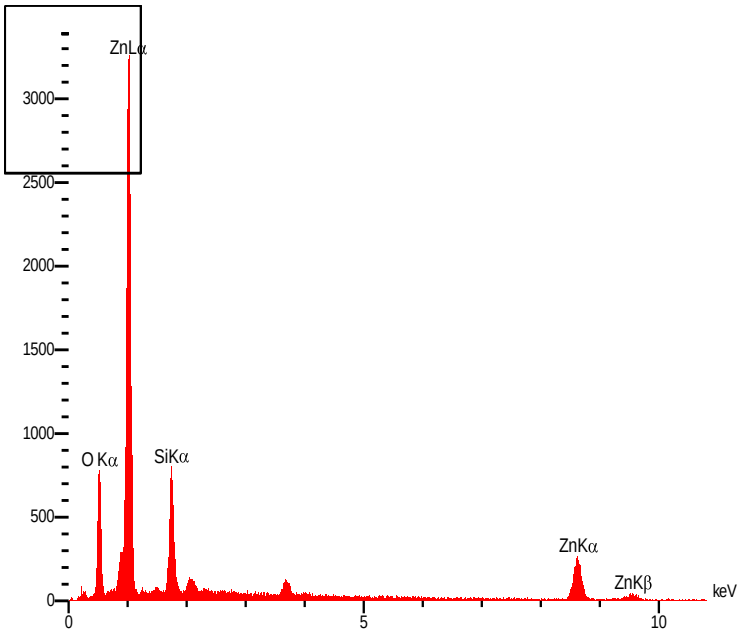

Figure 9-EDX Spectrum of ZnO nanoparticles for a sample of ZnO prepared using the hydrothermal methodand deposited by the spinning method.

Conclusion

ZnO NS has an average thickness of 26.10 nm for the sample was prepared by hydrothermal method and then deposited by the drop casting method (S1) with a temperature of 200 ° C while it was 21.77 nm for the sample was prepared by hydrothermal method and then by

spinning method at a temperature of 200 C on a glass substrate (S2). From the UV -visible spectroscopy, the effect of the deposition method on the absorbance can be seen. This analysis showed that theenergy gap values were recorded at 3.90 eV and 3.755 eV for both S1 and S2, respectively.

The XRD analysis confirmed that the material is crystallized, depending on the peaks in the analysis and the size of the nanoparticle calculated from this test . The average crystallite size of ZnO NPS was recorded to be (22.05, 22.46) nm for S1 and S2, respectively. The SEM analysis showed that the structure of the material was in the form of nanosheets and it shows the size and shape of the crystal. From the results, it is evident that the deposition method using spinning is better than the drop casting method (distillation)

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