Chapter

Study of Optical and Structural Properties of ZnS/rGO Nano Composites Prepared by Laser Ablation

Mohammed J. Jader and Wasan H. Jawad

Abstract

Through the physical process of laser ablation, zinc sulfide (ZnS/rGO) nanoparticles were created. From there, it was possible to estimate the crystal structure and crystallite size of X-ray diffraction (XRD) particles (D = 8.35 nm). The visible ultraviolet absorption spectrum has also been used to study optical characteristics. The Neodymium-Yak laser (1064 nm) with the pulsed laser energy of 800 mJ and 600 pulse at a frequency of 6 Hz in room temperature was used to form the Graphen Oxide as a Nano composite after it had been prepared by the hummer method and combined with zinc sulfide. This resulted in the generation of plasma that contributed to the formation of Nanoparticles. To determine the components of the material, several measurements were done on it, including FTIR, SEM, XRD and EDAX for samples. In this chapter, ZnS/rGO nanoparticles were prepared by laser ablation method as well as by hydrothermal chemical method, and optical and structural examinations for both were found. Hence, the laser ablation method proved to be highly efficient compared to the chemical method in terms of knowing the Nano scale sizes and the different energy gaps, which helps in finding multiple future applications for them.

Keywords: nano composite, ZnS nano materials, laser ablation, Zns/rGO, nano particles

1. Introduction

A variety of bottom-up production techniques for nanoparticles have been created for both the liquid (such as sol-gel and chemical reduction) and vapor phases (such as physical/chemical vapor deposition and flame synthesis). Each fabrication technique has benefits and drawbacks. For the purpose of creating different types of nanoparticles with precisely regulated structures on a laboratory scale, liquid phase technologies are efficient and utilised. By using a continuous flow reactor,

vapor phase techniques are superior at creating high purity nanoparticles. Solid nanoparticles are produced by the nucleation of supersaturated species that are created by precursor reactions and/or the evaporation of solids in both the liquid and gas bottom-up processes. According to Buzea et al. [1], nanoparticles exhibit some distinctive qualities that are not seen in bulk materials. According to Kim et al. [2], the most important property of nanoparticles is that it greatly depends on the size and size distribution of the particles in order to have specific properties (electrical, optical, magnetic, etc.).

This chapter will present Preparation of graphene oxide (GO) and ZnS disc with using laser ablation method, the results of the optical examinations obtained through the UV-Vis spectrometer and the synthetic through XRD devices (FTIR, SEM, EDX) of the ZnS/rGO nanocomposite prepared by the laser ablation method. Liquid phase pulse (PL-AL) and (hydrothermal) method are discussed.

2. Preparation of graphene oxide (GO)

Graphene oxide was prepared using the Hummer modified method, which is considered one of the most common methods in the production of large quantities of graphene oxide (1 g) of pure and fine graphite powder was added and (120 ml) of concentrated sulfuric acid H_2SO_4, and (13.3 ml) of graphene oxide. H_3PO_4 phosphoric acid, and stir the mixture using a magnetic stirrer. Then (6 g) of $KMnO_4$ potassium permanganate was gradually added to the mixture, and the mixture was stirred at a temperature of (50°C) for (12) hours. Hours, we notice the color change of the mixture to a dark brown color, and after 10 h it changes to a light brown color, and after completing (12) hours, (4 ml) of hydrogen peroxide H_2O_2 was added slowly in an ice bath, we notice the color change of the mixture from the color Light brown to yellow, then the ice bath was removed, the color of the mixture changed indicating the formation of graphene oxide (GO), then the graphene oxide was separated using a centrifuge at 8000 rpm for 15 min, where it was washed for the first time using (30%) of acid HCL (2–3 times), then it was washed with (5%) of acid HCL (2–3 times) also, then distilled water was used repeatedly (8–10 times) until the number becomes The pH of the solution is neutral 6–7), then it was washed twice with ethanol, then washing with (40 ml) of ether and only once, after that The resulting suspension was filtered using filter paper and dried at room temperature in order to obtain graphene oxide (GO) powder.

3. Preparation of the ZnS/rGO nanocomposite

ZnS/rGO was prepared by two methods, physical (pulsed laser ablation) and chemical (hydrothermal).

3.1 Preparation of (GO) solution

Graphene oxide (GO) powder (70 mg), prepared in the aforementioned manner in paragraph and weighed and dissolved in (70 ml) of distilled water, and in order to obtain a homogeneous solution, it was placed in an ultrasonic device for (30 min).

Figure 1.
Pressure system is used in this work.

3.2 ZnS tablet preparation

Zinc sulfide (ZnS) powder was used after being pressed into tablets of a certain thickness, whereby (4 g) of the powder was weighed per tablet, then the powder was placed inside a stainless steel cylinder after cleaning it with ethanol, it was pressed using a compressive strength tester Type JB/T3818-1999), shown in **Figure 1**, with compressive strength (2 MPa).

4. Results and dissection

4.1 UV-visible absorption spectra measurements

The absorption spectrum of ultraviolet-visible (UV-Vi) rays was studied for graphene oxide, prepared by the modified Humer method and mentioned in paragraph (3). **Figure 2** shows the stages of formation of graphene oxide (GO). **Figure 2** shows

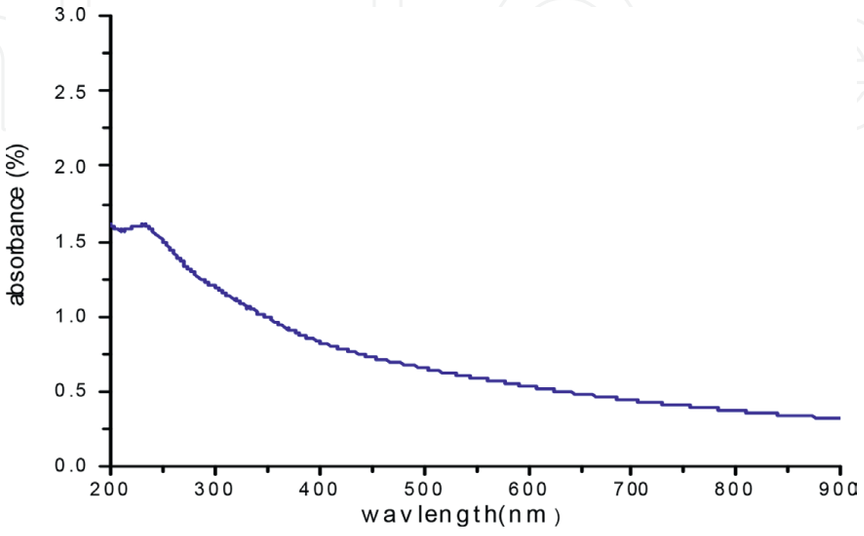

Figure 2.
Shows the UV-Vis absorption spectrum of graphene oxide.

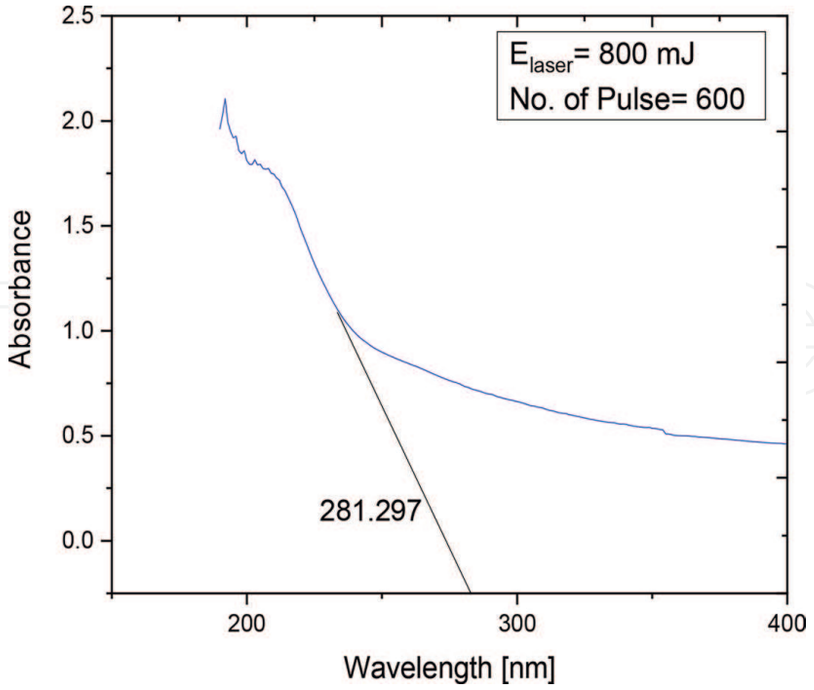

Figure 3.
Shows the Absorption Spectrum of sample (A).

the absorption spectrum of the aqueous solution of graphene oxide (GO), where it found an absorption peak due to GO at (230 nm) due to the electronic transition (π-π^*), as a result of the presence of the (C-C) bond [3].

Also, the absorption spectra of ZnS/rGO prepared by the hydrothermal and pulsed laser ablation method were analyzed using a Nd-YAG laser (wavelength 1064 nm, frequency 6 Hz, and pulse width 10 ns) for two samples only, the first sample (A) was prepared By the method of pulsed laser ablation, with a capacity of (800 mJ) and the number of pulses (600 pulse), while the second sample (B) was prepared by the hydrothermal method. **Figures 3** and **4** show the absorption spectra of the prepared samples, and through the results for sample (A), the highest value of the adsorption of the mixed compound was determined at a peak of 281.497 nm, and this indicates the occurrence of transitions of carbon bonds (C-C). By studying on zinc sulfide, it has the highest absorption at 336 nm wavelength in most of the experiments, as well as for graphene oxide, it has the highest absorption at 230 nm [3].

In this work, it was found that the highest absorption of the mixture was at the wavelength of 281.497 nm, which indicates that there are spectral transitions that occurred between the π-π^* transitions in the carbon (C-C) bond. The energy gap of the mixture was calculated using the method [4]. The Touc plot was about 4.942 eV, as shown in **Figure 5**.

Where the energy gap in most of the studies was 3.8 eV, as well as the wide band-gap 3.5 eV (3.8 eV), as well as zinc sulfide nanoparticles (ZnS-NPs) have recently received heightened thinking regarding their use in many applications [5].

The results for sample (A) indicate a shift blue spectral shift and this is consistent with the theoretical study indicating an increase in the energy gap of the synthesized ZnS nanoparticles as well as a slight amplification in the nanoparticles [6]. As for the results of the sample (B), the highest value of the adsorption of the compound was determined at a peak of 518.023 nm, and this indicates that transitions of carbon

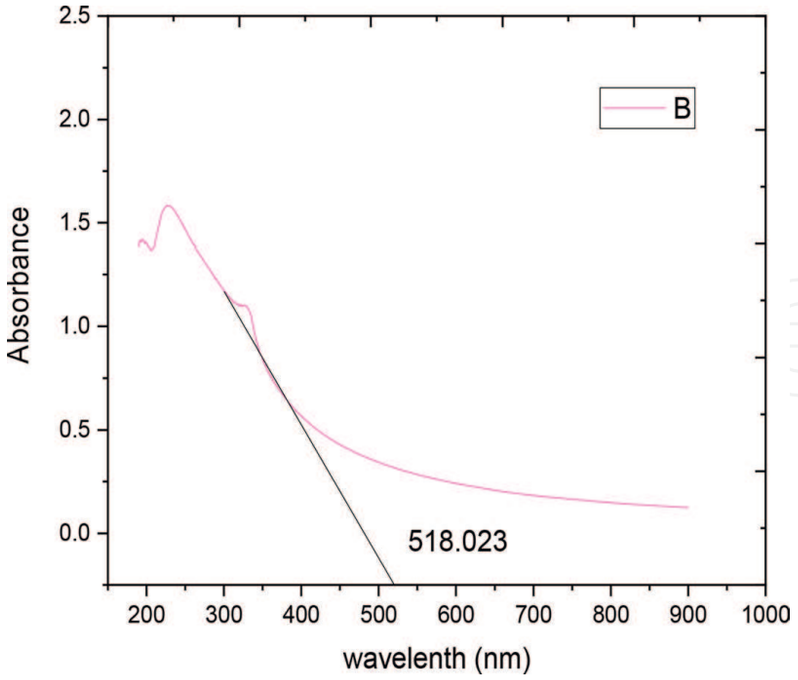

Figure 4.
Shows the Absorption Spectrum of sample (B).

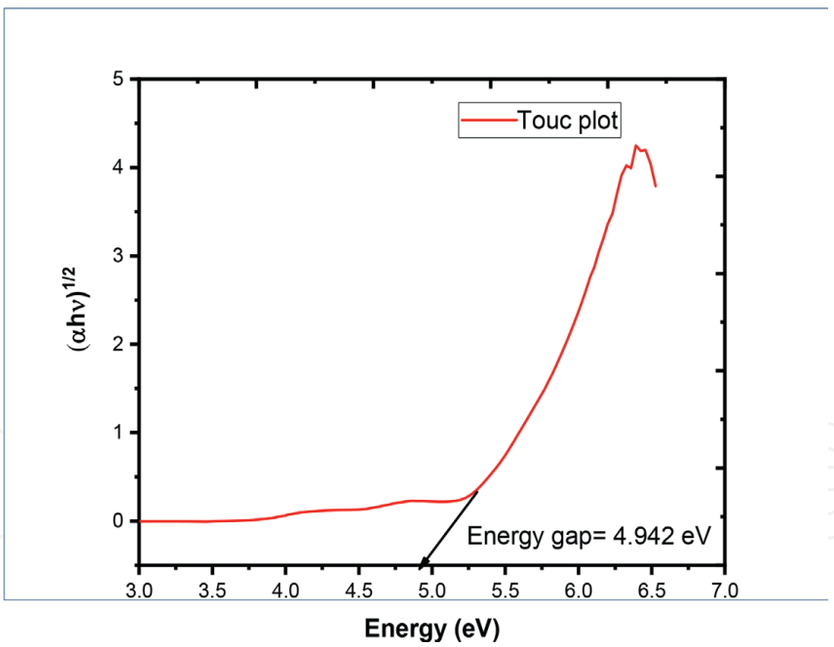

Figure 5.
Shows the energy gap of the sample (A).

(C-C) bonds also occurred. In this study, it was discovered that the mixture's peak absorption occurred at wavelength (281.297) nm, indicating that there were spectral transitions that took place in between transitions (-* in the C-C bond). In addition, the mixture's energy gap was determined using the Touc plot method and was approximately (2.983 eV), as shown in **Figure 6**. It is evident from the sample (B) results that there is a red shift, which results in a reduction in the energy gap of ZnS material.

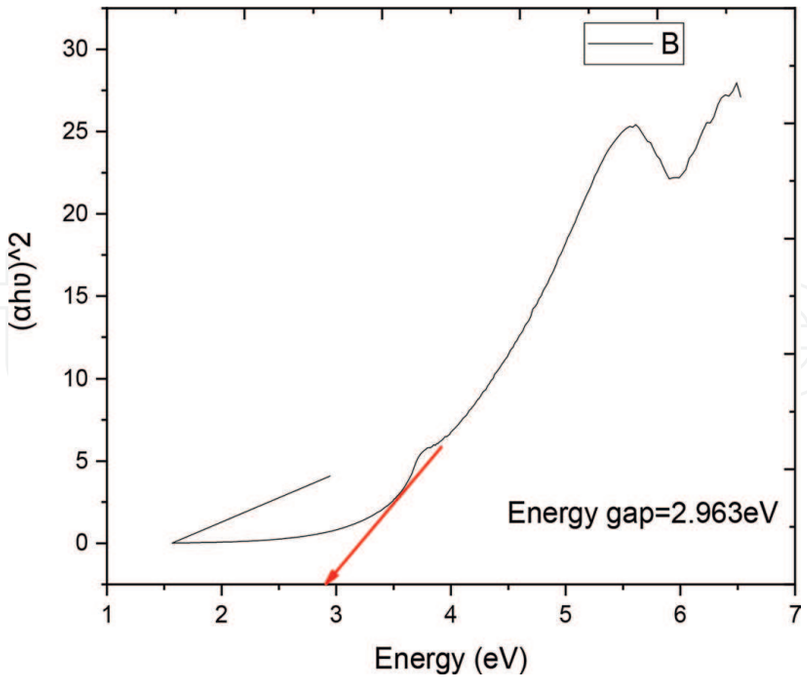

Figure 6.
Shows the energy gap of sample (B).

4.2 Results of X-ray diffraction (XRD) measurements

4.2.1 Results of X-Ray diffraction measurements

Using the X-ray diffraction spectrum for the purpose of studying the crystal structure of the samples prepared by the physical and chemical method. **Figure 7** shows the X-ray diffraction spectrum of the sample (A), where the (XRD) spectrum showed

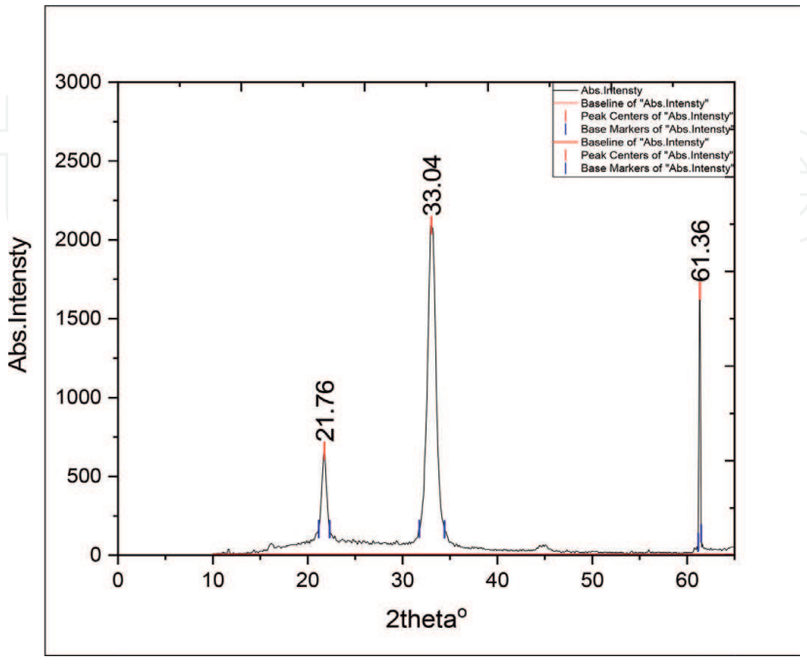

Figure 7.
Shows the (XRD) spectrum of the ZnS/rGo Nano composite prepared by the physical method.

a crystalline band at 2θ = 21.76°, 33.04°, 61.36°, The grain size was calculated using Scherer's equation after converting the angles from degrees to radians in addition to the values of the vertices.

The crystal size was calculated, and the results showed that the lowest value of the particle size was at the peak of 33.04°, and the diameter was about 8.359 nm, and this occurs due to the phenomenon of quantum confinement. Also, the average crystalline size of the particles was calculated and was about 25,233 nm, as shown in **Table 1**.

The X-ray diffraction spectrum of the sample (B), where the (XRD) spectrum showed a crystalline band at 2θ=(21.76, 33.04, 61.36) and the grain size was calculated using Scherrer equation after converting angles from degree scale to Radians plus vertices values.

Calculations of the crystal's size revealed that the lowest particle size value—33.04—was found at the peak, and the diameter—approximately 8.3596 (nm), which is caused by the phenomenon of quantum confinement. Additionally, the average particle size was determined to be around (25.23373) nm.

4.3 Results of Fourier Transform Infrared (FTIR) measurements

The FTIR spectrum was studied to determine the functional groups present in each of the two samples prepared by physical and chemical methods, They often interact with water layers and create a collection of chemical interactions. The FTIR spectra of ZnS/rGO for sample (A) is depicted in **Figure 8**. Experiments revealed that the peaks seen between 1636.01 and 3329.17 cm^{-1} are caused by the bending vibrations of adsorbed water molecules and the stretching vibrations of straight hydroxyl groups. Alkoxy and epoxy groups can also be found in the combination. The planar C=C band and the aromatic group vibrations in rGO [7] are what cause the peak to appear at 1636.01 cm^{-1}. However, they were marginally displaced to the lower frequency for ZnS-rGO at the mixed Nano composite [8].

Figure 9 shows the FTIR spectrum of ZnS/rGO for sample (B), through experimentation, it was shown that the peaks seen between 1636.12 and 3280.13 cm^{-1} are caused, respectively, by the stretching vibrations of the hydroxyl groups and the bending vibrations of the adsorbed water molecules. Alkoxy and epoxy groups are also present in the combination in the sample. The planar (C=C) band and the vibrations of the aromatic groups in rGO are responsible for the resultant peak at 1636.12 cm^{-1}. Notably, with the exception of being slightly displaced to the lower frequency, all of the aforementioned peaks were at ZnS-rGO (mixed Nano composite). This is explained by the chemicals' interaction with rGO and ZnS. In order to explain the absorptions at 559.81 and 408.54 cm^{-1}, the stretching of the vibrations of the ZnS bonds.

No.	Intensity	2 theta°	FWHM	Peak center	Crystallite size (D) nm	D Average (nm)
1	446.58	22.3	0.66757	21.76	12.11814	25.23373
2	2396.34	34.42	0.99123	33.04	8.359659	
3	292.11	61.48	0.16727	61.36	55.2234	

Table 1.
Shows the data of the XRD spectra of a compound for the sample (A).

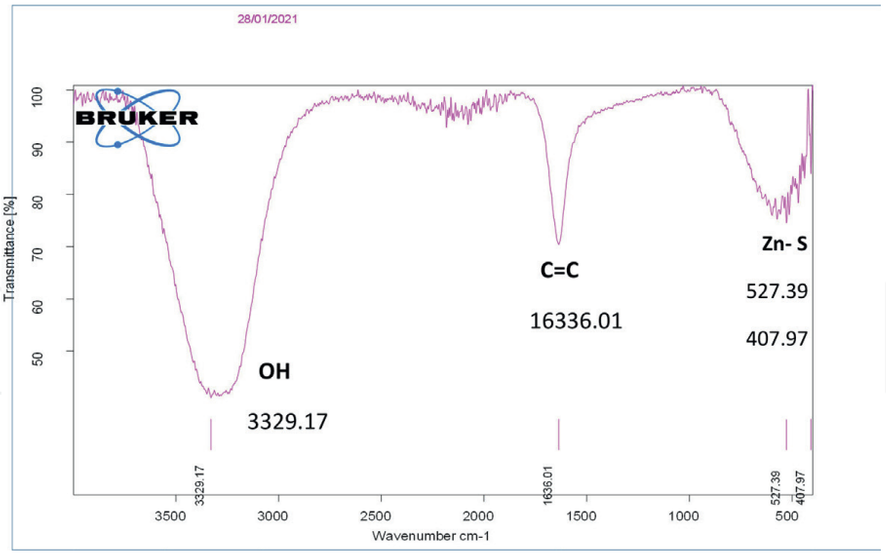

Figure 8.
Shows the FTIR spectrum of the sample (A).

4.4 Results of SEM and EDX scanning electron microscopy measurements SEM and EDXS analyses

Using a SEM device to identify the morphological characteristics of the prepared ZnS/rGO Nano composite samples, and by studying part of one of the images of the sample (A) at 200 nm in **Figure 9**, the results showed the formation of nanoparticles with different dimensions and measurements of their diameters, which were about 54 nm, in addition to the presence of particles with diameters Less, and this formation is due to the occurrence of quantum confinement phenomenon. Results of SEM measurements for samples (A,B) with distribution function of particles is given by **Figures 10-14**.

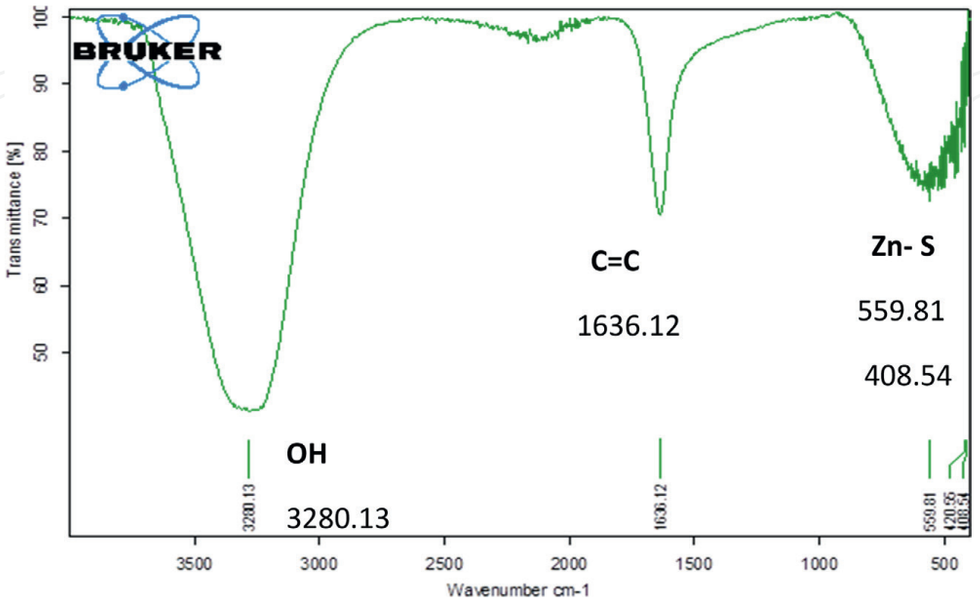

Figure 9.
Shows the FTIR spectrum of the sample (B).

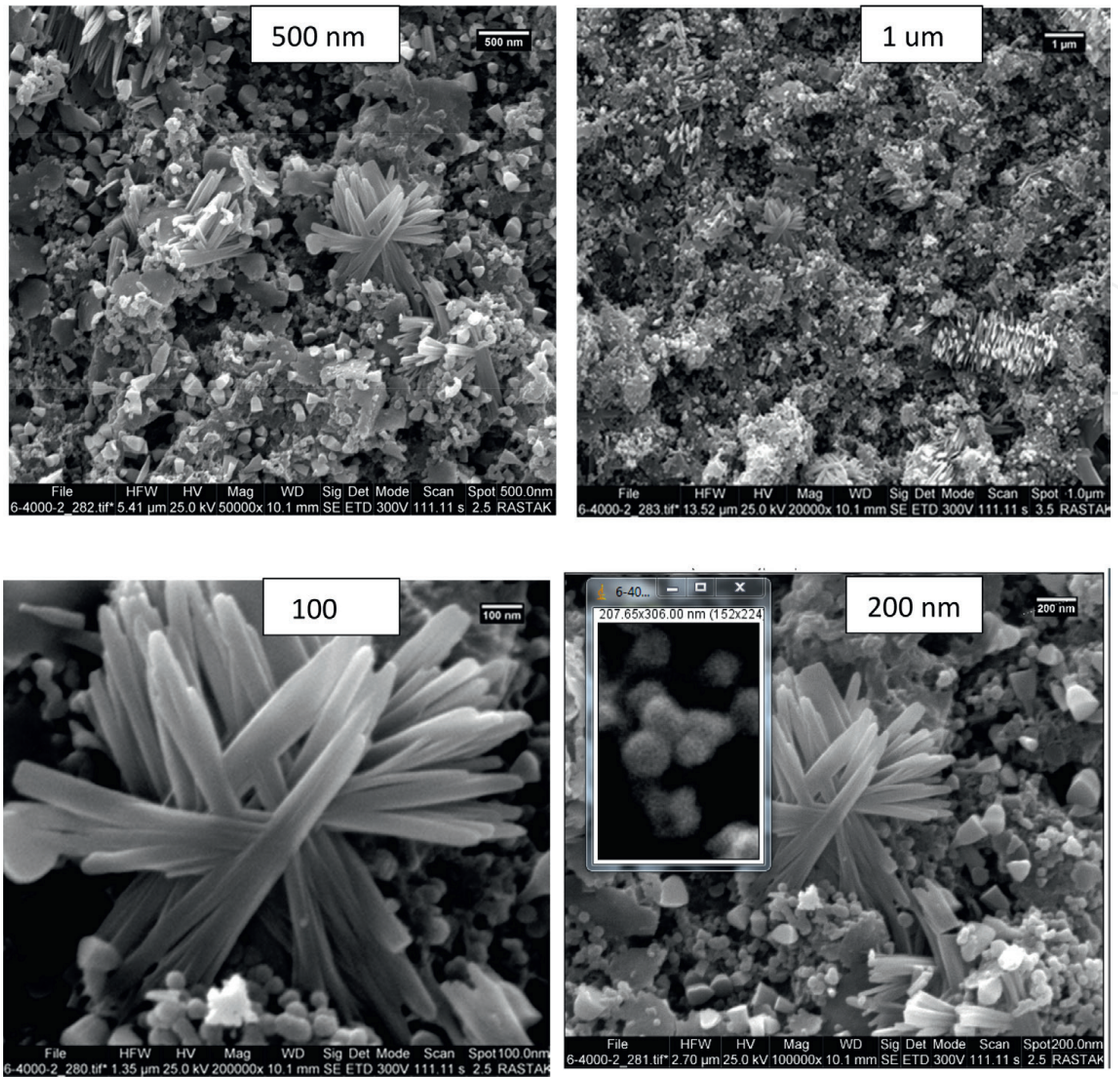

Figure 10.
Shows the SEM images of the sample (A).

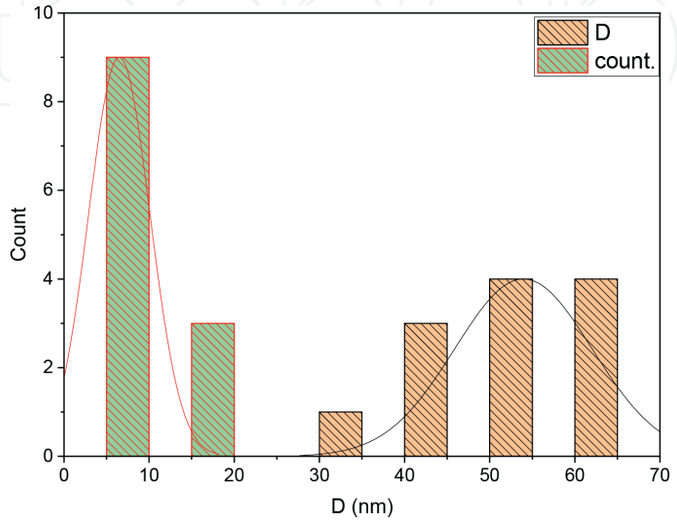

Figure 11.
Distribution function of particles of SEM in sample (A).

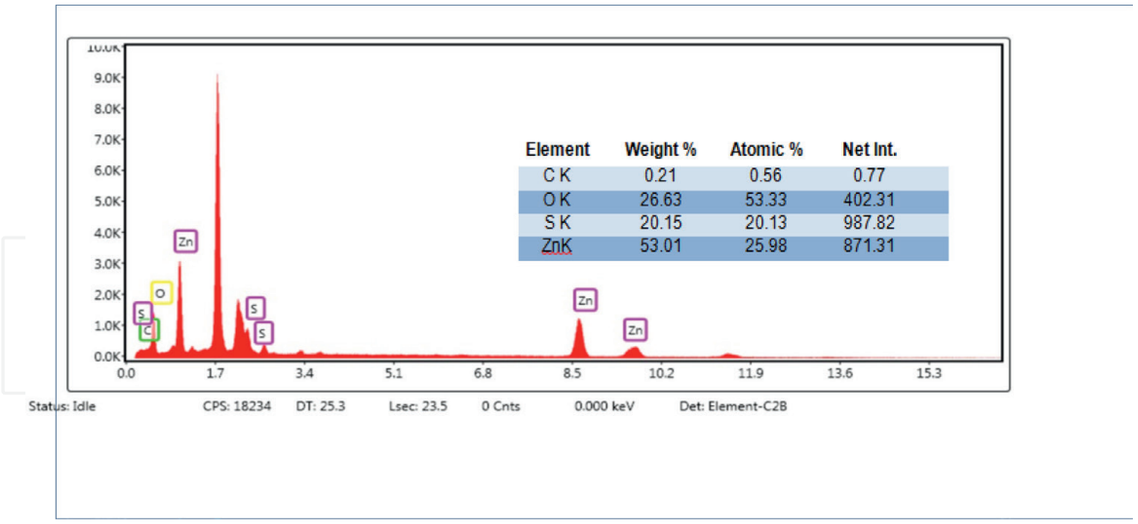

Figure 12.
EDAX for the ZnS/rGo complex with the element ratios of the sample (A).

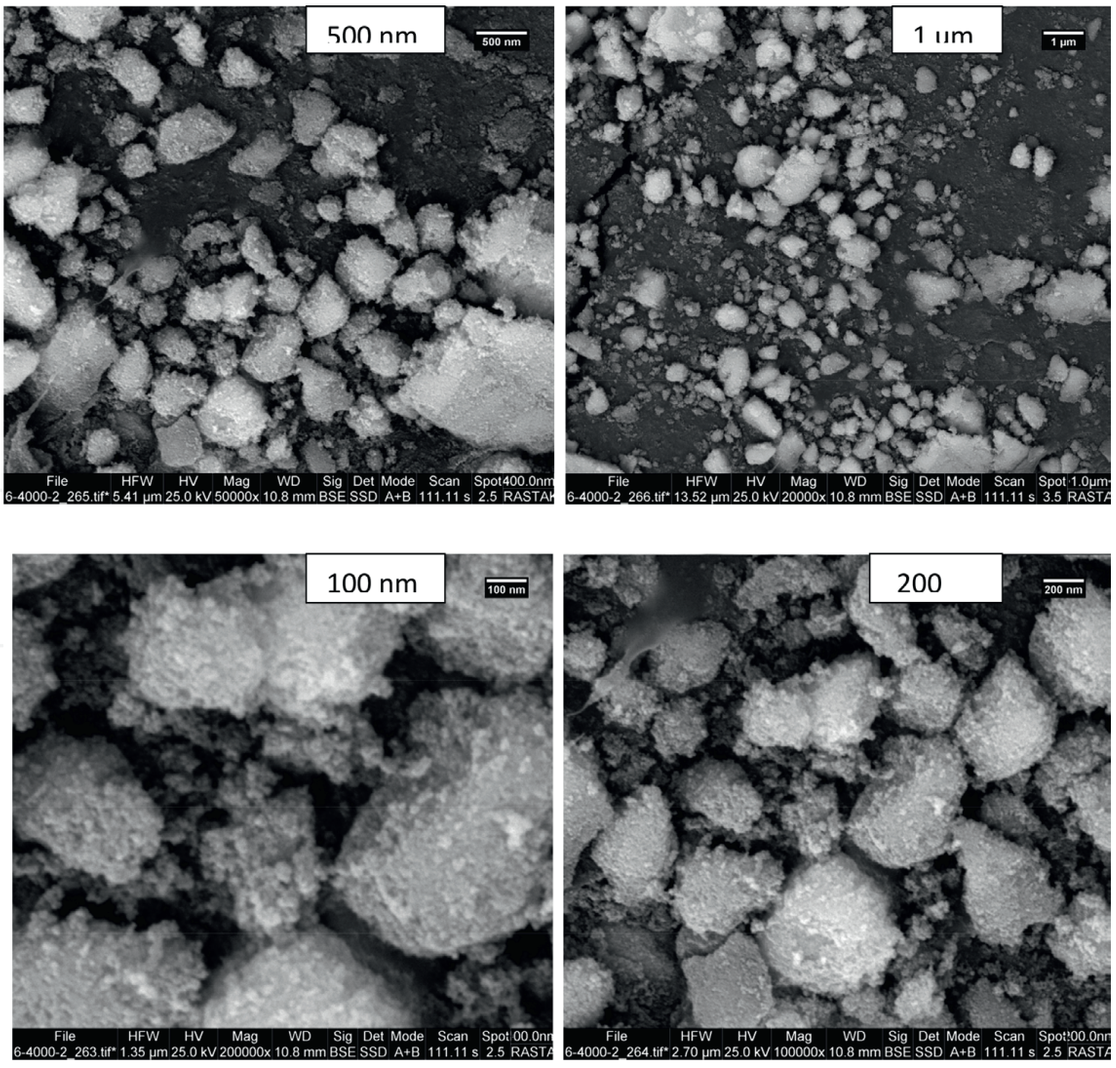

Figure 13.
Shows the SEM images of the sample (B).

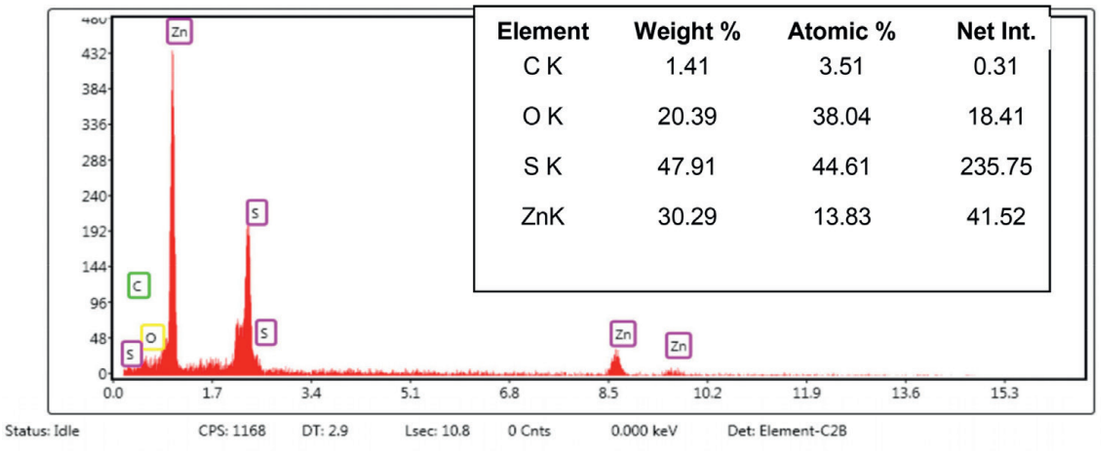

Figure 14.
Shows the distribution function for a portion of the SEM graph of the sample (B).

5. Application of removing dye from water using ZnS/rGO nano composite

The Nano composite ZnS/rGO prepared by the two methods was applied to remove the methylene blue dye (C16 H18 N3SCl. 3 H_2O) which is used in leather and textile coloring (4 mg) of the dye was dissolved in (100 ml) of distilled water and then (2 ml) was added From ZnS/rGO of sample (A) to (2 ml) of dye, then examining the samples by UV-visible spectroscopy. **Figure 15** shows the result of adding ZnS/rGO to sample (A) to the dye and its effect on removal. We note that the peaks for each (C16 H18 N3SCl. 3 H_2O + ZnS/rGO) from (5 min), (10 min) and (15 min) are almost similar and have lower adsorption intensity compared to ZnS/rGO. This indicates that The prepared ZnS/rGO Nano composite is capable of absorbing dyes and

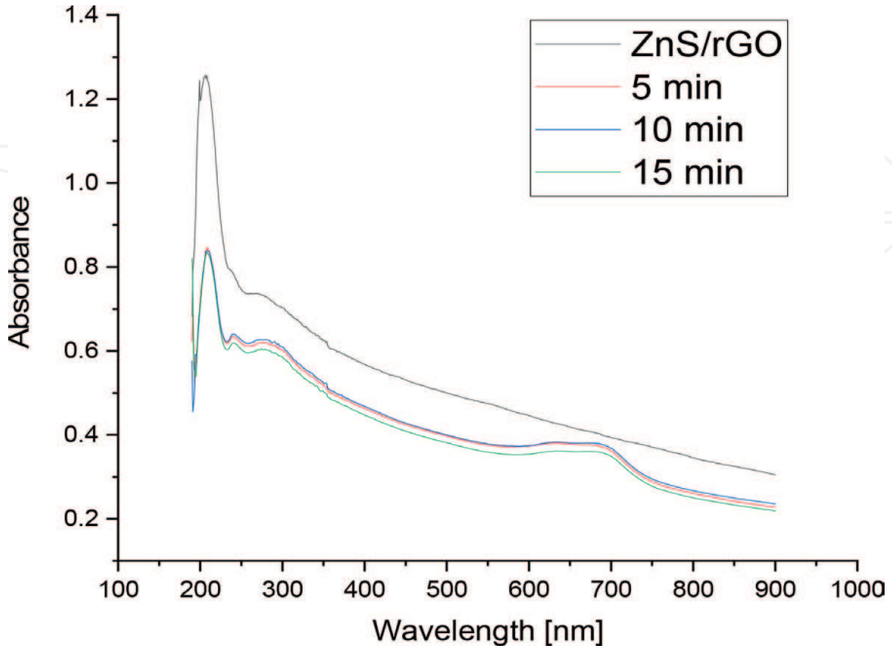

Figure 15.
Shows a UV-Vis spectrum showing the effect of the ZnS/rGO nano composite of the sample (A) on the removal of dye.

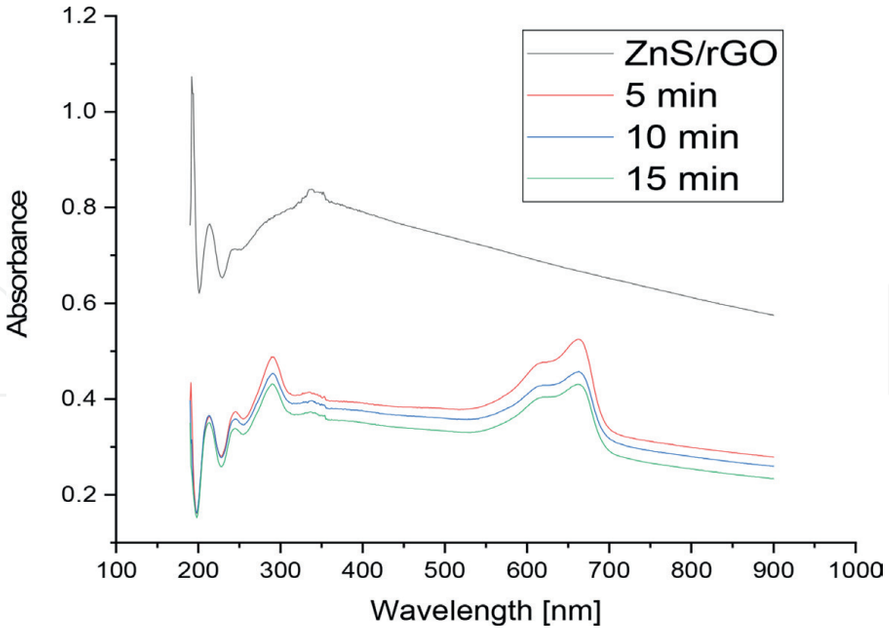

Figure 16.
Shows a UV-Vis spectrum showing the effect of the ZnS/rGO Nano composite of the sample (B) on the removal of dye.

removing pollutants from the water. Then (2ml) of ZnS/rGO was added to sample (B) to (2 ml) of the dye and then the samples were examined by UV-visible spectroscopy, **Figures 15** and **16** shows the result of adding ZnS/rGO to sample (B) to the dye and its effect on removal the peaks for each ((C16 H18 N3SCl. 3 H_2O + ZnS/rGO from (5 min) and (10 min) and (15 min) be satisfied It is almost opaque and has a lower adsorption intensity compared to ZnS/rGO. This indicates that the prepared ZnS/rGO Nano composite is capable of absorbing dyes and removing pollutants from water.

6. Conclusion

By studying pulsed laser ablation and comparing it with one of the chemical methods, it was found that it is the most suitable method for finding nanoparticles of small sizes due to the occurrence of the phenomenon of quantum confinement by the induction plasma. However, the density of nanoparticles is in a small proportion compared to chemical methods. Laser deamination is one of the important techniques in obtaining small nanoparticles with low densities, and this process is important in the manufacture of thin films as well as in the grafting process of some semiconductors used in electronic applications and detectors. The difference in the energy gap leads to the emergence of new physical properties.

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