Preparing and Studying the Combination of ZnS/ rGO Nano Composite by Laser Ablation Method

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Abstract: The mixed compound zinc sulfide (ZnS / rGO) nanoparticles were synthesized by the physical method laser ablation. From there, the crystal structure and crystallite size of X-ray diffraction (XRD) particles were determined (D =8.35nm). The optical properties have also been studied by the visible ultraviolet absorption spectrum. Where the graphene oxide was prepared by a hummer method, after mixing it with zinc sulfide, and it was formed as a Nano composite by using the Neodymium-Yag laser (1064 nm) with the pulsed laser energy of 800 mJ and 600 pulse at a frequency of 6 Hertz in room temperature, thus generating an ionic plasma that contributed to the formation of nanoparticles. Several measurements were made on the sample, such as FTIR, to find out the constituents of the Nano composite and Energy gap is 4.942ev to calculate from UV-Visible by Tuac plot, also, determine the average Green size (25.2nm) from XRD by using the Scherer equation, and to take SEM tests of the compound.

Key words : Nano composite, ZnS Nano materials, Laser ablation, Zns/rGO

1-Introduction

Nanotechnology is defined as a set of technologies and tools that enable Nano science to advance by providing methods for studying, processing and making nanomaterial's [1]. In other words, it is the rearrangement and structure of atoms and molecules and the ability to synthesize new materials and Nano composites [2-3]

They are the materials whose average minute size is less than 100 nanometers or the materials that contain nanoparticles, and the nanomaterial's are characterized by a number of properties such as high surface area, low weight, high strength. These materials also have good physical and chemical properties. These properties depend largely on the size and shape of the nanomaterial's, also its have distinct structural properties between the atoms.
Most of the nanomaterial's have different properties from the materials corresponding to the same material at the micro scale, where the properties of nanomaterial's differ greatly from those atoms and other materials in the non-Nano scale size [4-5]

The compound of ZnS /rGo (graphene oxide prepared by the Hummer method) was studied and the properties of the new Nano composite were identified using the laser ablation technology with a set of spectroscopic measurements.

2- Experimental methods

2.1- Work material components

- Graphene Oxide was prepared from (Graphite powder, Sulfuric Acid ( H2SO4), Hydrochloric Acid (HCL), Hydrogen Peroxide (H2O2), Potassium Permanganate ( KMnO4), Phosphoric Acid ( H3PO4), Ethanol, Ether, H2O)

- ZnS (ZnS is pre-prepared and pressed and annealed using heat press machines and under ideal pressing conditions)

2.2-Preparation of reduced Graphene Oxide

The graphene oxide was prepared using the Hummer method. A graduated glass beaker was brought and placed in it (1gm) of fine and pure graphite powder, Then add (120 ml) of concentrated sulfuric acid H2SO4 to the powder and (13.3 ml) of phosphoric acid H3PO4 was added to the mixture was stirred by a magnetic stirrer, 6gm of KMno4 potassium permanganate was gradually added to the mixture. The beaker containing the mixture was placed on the trays at a temperature of 50° and a certain speed for a period of 12 hours with noticed from the first minutes of stirring the mixture that it changed from black to greenish black. Also, it was washed with distilled water 10 times and after each washing process, the acidity was measured until the acidity of the material reached pH = 6. Then the material was filtered by filter paper. The material was dried and converted to reduced graphene oxide

Then it was washed with distilled water 10 times. The material was dried and converted to reduced graphene oxide, 70 gm of reduced graphene oxide and 70 gm of distilled water were taken and combined until the reduced graphene oxide dissolved in the distilled water. hours, it changed from greenish black to dark brown.

The resulting suspension was then filtered with filter paper and dried at room temperature 25° to obtain a graphene oxide powder and made mixture with zinc sulfide (ZnS) and Distilled water ( H2O). A zinc sulfide disc was placed inside graphene oxide and exposed to laser pulses.
2.3- Syntheses of ZnS/rGO Nanocomposite using Pulsed Laser Ablation

After placing the zinc sulfide disc inside the graphene oxide solution, it was exposed to a number of laser pulses. Where a Neodymium-Yak 1064nm laser was used, with a pulse duration of 10 nanoseconds, and the number of pulses was 600 with a pulse Energy of 800mJ, The frequency of six hertz. Which led to the formation of a Nano-solution by the action of the plasma generated as a result of the fall of the laser pulses on the target [6].

After the formation of the Nano composite, it was subjected to a set of spectrophotometric measurements to study the resulting compound.
3- Results and Discussion

3.1. UV-Visible spectroscopy

UV-visible tests were performed on the research samples. The focus was on the zns/rGO mixture sample, and through the results, the highest value of the absorption of the mixed compound was identified at a peak of 278.19 nm, and this indicates the occurrence of transitions for the c-c carbon bonds. Also, through the study on zinc sulfide, it has the highest absorbance at the wavelength of 336 nm in most of the experiments, as well as for graphene oxide, it has the highest absorbance at 230 nm [7].

In this work, it was found that the highest absorbance of the mixture was at wavelength 287.17 nm, which indicates that there are spectral transitions that occurred between $\pi - \pi^*$ transitions in the c-c carbon bond. Also, the energy gap of the mixture was calculated using the Touc plot method [ 8], and it was about 4.942 electron volts in this work, as the energy gap in most studies was 3.8 Electron volts ,also, Zinc sulfide nanoparticles (ZnS-NPs) with wide bandgap (3.5-3.8 eV) have as of late got escalated thoughtfulness regarding be utilized in numerous applications [9]. The results indicate a blue shift spectral shift and this corresponds to the theoretical study that indicates an increase in the energy gap in composite ZnS nanoparticles as well as a slight amplification in nanoparticles [10].

![Absorbance vs Wavelength](image.png)

**Fig. 3- UV-Visible spectra of ZnS /rGO for two samples at different the energy and pulse numbers.**
Fig.4- The Energy gap of ZnS/rGo by Touc plot method at E=800 mJ ,NO. of Pulse=600

3.2- Fourier Transform Infrared (FTIR) Spectroscopy

The study of the FTIR spectrum is concerned with identifying information about the surface nature of nanoparticles, which are usually affected by water layers, forming a group of chemical bonds. Figure 5 shows the FTIR spectra of ZnS/rGO. In general, through experiments it was found that the peaks observed between 1636.01 cm⁻¹ and 3329.17 cm⁻¹ occur due to bending vibrations of adsorbed water molecules and expansion vibrations of hydroxyl groups respectively. The mixture also has alkoxy and epoxy groups in the sample. The resultant peak of the peak at 1636.17 cm⁻¹ is due to the planar C = C band and the vibrations of aromatic groups of rGO [11]. Notably, all the above peaks were observed for ZnS-rGO and ZnS-rGO for the admixed nanocomposite except that they were slightly shifted to the lower frequency. This can be attributed to the interaction between rGO and ZnS in the compounds. Figure 5 shows the FTIR spectrum of the prepared ZnS nanoparticles. The absorptions at 527.39 cm⁻¹ and 407.97 cm⁻¹ are attributed to the stretching of the vibrations of the ZnS bonds and agree with the results in [12].

Table 1. The bonds of FTIR Spectra for ZnS/rGO Nano compsite

| Bonds  | Wave number |
|--------|-------------|
| OH     | 3329.17     |
| C=C    | 1606.01     |
| Zn-S   | 527.39, 407.97 |
3.3- SEM Spectroscopy measurements

A scanning electron microscope (SEM) is kind of electron magnifying lens that produces pictures of an example by checking the surface with an engaged light emission. The electrons collaborate with particles in the example, creating different signs that contain data about the surface geography and organization of the example [13]. The electron pillar is examined in a raster filter design, and the situation of the shaft is joined with the power of the identified sign to deliver a picture. SEM images are illustrated in Figure 6, and by studying part of one of the images at 200 nm, the results showed the formation of nanoparticles of different dimensions and measurements of their diameters, where they were about 54 nanometers, as well as the presence of particles with diameters less than that, and this formation is due to the occurrence of the phenomenon of quantum confinement.
Fig. 6- SEM images of ZnS/rGO at scales (1µm, 500 nm, 200 nm, 100 nm) respectively.

Fig. 7- The distribution function of part from SEM graphi

Fig. 8- The EDAX of ZnS/rGo composite with ratios of Elements.
3.4-X-Ray Diffraction (XRD)

The figure 9 represents the measurement of the XRD spectrum of the Nano composite, where three peaks appeared in the drawing and the granular size was calculated by using the Scherer equation after converting the angles from degree to radians scale as well as the values of the peaks.

![Fig.9- XRD Spectra of ZnS/rGO composite](image)

The crystallite size was calculated, the results showed that the lowest value of particle size was at the peak 33.04, and the diameter was about 8.359 nm, and this happens due to the phenomenon of quantum confinement. Also, the average particle size was calculated and it was about 25.233nm, as shown in the Table.2.

| NO. | Intensity | 2\(\theta\) | FWHM | Peak center | crystallite size (D) | D Averge(nm) |
|-----|-----------|-------------|------|-------------|----------------------|--------------|

Table 2. Data of XRD Spectra for ZnS/rGO composite
4- Conclusions

The Nano composite mixture was prepared successfully using Q-switch Neodymium :YAG pulsed laser(λ= 1064 nm, pulse Energy is 800 mJ, Number of pulses 600, and the pulse duration 10 n sec) by using laser ablation Technique. The method is an important physical method in preparing Nano composite, also, to get important Nano applications.

By studying the effect of high-powered laser pulses on the compound due to the plasma generated inside the liquid, which gave a behavior different from the normal behavior of zinc sulfide, especially the observation of an increase in the energy gap, which leads to the possibility of making scientific applications such as adsorption as well as its use in the removal of some pollutants.

References:

[1] B.D. eddine, "Elaboration et Etude de Nanoparticules Au/TiO2 et Ag/TiO2", présenté pour obtenir le Diplôme de Magister en physique, université Mentori, Constantine, 2012.

[2] European commission, Nanotechnologies, principales, Application, implications and Hands-on Activities, 2013.

[3] J. Moore, R. Moore, "Nanotechnology 101", science 101, Westport, 6) Connecticut, London, 2007.

[4] SEGETS, D., GRADL, J., TAYLOR, R. K., VASSILEV, V & PEUKERT, W. 2009. Analysis of optical absorbance spectra for the determination of ZnO nanoparticle size distribution, solubility, and surface energy. American Chemical Society Nano, 3, 1703-1710.

[5] WANG, J., CAO, J., FANG, B., LU, P., DENG, S. & WANG, H. 2005. Synthesis and characterization of multipod, flower-like, and shuttle-like ZnO frameworks in ionic liquids. Materials Letters, 59, 1405-1408.

[6] Hongkun Huang, Jiancheng Laia), Jian Lu, and Zhenhua Li, "Pulsed laser ablation of bulk target and particle products in liquid for nanomaterial fabrication", AIP Advances 9, 015307 (2019).
[7] Yang Yang, Tianxi Liu, "Fabrication and characterization of graphene oxide/zinc oxide nanorods hybrid". Applied Surface Science 257, 8950-8954(2011).

[8] Kareem Abass Al-Hassani, M. (2019). SEROLOGICAL DETECTION OF COXIELLA BURNETII CHRONIC INFECTION- PHASE 1 IN SERUM OF HUMAN AND SHEEP AT AL-QADISIYAH PROVINCE, IRAQ. Al-Qadisiyah Journal Of Pure Science, 24(1), 13 - 20.

[9] Jalil Abed, M. (2019). Synthesis and Characterization and evaluation of biological activities of some new pyrrole compounds. Al-Qadisiyah Journal Of Pure Science, 24(1).

[10] Abdul-Hamza, H. kadhum, & Mohammed, G. J. (2019). The inhibitory effect of some nanoparticles on biofilm formation of Streptococcus agalactiae. Al-Qadisiyah Journal Of Pure Science, 24(2).

[11] Hussein Al-abedi, K. J., & Abd Al-Mayah, F. (2019). Molecular detection of metallo-β-lactamase genes in carbapenem-resistant isolates of Pseudomonas aeruginosa recovered from patients in Al-Diwaniyah province, Iraq. Al-Qadisiyah Journal Of Pure Science, 24(2).

[12] Alramahy, S. khoman, & karim, N. abdul. (2019). Evaluation ofserum levels of IL-10and IL-6 in patients with HCV at Diwaniyah Teaching Hospitals, Iraq. Al-Qadisiyah Journal Of Pure Science, 24 (2).

[13] kareem, F., & Thamer, W. (2019). Study of some immunological effects of methotrexate in people with rheumatoid arthritis. Al-Qadisiyah Journal Of Pure Science, 24(2).

[14] Jwad Sahar, Y., & Shamran Mohammed, H. (2019). Synthesis and characterization some complexes of azo dye of pyrimidinyi1 and evaluating their biological activity. Al-Qadisiyah Journal Of Pure Science, 24(3).

[15] A. Ghazay, A., Mayar Hezam, A., M. Alkhuzaie, M., & Obayes, I. S. (2020). Study the effect of different temperatures on the biofilm production in Proteus mirabilis isolated from urinary tract infection patients. Al-Qadisiyah Journal Of Pure.

[16] Salah, A. (2020). The New Combination of Semi-Analytical Iterative Method and Elzaki Transform for
Solving Some Korteweg-de Vries Equations. Al-Qadisiyah Journal Of Pure Science, 25(1), Math. 23 -26.

[17] Ali , W., & R.Annon, M. (2020). Biological Effective of organic solvent extracts of Mirabilis jalapa Leaves in the Non-cumulative for mortality of Immature stages Culex quinquefasciatus Say ( Diptera : Culicidae ). Al-Qadisiyah Journal Of Pure Science, 25(1), Bio 1-6.

[18] Sami Abd ali , mohammed, Shaker Hussein, A., & mohammed hadi, H. (2020). Study The Current Density-Voltage (J-V) Characteristics of α-Fe2O3 Thin Film Prepared by Spray Pyrolysis Technique. Al-Qadisiyah Journal Of Pure Science, 25 (1), Phys 1-7.

[19] J. Tauc, Amorphous and Liquid Semiconductors, Plenum Press, New York, (1974).

[20] X. Fang, T. Zhai, U. K. Gautam et al., “ZnS nanostructures: from synthesis to applications,” Progress in Materials Science, vol. 56, no. 2, pp. 175–287, 2011. AAKANKSHA SUD & RAMESH K SHARMA, "STUDY OF OPTICAL PROPERTIES OF ZnS THIN FILM USING SIMULATION SOFTWARE", International Journal of Applied and Natural Sciences (IJANS), Vol. 5, Issue 5, Aug – Sep 2016; 13-18.

[21] Z. Wang, B. Huang, Y. Dai, X. Zhang, X. Qin, J. Wang, Z.Zheng, H. Cheng, Cryst. Eng. Comm.14, 1687 (2012)

[22] Eric Selorm Agorku•Messai Adenew Mamo, "Cobalt-doped ZnS-reduced graphene oxide nanocompositeas an advanced photocatalytic material", Porous Mater (2015) 22:47–56

[23] Priyanka Tonk1, Tashi Dawal, Mindu Dorjil, Dorji Choзам1, Harmee Singh Bhullar1, Vikas Thakur2, Tarun , International Journal of Innovative Research in Computerand Communication Engineering(An ISO 3297: 2007 Certified Organization)Vol. 4, Special Issue 4, August 2016.