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SYNTHESIS AND CHARACTERIZATION OF MOLIBDENUM SULFIDE NANOPARTICLES BY A NEW CHEMICAL REACTION FORMULATION

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This research is presents a new formulation to obtain MoS2 nanoparticles using chemical reaction controlled and using non-hazardous compounds and easy handling. MoS2 nanoparticles of 5 nm size with hexagonal structure were obtained and characterized by HRTEM. From UV-Vis spectroscopy were determined the direct as indirect energies band gap of 3.13 eV and 2.78 eV, respectively. Chemical composition was corroborated by X-Ray Photoelectron Spectroscopy, while Fourier Transform Infrared only show the functional group presents in the dispersive media for MoS2 nanoparticles.

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1. Introduction

For two centuries, Molybdenum sulfide (MoS_2) was used as lubricant material to reduce the friction wear in machinery [1]. At the end of the last century, the number of studies around this material increased in order to improve the aeronautical technology. Additionally, the MoS_2 is used as a catalyst in the petroleum industries [2], in order to remove the sulfur from the carbides and in other reactions due to its high tolerance to contaminants such as sulfuric acid.

The chemical compound is inorganic, solid, with laminar structure it appears as dark metallic gray and its hardness as low as graphite. The laminar structure, composed by three layers has molybdenum atoms in the central layer while in the lateral layers are located sulfur atoms [3].

The state of the art on molybdenum chalcogenides nanoparticles, it has been recently reported similar to graphene but formed by three layers [4]. Some transition metal dichalcogenide materials such as MoS_2 are semiconductors, for example, for three of the monolayers of molybdenum disulfide (MoS_2) is reported a direct band gap of 1.9 eV and an indirect band gap of 1.2 eV [5-7]. It has also been reported that two of the existing MoS_2 crystalline structures are the 2H and the 3R, that correspond to different types of stacks of the monolayers, where these stacking forms are similar to those observed in graphene and where these materials, 2H-MoS_2 and 3R-MoS_2 have similar band structures [7].

This article describes a new process for MoS_2 nanoparticles using a new formulation by controlled chemical reaction.

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2. Experimental

The synthesis of the material, Molybdenum Sulfide nanoparticles (MoS_2), was carried out by the aggregation technique in chemical reaction. The main conditions were room temperature (24 °C), normal atmosphere and aqueous solutions.

In this section, the formulation used to elaborate MoS_2 nanoparticles is described. Firstly, in a beaker 1 mililiter of Amonium Molibdate Tetrahidrated (0.01M) is added, then 0.1 mililiter of concentrated acetilacetone [1]is aggregated, homogenizing the solution mixed with ultrasonic vibration. Posteriorly, 0.1 mililiter of rongalite and 1 mililiter of tiourea is incorporated in this order, applying ultrasonic vibration again during 1 to 2 minutes. The used equipment to characterize the MoS_2 nanoparticles obtained were: TEM-HRTEM, Jeol-Jem 2010F, UV-vis, Cary WIN 60. XPS PHI-5100, and FTIR spectrometer IS10 Nicolet Thermo scientific.

3. Results

The first characterization presented is the High-Resolution Electron Transmission Microscopy (HRTEM). A sample of the suspended nanoparticles synthetized was dropped on the carbon coated copper grid. Figure 1, shows in part a) a contrast micrography, with a work scale of 2 nm, electron diffraction lines can be observed, when electrons pass through of a crystalline structure of the Molybdenum Sulfide obtained. On that image, three different interplanar distances of 2.30, 2.65 and 1.64 Å were located, which corresponds with PDF# 37-1492 pattern for MoS_2 compound hexagonal [8,9]. This set of interplanar distances correspond to the Miller indexes (103), (101) and (106), respectively.

Part b) of Fig. 1 shows the Fast Fourier Transform (FTT) of the image a), were two interplanar distances were located, being one of them different to previous above mentioned, d4=2.736 Å with Miller indexes (100). The four distances identify the same referred compound, hexagonal MoS_2. Using this characterization an estimation of the nanoparticles size of 5 nm was obtained.

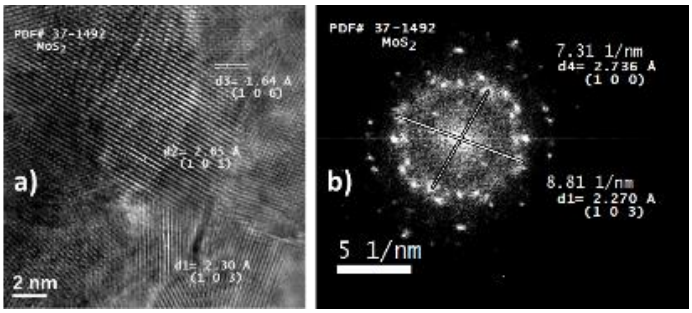

Fig. 1. High Resolution Transmission Electron Microscopy of MoS2 nanoparticles a) Micrograph and b) Fast Fourier Transform.

The absorption response study is presented in the 200-900 nm range in the Fig. 2. The absorption from 900 until 400 nm around remains low and almost constant, but from 400 until 368 nm the absorption increases 7 times, therefore, there is an absorption threshold. In order to evaluate its energy band gap, direct and indirect, the Tauc method was used.

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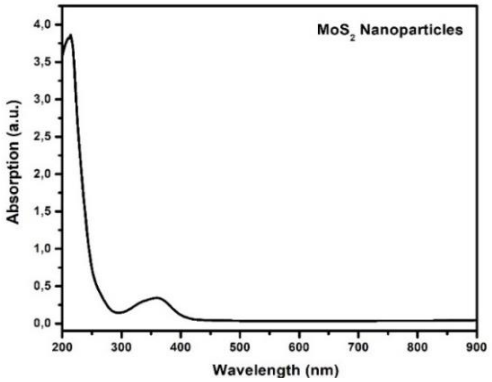

Fig. 2. Absorption spectrum of the MoS2 nanoparticles synthetized.

In Fig. 3, the procedure to evaluate the direct energy bandgap is shown, a value of 3.13 eV was obtained, even if the value reported in bulk is 1.8 eV, this is due the nanoparticles size reported by TEM[9-13].

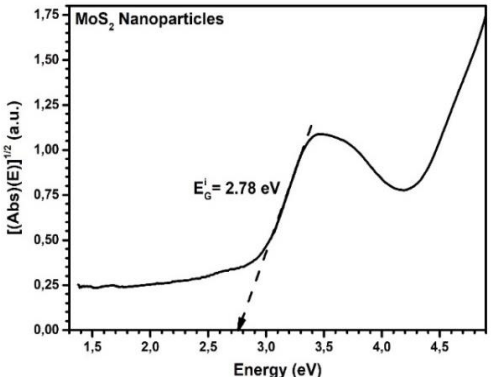

Fig. 3. Direct Energy Band Gap using the graphic Tauc method for MoS2 nanoparticles.

Additionally, in Fig. 4 is depicted the calculation of indirect energy bandgap for MoS_2, resulting in 2.78 eV value due the nanoparticles size, while in scientific references values of 1.23 to 1.29 eV were reported for bulk material [13].

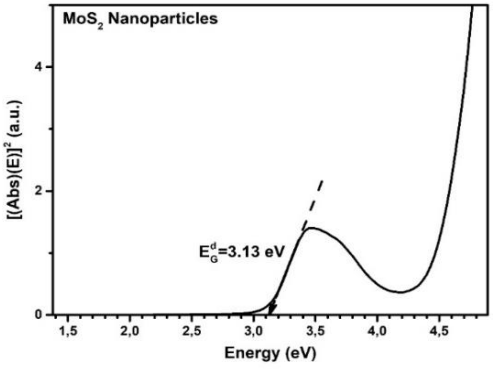

Fig. 4. The graphic Tauc method in order to obtain Indirect Energy Band Gap for MoS2 nanoparticles.

At Fig. 5 the X-Ray Photoelectron Spectrum the presence of the Binding energy values 413.5, 396.25, 233 and 230 eV for Molybdenum and 168 and 161.5 eV for Sulfur are presented. The other elements detected are due to the substrate used in order to deposit the MoS_2 nanoparticles by drop coating. As can be observed, the Carbon is closed to the value reported in Handbook, which correspond to the equipment calibration.

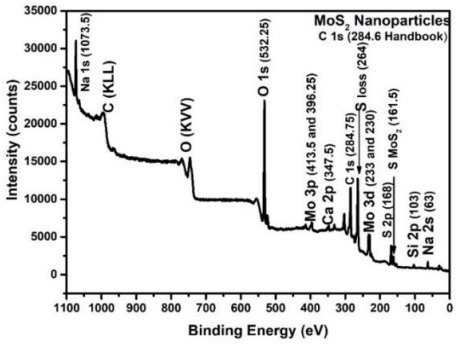

Fig. 5. XPS survey spectrum of MoS2 nanoparticles suspension where the mostly signals were identified.

In order to probe the MoS_2 compound presence were practiced High Resolution XPS around the signals O 1s, C 1s, S 2p, S 2s and Mo 3d obtaining the results presented in Fig. 6, Fig. 7, Fig. 8 and Fig 9. The deconvolution process allow identify the binding energies related with the molybdenum sulfide.

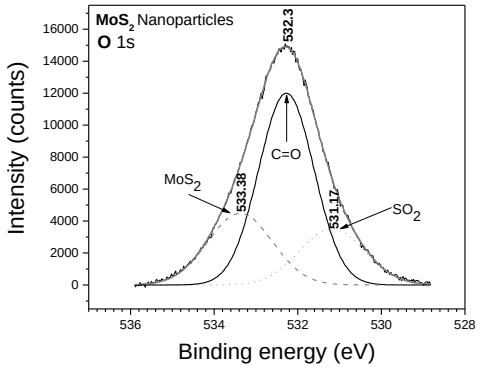

Fig. 6. High Resolution XPS spectrum, deconvolution and smooth, for the signal of Oxygen 1s, as indicated on the plot.

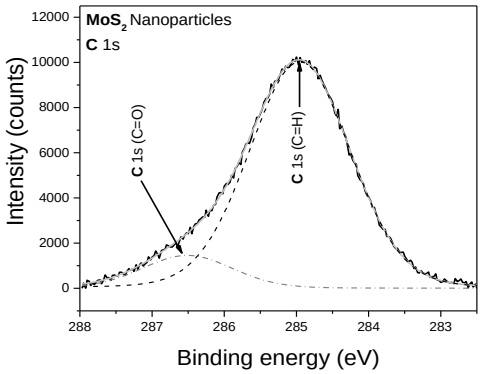

Fig. 7. High Resolution XPS, deconvolution and smooth, for the signal of Carbon 1s, as shown on the plot.

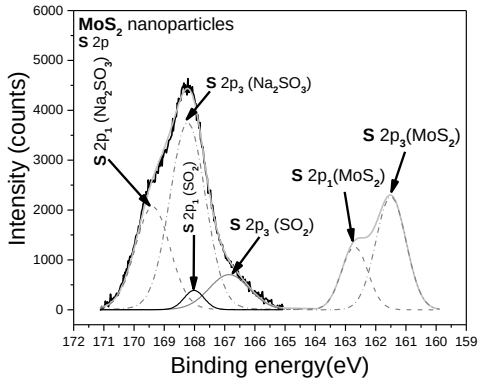

Fig. 8. High Resolution XPS and corresponding deconvolution and smooth of Sulfur 2p as indicated on the plot.

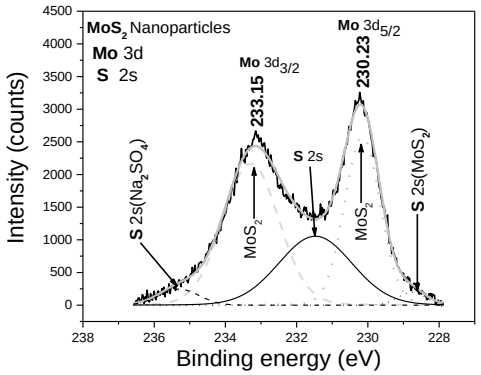

Fig.9. High Resolution XPS spectra and corresponding deconvoluted and smoothed spectra, for the signals of Molybdenum 3d and Sulfur 2s.

The FTIR results presents three principal peaks, the functional group O-H centered in 3379 cm^{-1}, the band of 1643 cm^{-1} represents the functional group C=O and the functional group C-O for the band of 1211 cm^{-1}. Any way this is the chemical composition of the liquid suspension where are immerses the MoS_2 nanoparticles.

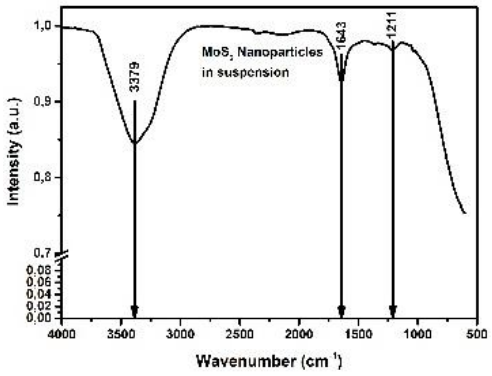

Fig. 10. Fourier Transform Infrared Spectroscopy of the MoS2 nanoparticles suspension.

4. Conclusions

MoS_2 nanoparticles were synthetized, hexagonal structured was obtained and corroborated by HRTEM. The synthesis method developed in order to obtain Molybdenum sulfide nanoparticles is simplified using chemical reaction controlled and using non-hazardous compounds and easy handling. The chemical composition and the oxidation states were concerning using X-Ray Photoelectron Spectroscopy technique. The Fourier Transform Infrared spectroscopy contribute to qualify the suspension media.

Acknowledgments

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