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Research Article

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Optical and Surface Studies of MoS_2 Sheets Functionalized with Zincon

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Abstract

Past research over elements has concluded a noteworthy role of zinc (Zn) in prostate cancer (PCa) Healthy prostate has a higher amount of Zn present whereas, during prostate malignancy, the Zn concentration reduces. It has been also observed that in electrochemical sensing, hydrogen and Zn both get reduced at about the same potential -1.2 V causing interference between them. Exploring this interference and reduction we intended to develop a platform that could modify the surface of electrodes. For this purpose, Molybdenum disulfide (MoS_2) sheets having a dimension of 0.5 - 0.8 µm were synthesized through the hydrothermal method and subsequently chemically functionalized with Zincon. Further MoS_2 - Zincon complex was analyzed via FTIR, SEM and UV-Vis, which confirmed the formation of MoS_2 - Zincon complex. In UV-Vis analysis of Zincon, the peak at 300 nm was found to be blue and shifted towards 298 nm after the formation of the complex also Zincon peaks at 528 nm was red - shifted to 557 nm after could be recognized bonding of Zincon with MoS_2. SEM images clearly showed that the flowers like structure of Zincon were distributed over MoS_2 sheet. FTIR absorption band at 1102 cm^{-1} and 753 cm^{-1} contributed to =C-H from Zincon and their disappearance after Zincon complexed with MoS_2 sheet confirmed the formation of the MoS_2 - Zincon complex.

Keywords

Prostate cancer, Non-covalent interaction, Oxidation potential

Introduction

PCa is one of the major health issues in the world, and it is the fifth most common type of cancer in men [1]. Early detection, diagnosis, and treatment are identified as important steps for curing it. Detection of highly sensitive tumor markers in human serums is a key point for the treatment of PCa Digital rectal examination measurement of serum prostate - specific antigen (PSA) and trans rectal ultrasound are the diagnostic tools frequently used to detect PCa[2].

However, a rise in PSA level does not surely indicate the occurrence of PCa, as other health conditions such as benign prostatic hyperplasia, prostatitis or inflamed prostates, etc. can also lead to an increase in PSA. And some men with PCa do not show an elevated PSA level, while some others with elevated levels do not possess PCa [3], so another reliable method, as well as biomarkers, are required to confirm the presence of PCa. In the case of cancerous prostate cells does not show the ability to concentrate Zn, as result Zn levels decrease dramatically [4]. Thats why prostate malignancy and Zn level show a strong inverse correlation with PCa progression, and hence sensing Zn level has been suggested as an excellent candidate biomarker for PCa diagnosis [5].

Recent studies reported that Zn concentration significantly drops even in the early stages of PCa [6]. Since there is a large difference in Zn content between the malignant and normal prostatic fluids (1 and 9 mmol/g), therefore free / increased Zn ions detection can be a reliable method for the early diagnosis of PCa [7].

Detecting the presence of Zn^{2+} ions in the prostatic fluid is widely considered a useful biomarker for PCa, there have been only a few studies reporting the detection of Zn^{2+} [8, 9]. These studies have used highly complex instrumented methods such as inductively coupled plasma mass spectrometry (ICP-MS) [10] and Atomic absorption spectroscopy (AAS) [9]. AAS is the common method for the determination of Zn concentration however, high cost is a major factor in their wide use. Colorimetry or UV-Vis spectrophotometry [11] of the zinc reagent Zincon [(o-2- (2-hydroxy-5-sulfophenylazo) benzylidene hydrazinobenzoic acid) [12] can also be used for the detection of other metals such as copper and mercury detection; so Zincon is a choice for detection of Zn ion in the serum samples.

Zincon is a synthetic material that has been used for the analysis of metallic ions such as copper and Zn [13]. Qin et al. used Zincon to make an amperometric sensor for phenol detection [14]. In that research, Zincon was electropolymerized on the surface of carbon paste by cyclic voltammetry. The performance of the sensor was studied at different PH and scan rates and the detection limit of the sensor was 9 μmol L^{-1}. The electrochemical behavior of Zincon has not been studied so far.

Some materials and their nanostructure including silicon nanowires and carbon nanotubes, have been actively examined to improve the sensitivity in detecting biomolecules. Furthermore, two-dimensional materials, including graphene and transition metal dichalcogenides have shown great potential for ultra-sensitive biosensors [15].

Based on the above theory, we have developed a composite, which could suitably modify the electrode surface to avoid interference and improve the selectivity of Zn detection. Due to the large complexation constant of Zincon [16] with Zn, Zincon was used to functionalize the hydrothermally obtained MoS_2 sheet. Herein we report optical and surface morphologies of hydrothermally obtained MoS_2 micro sheet chemically modified with Zincon.

Materials and Methods

Reagents and instruments

Ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}.4H_2O$), Thiourea ($CS(NH_2)_2$), Zincon, Zinc sulfate (ZnSO4), are purchased from Sigma Aldrich were used in their original form in the experiment. High quality deionized (DI) water was used in all experiments. Stainless steel hydrothermal autoclave was used to prepare MoS_2 micro sheet. Ultraviolet-Visible (UV-Vis) spectrophotometer and Fourier transform infrared (FTIR) spectrometer were used for characterization of the synthesized MoS_2 - Zincon. A scaaning electron microscope (SEM) was used to study the surface morphology of Zincon and MoS_2 - Zincon.

Synthesis of MoS_2 Sheet

MoS_2 sheet was prepared by adding 30 mM CH_4N_2S and 1 mM ($(NH_4)_6Mo_7O_{24}.4H_2O$) in 35 mL distilled water by stirring and sonication to form a transparent bluish solution. After that, the solution was transferred into a Teflon-lined stainless-steel autoclave and heated in the oven at 180 °C for 18 hr [17]. After centrifugation black product was obtained, it was washed with distilled water and ethanol several times and dried at 60 °C in a vacuum. The hydrothermally prepared sheet was washed with DI water.

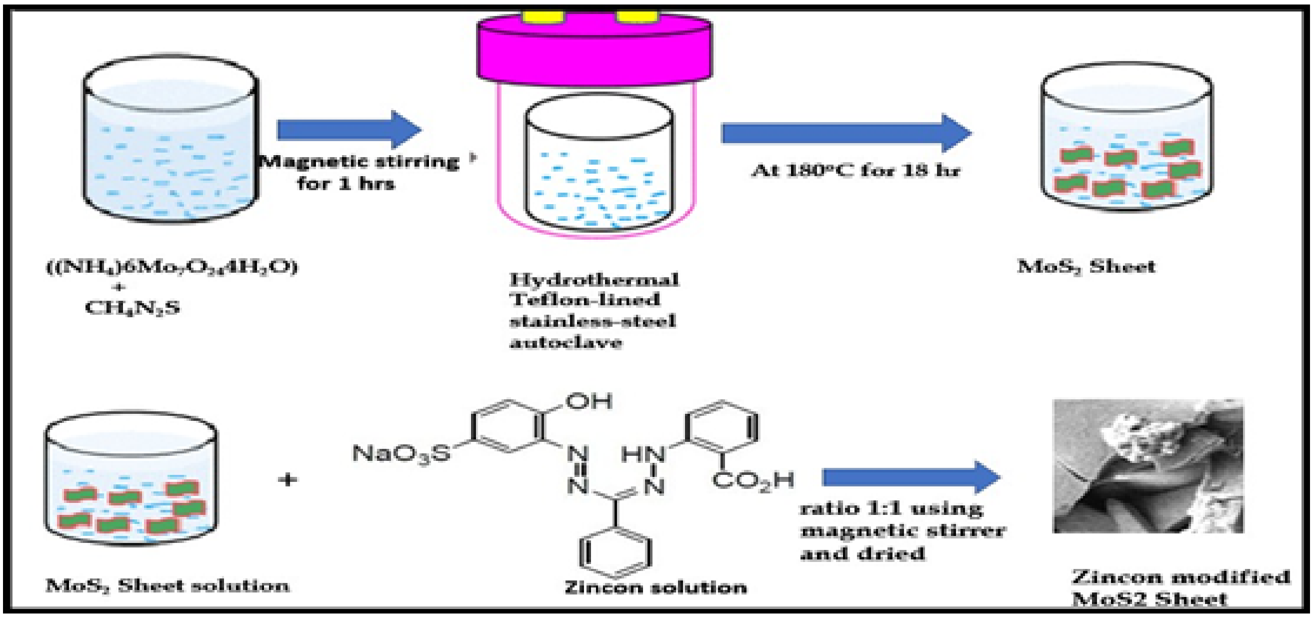

Figure 1: Scheme of preparation of MoS_2- Zincon complex.

Synthesis of MoS_2 - Zincon complex

Zincon solution was prepared by adding 0.02 g Zincon into 25 mL absolute ethanol and sonicated for 10 min; it was collected in a brown bottle and held for 12 hr at room temperature until completely dissolved [15].

The concentration of MoS_2 sheet solution was adjusted to the 1 mg mL^{-1} using DI followed by sonication for 120 min. MoS_2 - Zincon sheet complex was prepared by mixing Zincon solution and MoS_2 solution in a ratio 1:1 using a magnetic stirrer. The obtained solution was centrifuged at 7000 rpm and precipitate was collected. After washing three times with ethanol, it was dried naturally(Figure 1).

Results and Discussion

Material characterization

The prepared MoS_2 - Zincon was rinsed with ethanol and UV-Vis spectra of Zincon and MoS_2 - Zincon suspension solution were recorded. The FTIR spectra were also recorded.

From FTIR of MoS_2 sheet, it can be observed that there were absorption bands at 524, 610, 1071, 1605 and 3154 cm^{-1} (Figure 2a). Here the band observed at 524 cm^{-1} was due to Mo-S bonds present in the MoS_2 sample. Presence of band at 610 cm^{-1} was due to -SH bonds, 1071 cm^{-1} was due to -C-OH bond and 1605 cm^{-1} was due to -C=O group. Here bands at 524, 610, 1071, and 1605 cm^{-1} were attributed to MoS_2. The peak at 3670 cm^{-1} was also due to the stretching vibration of

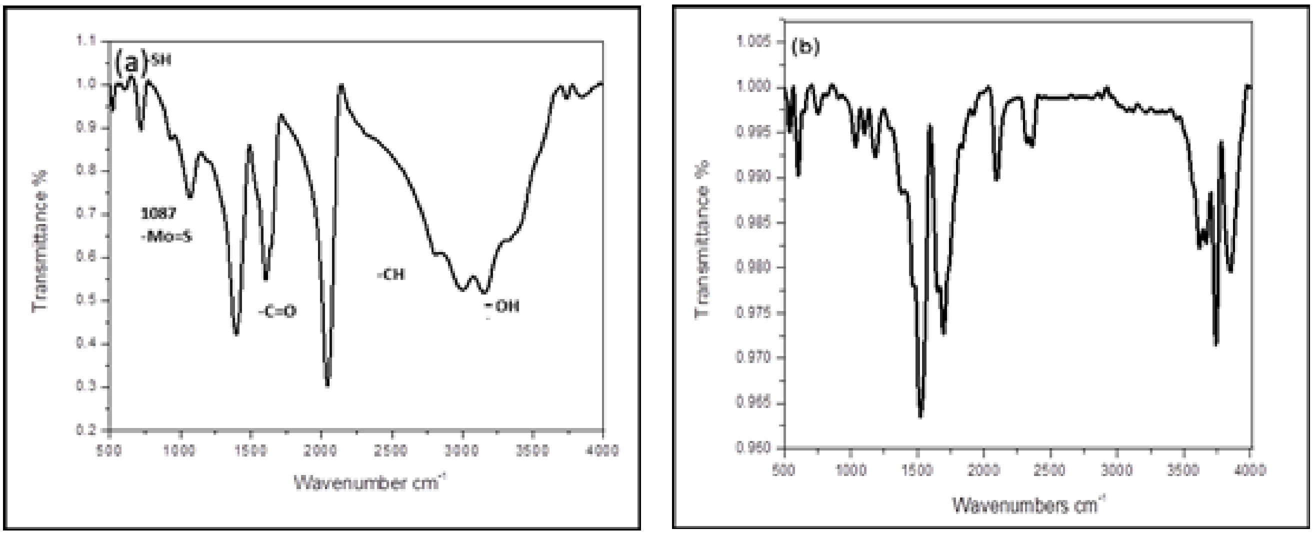

Figure 2: FTIR Spectroscopy of (a) MoS_2 sheet and (b) Zincon.

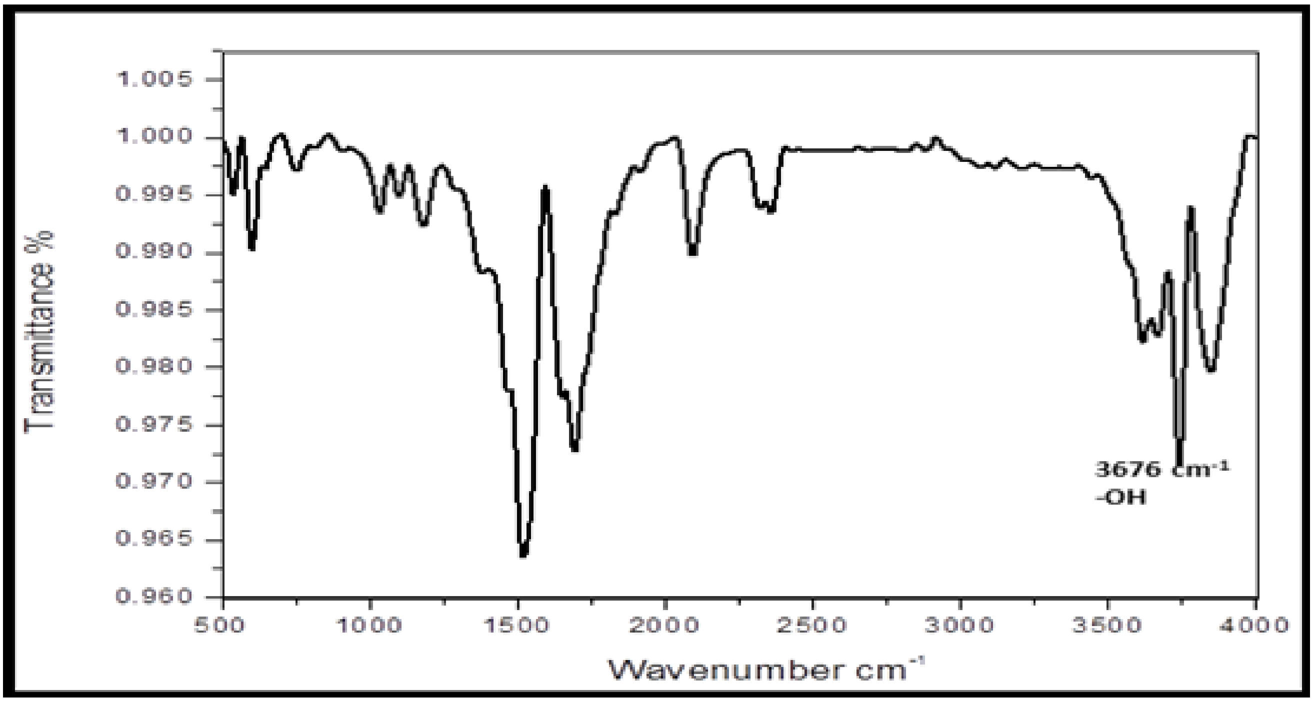

Figure 3: FTIR spectroscopy of MoS_2 - Zincon complex.

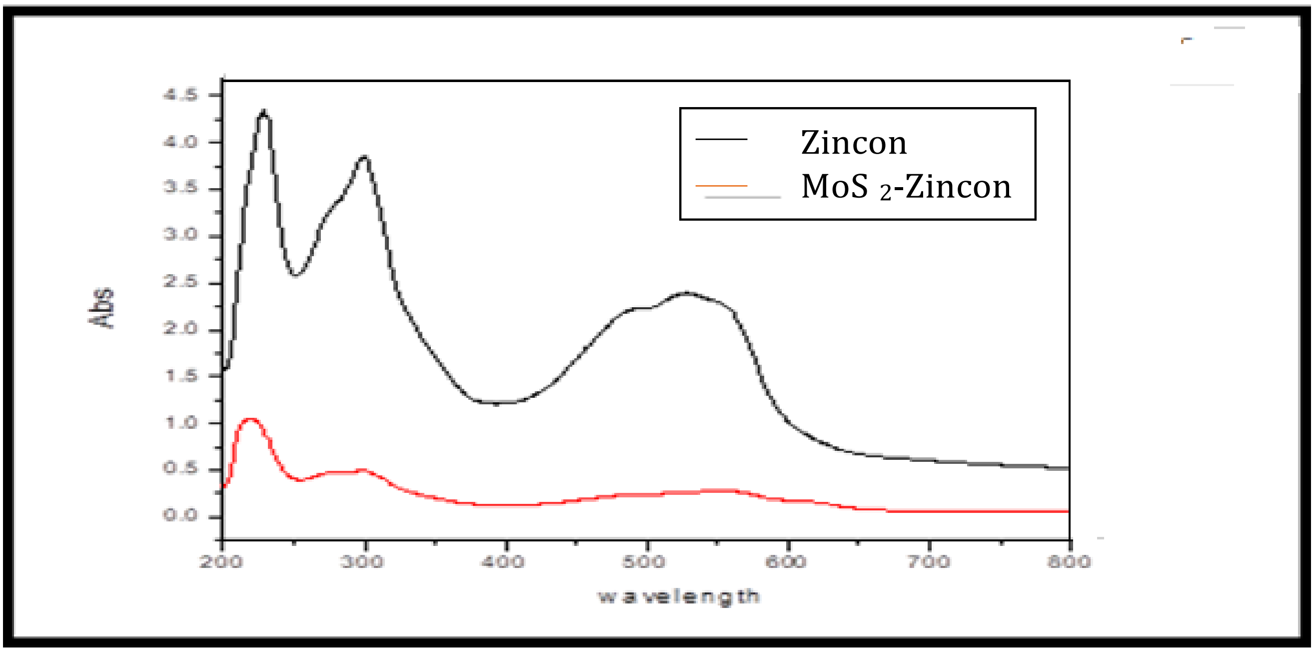

Figure 4: UV-Vis Studies of Zincon and MoS_2 - Zincon complex.

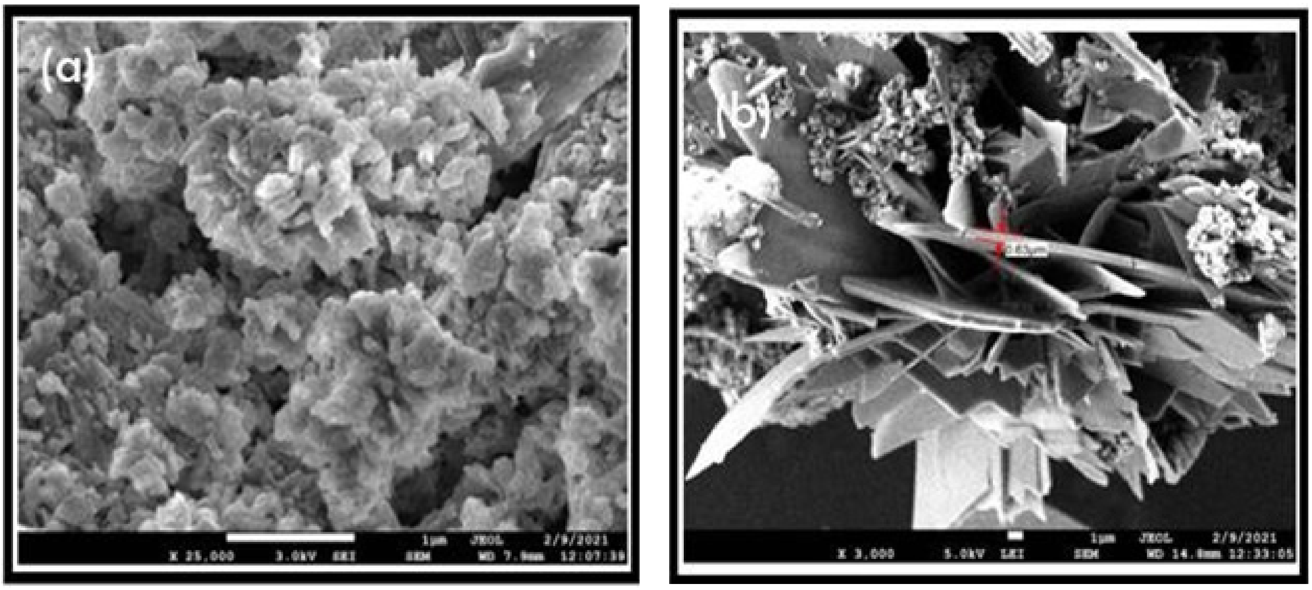

Figure 5: SEM images of (a) Zincon and (b) MoS_2 sheet with Zincon (width in micrometre range).

the hydroxyl group. In the FTIR of Zincon (Figure 2b) peak located at 1102 cm^{-1} and 753 cm^{-1} that contributes to =C-H from Zincon was absent after Zincon was complexed with MoS_2 sheet (Figure 3), this lends further support to MoS_2 - Zincon complex formation.

In UV-Vis analysis of Zincon, the peak at 300 nm was found to be blue and shifted towards 298 nm after the formation of the complex also Zincon peaks at 528 nm red - shifted to 557 nm after could be recognized bonding of Zincon with MoS_2 (Figure 4).

The SEM image of Zincon show flower - like structures (Figure 5), which was seen distributed on MoS_2 sheet having a width in 0.5 - 0.8 µm range (Figure 6).

Conclusion and Future Scope

We have developed a MoS_2 - Zincon complex platform which can be useful for Zn^{2+} ions detection. We synthesized MoS_2 micro sheet using hydrothermal method and successfully functionalized it with Zincon. Zincon was complexed with MoS_2 because of π-π interaction. All UV-Vis, FTIR, and SEM images establish the complex formation of MoS_2 - Zincon sheet. As Zincon has a large complex constant with Zn so this composite can be very useful for the detection of Zn quantity in human serum that is directly related to PCa.

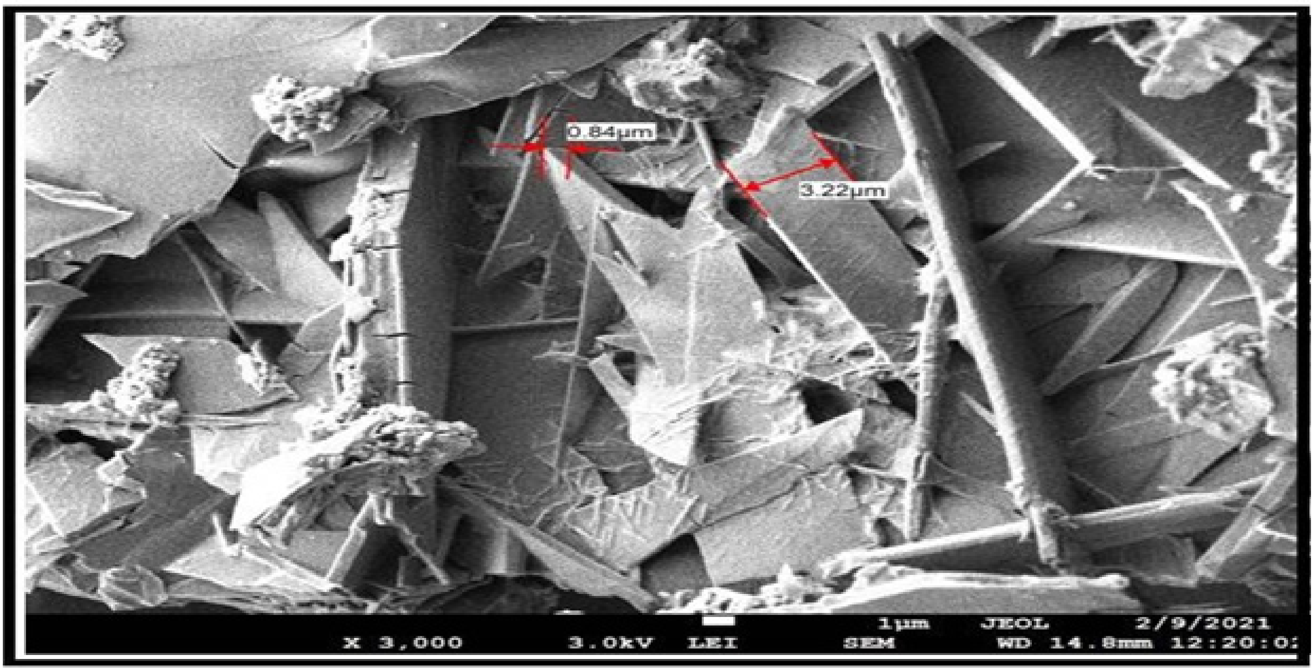

Figure 6: SEM images of MoS_2 - Zincon complex.

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