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Wet Chemical Synthesis and Optical Characterization of Manganese Sulfide Nanostructures

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ABSTRACT

In the present work, manganese sulfide nanoparticles were synthesized by chemical precipitation technique. UV-Visible spectrophotometer was used to determine the optical properties of MnS particles. The prepared particles displayed absorption maximum at 300 nm and band gap energy of about 3.6 eV. Other optical parameters, including the transmittance and absorption coefficient, were also determined using numerical equations. Electron microscopy (EM) images indicated that the prepared particles had a spherical shape with an average size of ~23 ± 1.1 nm. In addition, the FFT results suggested that the crystal structure of MnS NPs is hexagonal wurtzite.

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INTRODUCTION

Transition metal sulfides (TMS) nanomaterials have attracted a great deal of interest because of their special structure, electronic and optical properties. [1, 2]. Various applications are proposed in different fields such as catalysis, energy storage, optoelectronics and biomedicine. One of the significant p-type metal sulfides semiconductors is manganese sulfide (MnS), which possesses a large tunable band gap value of ~ 3 eV (visible-light region) [3]. It is regarded as an eco-friendly and sustainable material because of its low toxicity and utilization of elements that are abundant on Earth. At the same time, MnS nanostructures show pronounced absorption of visible light which makes it suitable for use in photocatalysis, optothermal technologies and for implementation within advanced optoelectronic devices. [3] Investigation on the optical properties of MnS NPs is very important for understanding its optical band gap, which governs amount of absorbance and emitting nature in the material. Moreover, they enable a deeper understanding of light-matter interactions at the nanoscale including surface-state contribution, quantum confinement effect, and exciton generation which are crucial to

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fabricate high-performance devices and catalysts [4]. These optical properties are generally investigated through different techniques such as UV-Vis spectroscopy, photoluminescence, and time-resolved technique generating qualitative and quantitative information about electronic transition energy-levels in the MnS NPs.

Manganese sulfide (MnS) features different crystal phases, such as α-MnS, β-MnS, and γ-MnS that have unique physical properties and chemical activity therefore, it is necessary to control its crystalline phase, particle size and morphological structure [5, 6]. Several synthetic methods have been developed for the preparation of MnS nanoparticles including hydrothermal, solvothermal and precipitation methods, but also green synthesis protocols [7-9]. Among these, chemical precipitation is the most commonly used because of its simplicity and being cost effective [10]. This approach provides the possibility to control the above particle growth and shape by tuning parameters like precursor concentration, temperature, pH, and addition of capping or coating agents [11].

MnS nanostructures are prepared in a facile and effective chemical precipitation method, and their structural constitution and optical properties are extensively investigated in this work. This effort is a spotlight with the method to correlate the preparation conditions, studies of the band gap and optical absorption properties changes shown above prove that MnS nanostructures may be used as multi-functional material of great significance to contemporary medical and engineering applications.

MATERIALS AND METHODS

To prepare MnS nanoparticles all the chemicals with 99% purity was used. Manganese chloride (from QualiKems Fine Chem), sodium sulfide Na_2S (from THOMAS BAKER), and sodium hydroxide (from CDH) were employed as starting materials. Deionized water was used as a medium for the reaction and for washing purpose.

Characterization

Both the size and morphology of MnS particles were determined using field emission scanning electron microscope (FESEM) and transmission electron microscopy (TEM) (Zeiss Model Sigma VP). The optical properties were measured using UV–Vis spectrophotometer (UV-1800 Shimadzu spectrophotometer, Japan) with a wavelength range of 200- 600 nm. To confirm the formation of the Mn-S bond, FTIR (IRAffin-ity-1S, SHIMADZU) was used.

Methodology

Preparation of MnS nanoparticles

Two solutions of Na_2S and $MnCl_2$ were prepared

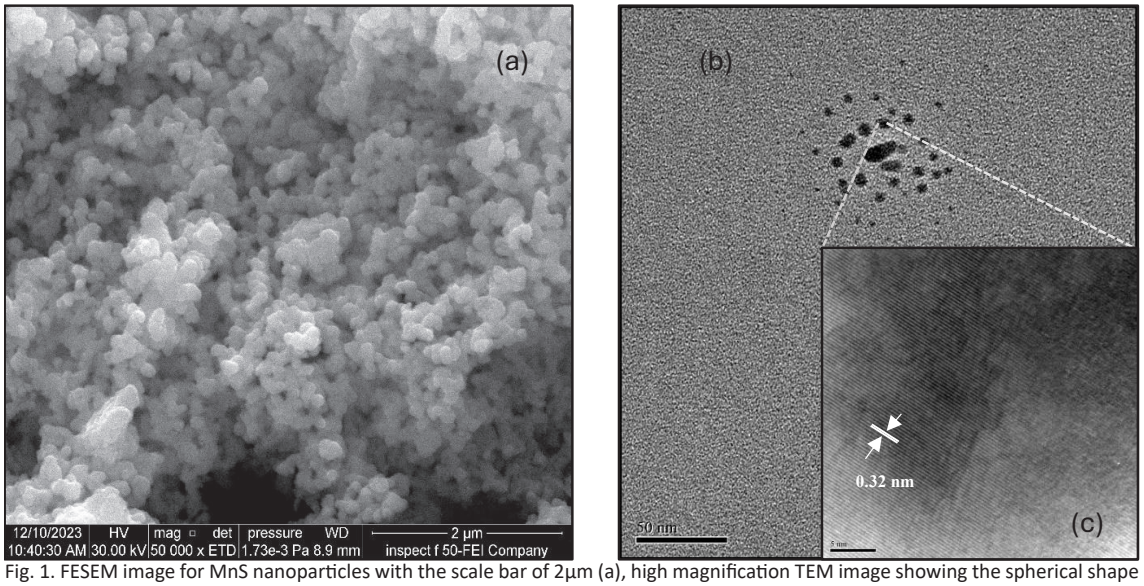

Fig. 1. FESEM image for MnS nanoparticles with the scale bar of 2µm (a), high magnification TEM image showing the spherical shape of MnS particles (b), and the inset shows an expanded view for MnS particle with the distance between adjacent planes of *d* = 0.32 nm.

separately by weighing 0.005 g of each salt and dissolving in 100 mL of deionized water, followed by stirring on a magnetic stirrer for half an hour to ensure complete dissolution and homogeneity. Sodium sulfide solution was slowly added to the manganese chloride solution under continuous stirring at 25 °C. The pH of the solution was adjusted to 9 by the addition of 0.1M NaOH. The mixture was then stirred for an additional one hour to facilitate complete reaction and nanoparticles growth. The resulting suspension was subjected to centrifugation at 4000 rpm for 25 minutes to separate the precipitated nanoparticles. The obtained product was then filtered, washed twice with deionized water to remove unreacted precursors, and subsequently dried in an oven at 100 °C for 2 hours**.**

RESULTS AND DISCUSSION

Structural properties of MnS nanoparticles

The morphology of the prepared MnS particles were studied using electron microscopy. It is clear from the FESEM image in Fig. 1a that MnS nanoparticles are nearly spherical with an average diameter of ~23 ± 1.1 nm. TEM image in Fig. 1b also showed that MnS particles have spherical shape. The crystalline structure of MnS particles was studied using Fast Fourier Transform (FFT) measurements from the ImageJ program as shown in the insert in Fig. 1c. The average distance between two neighbouring crystalline planes is found to be d = 0.32 nm, which complies with the spacing of the (111) plane of the hexagonal wurtzite structure. The calculated distance between MnS lattice fringes is consistent with the interplanar distance reported in previous studies [12].

Fourier transform infrared (FTIR)

The FTIR spectrum (Fig. 2) shows distinctive vibrational properties that conform the successful production for MnS. The low-frequency range between 500 and 600 cm^{-1} has a substantial absorption band, which is crucial for Mn–S stretching vibrations [13] confirming the formation of manganese sulfide. This finding which is consistent with previous findings on transition metal sulfides.[14] A large absorption band at around 3400 cm^{-1} is ascribed to O–H stretching vibrations, which are caused by hydroxyl groups and surface-adsorbed water molecules· H–O–H bending vibrations of water are attributed to a smaller band at about 1600 cm^{-1} [10].

Optical features of MnS nanoparticles

Absorbance

The first optical property for MnS nanoparticles was conducted is the optical absorption. As shown

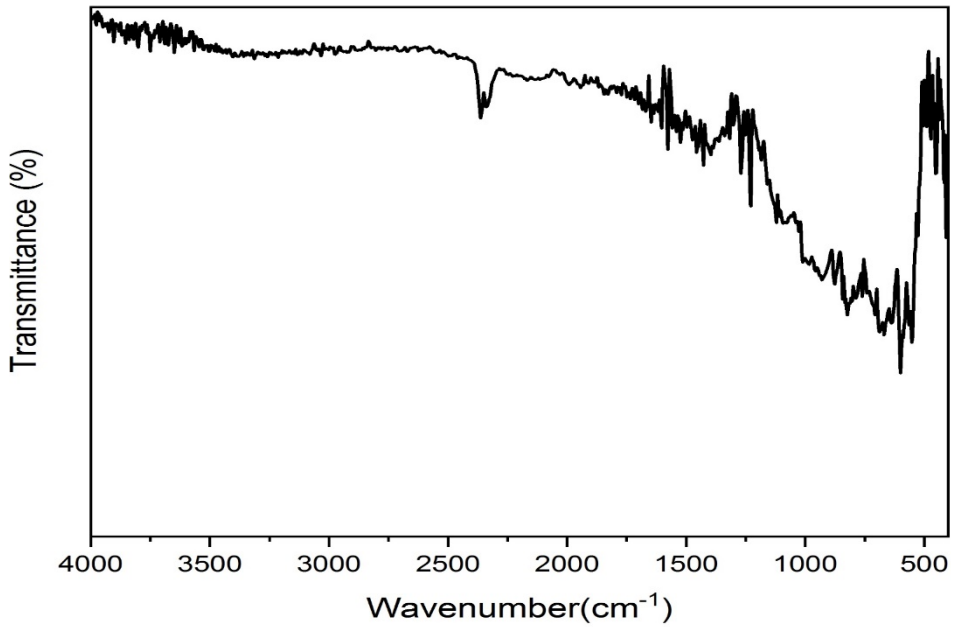

Fig. 2. FTIR spectrum for MnS nanoparticles showing the formation of Mn-S bond.

from Fig. 3a, the UV–Vis absorption spectrum of the MnS nanoparticles shows a strong absorption peak at 300 nm. This peak points to the impact of quantum confinement effects, which are frequently seen when particle sizes reach the nanoscale level. Compared to bulk MnS, the absorption edge shifts toward shorter wavelengths in such structures because the electronic energy levels become distinct and the particle become smaller in size. On the other hand, a weak tail in the visible spectrum can be a sign of localized states or surface defects in the band gap, which can trap photons and affect photocatalytic activity. The optical band gap of the prepared MnS nanoparticles was estimated from Tauc equation [15, 16]. The extrapolation of the linear part of the UV-Vis curve in Fig. 3b gives band gap value of 3.6 eV, which is higher than that of bulk MnS 3.1 eV [17].

Transmission spectrum

The transmittance spectrum of MnS nanoparticles (Fig. 4) demonstrates a progressive rise in transmission as wavelength increases between 200 and 550 nm. The transmittance is quite low at shorter wavelengths (200–300 nm), which is consistent with significant UV absorption. The π → π* electronic transitions of MnS are compatible with the material's ability to absorb

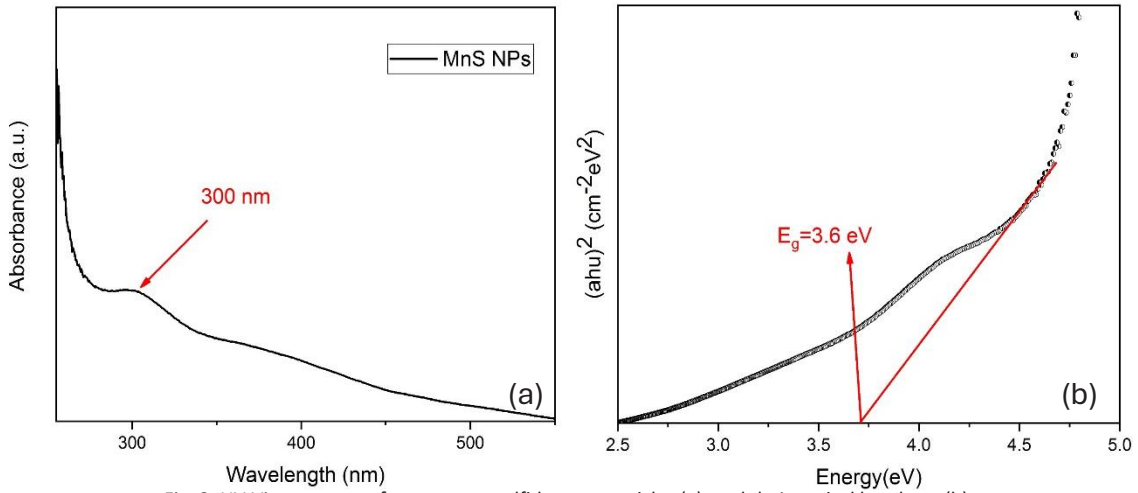

Fig. 3. UV-Vis spectrum of manganese sulfide nanoparticles (a), and their optical band gap (b).

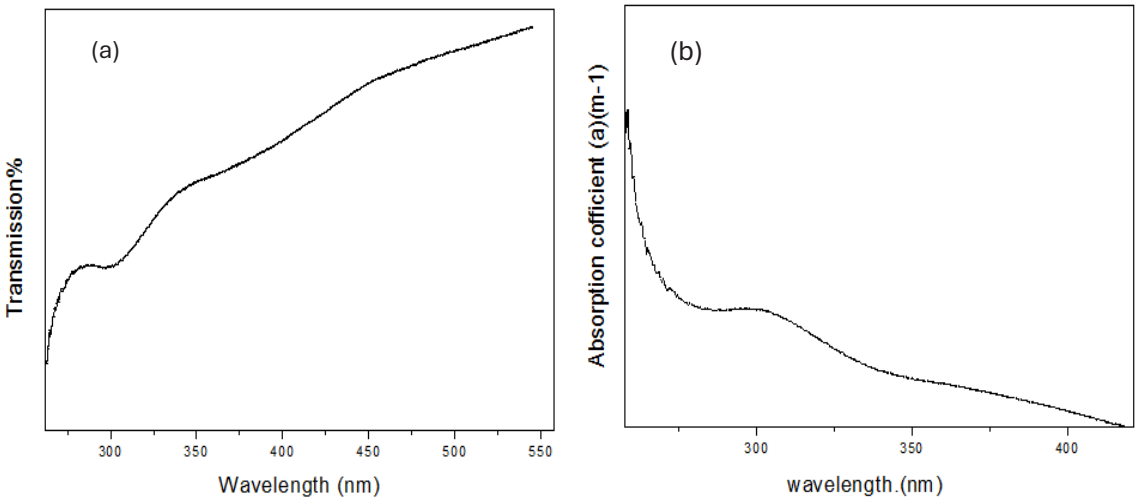

Fig. 4. Transmission spectrum of MnS particles (a) and the absorption coefficient of MnS particles formed by chemical precipitation method (b).

high-energy photons [11, 18].

A discernible rise in transmittance is seen between 300 and 400 nm. This transition area can be utilized to estimate the band gap energy and correlates to the optical absorption edge of MnS. When the wavelength passes 400 nm, the transmittance keeps increasing and obtains the maximum at ~550 nm in the visible range. This behavior indicates: simulation wavelength of the material is increased, it becomes more transparent to let pass visible light [19].

The absorption coefficient (α)

The absorption coefficient spectrum of MnS nanostructures (Fig. 4b) reveals a significant peak at roughly 300 nm, showing that the material absorbs most effectively in the ultraviolet region of the electromagnetic spectrum. This significant absorption at shorter wavelengths is often linked with electronic transitions from the valence band to the conduction band, which correspond to the inherent band gap energy of MnS. The position of this absorption edge gives an information for measuring the optical band gap, and its strength reflects the density of permitted electronic states and the crystallinity of the nanoparticles [20].

CONCLUSION

Manganese sulfide nanoparticles was prepared using simple and low-cost chemical precipitation method with manganese chloride and sodium sulfide as starting materials. FESEM image showed that MnS particles possess a spherical shape with an average diameter of ~23 ± 1.1 nm. According to the HRTEM image, the prepared particles exhibit a hexagonal wurtzite crystal structure with an interplanar spacing of d = 0.32 nm. The optical properties were studied using UV-Vis spectroscopy, it was found that MnS nanoparticles have a band gap of 3.6 eV, which is greater than of bulk MnS 3.1 eV, indicating a clear quantum confinement effect.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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