## Antibacterial and Optical Activities of Microwave Aided Zn<sub>2</sub>SnO<sub>4</sub> Nanorods

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(Received 10 January 2021; revised manuscript received 14 June 2021; published online 25 June 2021)

The zinc stannate ( $Zn_2SnO_4$ ) nanorods were synthesized via facile microwave assisted method using ammonia with cubic spinel structure. The crystallography and optical properties were studied using X-ray diffraction (XRD) and photoluminescence spectroscopy (PL). The morphology of the nanoparticles was observed using field emission scanning electron microscopy (FESEM). The antibacterial effect of  $Zn_2SnO_4$  nanoparticles tested against Gram-positive and Gram-negative pathogenic bacteria were investigated.

Keywords: Antibacterial activity, Zinc stannate, PL, Nanoparticles, Nanoarchitectonics.

DOI: 10.21272/jnep.13(3).03002 PACS number: 61.46.Km

#### 1. INTRODUCTION

The Zn<sub>2</sub>SnO<sub>4</sub> an inverse structure of AB<sub>2</sub>O<sub>4</sub> compound (space group Fd3m), has fascinated and unique properties rendering it suitable for a wide variety of applications such as chemical sensors, photoelectrical devices, transparent conducting electrodes, functional coatings and photocatalysts [1-3]. And also, as an important transparent semiconductor with wide band gap of 3.6 eV, Zn<sub>2</sub>SnO<sub>4</sub> is known to have high chemical sensitivity, high electrical conductivity and low visible absorption [4]. In order to realize the universal application of nanomaterials, the key point is to devise simple and efficient methods for their preparation on a large scale at low cost. Various methods have been employed to produce Zn<sub>2</sub>SnO<sub>4</sub> nanostructures such as mechanochemical synthesis, thermal evaporation method by heating metal or metal oxide powder at high temperatures, simple co-precipitation method and hydrothermal synthesis [5-7].

Metal oxide nanoparticles (NPs) are the most widely used antimicrobial agent in the food industry applications [8]. Gram positive and Gram-negative microorganisms are mentioned [9]. The antimicrobial activity of  $\rm Zn_2SnO_4$  NPs is mainly based on the following mechanisms: (a) release of  $\rm Zn^{2+}/Sn^{2+}$  ions which bind to electron donor groups in molecules containing sulphur, oxygen, or nitrogen, (b) disruption of DNA replication and (c) oxidative stress through the catalysis of reactive oxygen species (ROS) formation [10]. ROS contain the most reactive hydroxyl radical (OH), the less toxic superoxide anion radical ('O<sub>2</sub>-') and hydrogen peroxide with a weaker oxidizer ( $\rm H_2O_2$ ). This can damage DNA, cell membranes, etc., leading to cell death [11].

In the present work,  $Zn_2SnO_4$  nanorods were prepared by a microwave assisted method. The structural properties of the nanorods were characterized in detail. In addition, further development of wide range of optical behavior of  $Zn_2SnO_4$  nanorods and the antibacterial activity were also investigated.

#### 2. EXPERIMENTAL METHODS

## 2.1 Synthesis

The subsequent high purity chemicals such as zinc (II) nitrate, tin (II) chloride dihydrate and ammonia solution were used as precursors without further purification.

 $Zn_2SnO_4$  nanoparticles were prepared in different ratios of Zn and Sn (2:1, 1:1 and 1:2) by microwave-assisted precipitation method. Zinc (II) nitrate and tin (II) chloride aqueous solutions (50 ml) of appropriate amount were prepared and stirred together for 1 h 20 min to get a homogeneous mixture. Then ammonia solution was added to get a white precipitate and stirred at room temperature for 15 min. The product solution was transferred to a polypropylene capped autoclave bottle and the solution was irradiated by a microwave oven with the power of 600 W for 10 min. After irradiation, the solution was allowed to cool down naturally to room temperature. The schematic diagram for the preparation of  $Zn_2SnO_4$  nanorods is shown in Fig. 1.

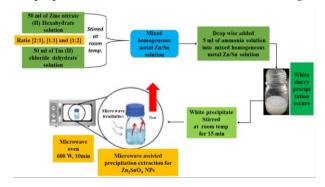


Fig. 1 – Schematic diagram for the formation of  $\mathrm{Zn_2SnO_4}$  nanorods

## 2.2 Antibacterial Assays

The antibacterial activity of microwave assisted Zn<sub>2</sub>SnO<sub>4</sub> nanorods was tested against *Streptococcus* pneumoniae, *Escherichia coli*, *Klebsiella pneumoniae* and *Shigella dysenteriae bacterial strain* were carried

 $The\ results\ were\ presented\ at\ the\ International\ Conference\ on\ Innovative\ Research\ in\ Renewable\ Energy\ Technologies\ (IRRET-2021)$ 

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out in agar by well diffusion method. The antibacterial activity was tested at a concentration of 1 and 1.5 mg/ml of the  $Zn_2SnO_4$  nanorods dispersed in dimethylsulphoxide (DMSO). The zone of inhibition levels (mm) was measured subsequently after 24 h at 37 °C. For positive control, standard antibiotic Amoxicillin (30 µg disc) was used.

#### 2.3 Characterization Techniques

The structural properties were investigated from the X-Ray diffraction patterns obtained using X'PERT PRO Panalytical Diffractometer. The morphology of Zn<sub>2</sub>SnO<sub>4</sub> nanorods was examined by FESEM (Carl Zeiss Ultra 55) with EDAX (Inca). The functional groups were analyzed from FT-IR spectra in the range of 400-4000 cm<sup>-1</sup>. Photoluminescence (PL) spectra were taken using a spectrometer JASCO spectroflurometer FP-8200 to study the optical properties.

#### 3. RESULTS AND DISCUSSION

#### 3.1 FESEM Analysis

The surface morphology of microwave assisted synthesis of all  $\rm Zn_2SnO_4$  nanorods was examined through FESEM analysis is shown in Fig. 2a, b. FESEM images clearly show the synthesized  $\rm Zn_2SnO_4$  exhibits, rod like structure and average particle size in the nanoscale range. The formation of nanorods may be due to two reasons such as crystal nucleation and crystal growth direction. The growth mechanism of  $\rm Zn_2SnO_4$  nanorods can be explained in terms of chemical reactions and crystal growth, as follows. From the crystallization point of view, the synthesis of an oxide during an aqueous solution reaction is expected to experience a hydrolysis-condensation process. Growth of  $\rm Zn_2SnO_4$  nanorods occurs according to the reaction.

$$Zn(s) \xrightarrow{\Delta} Zn(g)$$

$$Sn(s) \xrightarrow{\Delta} Sn(g)$$

$$2Zn(g) + Sn(g) + 2O_2 = Zn_2SnO_4(s).$$
(a)
(b)
(c)

Fig. 2 – (a), (b) SEM images of  $Zn_2SnO_4$  nanorods

#### 3.2 Photoluminescence Spectroscopic Studies

The photoluminescence spectra of microwave assisted  $\rm Zn_2SnO_4$  nanorods are shown in Fig. 3 (P1-P3). The  $\rm Zn_2SnO_4$  nanorods measured at the excitation wavelength of 460 nm. The two blue-green emission, four green emissions, and orange-yellow emission are located at (484, 499, 508, 519, 526, 541, 555, 566, and 584 nm), (484, 498, 508, 523, 540, 551, 566, and 582 nm) and (484, 499, 509, 519, 526, 541, 555, 566, and 579 nm) for P1, P2 and P3, respectively. The blue-green emission found to be (484-499 nm) for all  $\rm Zn_2SnO_4$  nanorods, which is attributed to oxygen vacancies [16, 17]. The green emission observed at (508-

551 nm) for P1, P2 and P3 samples respectively, usually the oxygen vacancies existing in  $Zn_2SnO_4$  [18, 19]. The yellow-orange emission centered at (566 nm and 579 nm) for  $Zn_2SnO_4$  nanorods respectively, due to the interaction between oxygen vacancies, tin interstitials and oxygen interstitials can be accountable for the yellow-orange emission [20], and defects has formation of a huge number of trapped states and sum of meta stable energy levels in the band gap of the as-synthesized  $Zn_2SnO_4$  NPs.

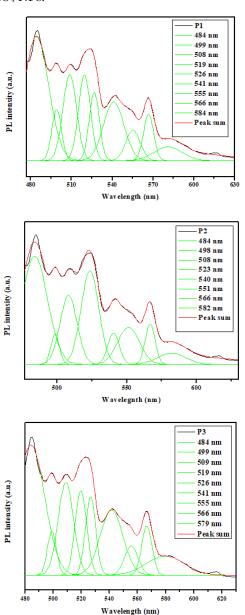


Fig. 3 – PL spectra of Zn<sub>2</sub>SnO<sub>4</sub> NPs

However, for the P3 sample, green emission values (579 nm) increased as compared to the P2 (582 nm) and P1 (584 nm) for Zn<sub>2</sub>SnO<sub>4</sub> nanorods samples, respectively. From the optoelectronic application generally depends on decrease in defect level, which in mainly influenced via electron phonon coupling interaction. In the present work, the P3 samples emission decreased as compared to P1 and P2 samples, this results sustenance for the future development of optoelectronic application.

#### 3.3 Antibacterial Activity

Fig. 4a, b shows antibacterial activity of microwave assisted Zn<sub>2</sub>SnO<sub>4</sub> NPs tested against Streptococcus pneumoniae, Escherichia coli, Klebsiella pneumoniae and Shigella dysenteriae bacterial strains to determine by the well diffusion method. Zn<sub>2</sub>SnO<sub>4</sub> NPs and amoxicillin show the antibacterial activity, which clearly shows the inhibition zone and specifies the biocidal action of Zn<sub>2</sub>SnO<sub>4</sub> NPs. The maximum zone of inhibition was observed E. coli as compared to the other S. pneumoniae, K. pneumoniae and S. dysenteriae bacterial strain (Fig. 5). In the present work, increasing the concentration (P3) of Zn<sub>2</sub>SnO<sub>4</sub> NPs the inhibition zone also gets increased.

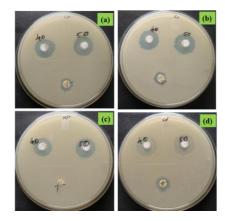


Fig. 4 - Progressive antibacterial activity of G+ and G- bacteria

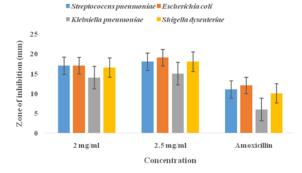


Fig. 5 – Zone of inhibition for various bacterial strain treated with  $\rm Zn_2SnO_4~NPs$ 

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The antibacterial activity generally depends on production of reactive oxygen species (ROS) [21-23]. This ROS on the surface of these nanoparticles in light causes oxidative stress in microbial cells membrane, ultimately leading to the death of the cells.

The ROS production can be given in equation form as the following:

$$Zn_2SnO_4 + h\nu \rightarrow e^- + h^+$$
  
 $h^+ + H_2O \rightarrow OH + H^+$   
 $e^- + O_2 \rightarrow O_2^-$   
 $O_2^- + H^+ \rightarrow HO_2^-$   
 $HO_2^- + H^+ \rightarrow H_2O_2^-$ 

The Zn<sub>2</sub>SnO<sub>4</sub> nanorods through defects can be activated via both UV and visible light, electron-hole pairs  $(e^-h^+)$  can be created. The holes fragmented H<sub>2</sub>O molecules hooked on  $OH^-$  and  $H^+$ . Dissolved  $(O_2)$  can be converted to  $({}^{\cdot}O_2 {}^{-})$  radical anions. The  $({}^{\cdot}O_2 {}^{-})$  superoxide radical anions in turn react with H+ to create (HO2') radicals. The hydrogen ions (H+) react with (HO2·) to produce molecules of H<sub>2</sub>O<sub>2</sub>. The production of H<sub>2</sub>O<sub>2</sub> be able to penetrate the cell membrane and finally the bacteria die [24]. On the other hand,  $Zn^{2+}/Sn^{2+}$  ions released by  $Zn_2SnO_4$  come into contact with microbial cell membranes, cell membranes with (-) charge and Zn<sup>2+</sup>/Sn<sup>2+</sup> ions with (+) charge mutually attract. The Zn<sup>2+</sup>/Sn<sup>2+</sup> metal ions penetrate hooked on the cell membrane and react by sulfhydryl groups inside the cell membrane. As a result, the microbe synthetase activity is damaged and cells lose their ability to divide cells, which leads to the death of bacterial cells.

### 4. CONCLUSIONS

In summary, the Zn<sub>2</sub>SnO<sub>4</sub> nanorods were prepared and XRD patterns showed that synthesized nanorods exhibits spinel cubic structure. Nanorod-like morphology and chemical composition were observed through FESEM and EDAX spectra. In case of FT-IR spectra, the Zn-Sn-O stretching bands were observed at 502, 475 and 460 cm<sup>-1</sup> for all Zn<sub>2</sub>SnO<sub>4</sub>.

#### **ACKNOWLEDGEMENTS**

Authors are grateful to the Management of Wollega University, Ethiopia and Academy of Maritime Education and Training Deemed to be University, India.

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# Антибактеріальна та оптична активність нанострижнів Zn<sub>2</sub>SnO<sub>4</sub>, синтезованих під дією мікрохвиль

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Нанострижні станату цинку  $(Zn_2SnO_4)$  синтезували простим методом з використанням мікрохвиль, застосовуючи аміак з кубічною структурою шпінелі. Кристалографію та оптичні властивості вивчали за допомогою рентгенівської дифракції (XRD) та фотолюмінесцентної спектроскопії (PL). Морфологію наночастинок спостерігали за допомогою автоелектронної скануючої мікроскопії (FESEM). Досліджено антибактеріальну дію наночастинок  $Zn_2SnO_4$ , протестованих проти грампозитивних та грамнегативних патогенних бактерій.

**Ключові слова:** Антибактеріальна активність, Станат цинку, Фотолюмінесценція (PL), Наночастинки, Наноархітектоніка.