# Zno: Sno<sub>2</sub> Nano-Composite by Laser Ablation Method to Fight Diseases-Causing Bacterial and Fungi

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#### **Abstract**

Nano-particles of zinc oxide (ZnO) and tin oxide (SnO2) have been produced by the process of pulsed laser ablation in water. the optical, structural, morphological, and of all samples (ZnO, SnO2, and ZnO: SnO2 composite) Nano-particles were examined by employing UV-Vis spectroscopy, X-ray diffraction (XRD), atomic force microscopy, and evaluation of anti-bacterial and antifungal properties respectively. The XRD patterns demonstrate that generated ZnO Nano-particles are nano-Ocrystalline and have a hexagonal wurtzite structure, whereas the structure of tin oxide is tetragonal rutile. It was discovered that the direct optical energy gap of each and every sample fell somewhere in the range of (4.8), (4.8), and (4.9) eV, respectively. Anti-bacterial and antifungal activities can be observed in the Nano-particles that were produced. Keywords: ZnO, SnO2, laser ablation, zinc oxide, nano-composite, anti-bacterial, antifungal

#### 1. Introduction

Since nanotechnology has been employed to manufacture particles with dimensions in the nanometer range, the anti-bacterial capabilities of zinc oxide Nano-particles (also known as ZnO-NPs) have garnered a lot of interest from researchers all over the world. microbes can range in size from hundreds of nanometers to tens of micrometers. There are many different kinds of microbes in this range. ZnO is an example of a semiconducting II-VI metal oxide that has a broad band gap of 3.37 eV. ZnO-NPs offer very appealing features from an anti-bacterial standpoint. Because of their larger specific surface area and smaller particle size, which together lead to an increased particle surface reactivity. SnO<sub>2</sub> is an n-type material that has a band gap that ranges from 3.5 to 3.6 eV. ZnO and SnO<sub>2</sub> are two potential materials that could be used in a variety of applications. ZnO and SnO<sub>2</sub> can be mixed together to produce a wide variety of composite materials, such as ZnO/ SnO<sub>2</sub>, ZnSnO<sub>3</sub>, Zn2SnO<sub>4</sub>, as well as Zn-doped SnO<sub>2</sub> and Zn-doped ZnO. There have been numerous ZnO/SnO2 structures developed, such as nano-fibers, nano-rods, and Nano- flowers [1-5]. Nanosized linked ZnO- SnO<sub>2</sub> composites are crucial in many domains of chemistry, physics, and solid state physics due to the size-dependent physical and chemical properties that they exhibit [6]. Using coupled oxides like ZnO and SnO<sub>2</sub>, which are both n-type semiconductors, could improve charge separation and expand the photooxidation energy range. This would result in changes to optical properties like band gap, refractive index, and extension coefficient, all of which are essential for optoelectronic applications [7-9]. It is

properties believed that investigating the composites will be advantageous because the recombination of electron hole pairs, which is directly related to the properties of the material, can be easily modified by the connection of two types of semiconductors with differing band gaps [10]. Both of these materials are notable for their excellent optical transparency and low resistance throughout the visible spectrum, as well as their enormous band gaps. In addition, the high chemical stability of these compounds makes them particularly well-suited for use in applications involving semiconductors. In this research, we have described the production of ZnO,SnO2 NPs and ZnO:SnO2 by nanosecond Nd:YAG laser ablation of samples target immersed in distilled water at room temperature. Additionally, we have studied the characteristics of these compounds and evaluated their anti-bacterial and antifungal activities.

# 2. Experimental part

In the initial step of the process, the two powders of zinc and tin were thoroughly ground by a ceramic grinder and filtered into very small particles. After this, they were pressed with 5 tons for ten minutes to produce a solid pellet that had a diameter of 1.5 centimeters. In the second step, a Nd: YAG laser of type HUAFEI, operating at 1064 nanometers with a pulse duration of 250 nanoseconds, was used. Each pellet was positioned at the bottom of a glass container that held 5 mL of distilled water. The process of ablation was carried out at a standard pressure and in open air, using a laser with an energy output of 480 mJ per pulse for a duration of ten

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minutes in order to produce nanoparticles, as shown in figure 1. A colloidal solution taken with a ratio of 1:1 , mixed with a magnetic stirrer for an hour at a temperature of 40 degrees Celsius, and then placed in an ultrasonic machine for an hour in order to generate a more homogeneous colloidal solution of ZnO: SnO $_2$  nano-composite, as shown in figure 1.

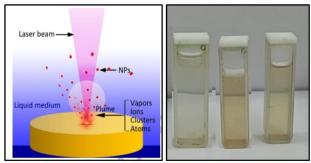


Figure 1: Schematic diagram of laser ablation method and samples (on left SnO<sub>2</sub>, ZnO and ZnO: SnO<sub>2</sub> composite)

## 3. X-ray diffraction of samples

X-ray diffraction (XRD) is a technique that uses an X-ray diffractometer (Model Brucker D-8with Nickel filtered Cu K (wavelength = 0.15404 nm) radiation in order to examine the phase formation and purity of ZnO-NPs that were generated using plus laser ablation method and deposited on substrate using drop casting method. According to the results of the XRD examination, there were three different diffraction peaks located at 31.2, 34.0, and 47.1, which corresponded to (100), (002), and (102) (figure 2a) .In accordance with the hexagonal crystalline structure of ZnO, each and every peak in the diffractogram has been assigned an index. These findings are in accordance with the Standards, JCPDS No. (36-1451). The Shrrer equation was used to determine that the average grain size of the zinc oxide Nano-particles that were generated in the process of pulse laser ablation was 39.94 nm. [11,12]. The diffraction pattern of SnO<sub>2</sub> peaks can be seen at (110), (211), and at a 2 diffraction angle of 26, 51.8 degrees in successive order in the XRD results of the SnO2 sample shown in Figure (2b).

Cassiterite crystal phase with tetragonal rutile structure (JCPDS No. 41-1445) [13]. These peaks correspond to the cassiterite crystal phase. Crystals that are, on average, 53.5 nanometers in size. The XRD patterns of the ZnO: SnO2 composite are displayed in Figure (2c). Crystalline ZnO has been successfully grown on the exterior of the SnO2 nanoparticles, as can be observed. This was a very important step in the process. where the findings of the XRD analysis showed that the typical peaks of SnO2 and ZnO Nano-particles are located at 26.4 and 31.0 respectively. [14].

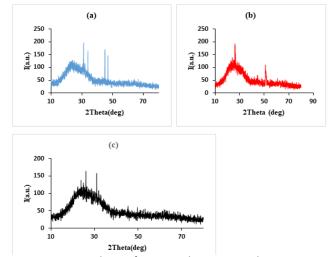


Fig.2: XRD analysis of (a)-ZnO,(b)- SnO2 and (c)-ZnO: SnO2 thin films.

Figure(3a-c) shows two-dimensional images of the surfaces of zinc oxide and tin oxide films prepared by laser ablation and deposited on glass bases by droplet casting method, with four drops on each substrate at a temperature of 80 °C, and left to dry completely for an hour. We note Nano-particles of different sizes and within the nanoscale distributed over the surface is in the form of peaks to the top with a spherical and semi-spherical shape, and others have pointed peaks. We notice in the composite film that the particles are lined up horizontally in the form of peaks, and the concentration and size of the particles are larger. Perhaps the reason is due to a larger number of interacting particles during the preparation process.

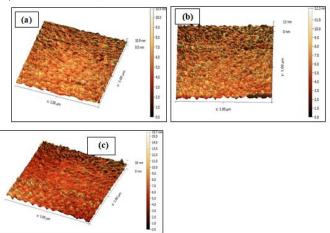


Figure 3: AFM image of (a)-ZnO,(b)-SnO2 and (c)-Zn:SnO2 composite.

FTIR spectroscopy is typically utilized for the purpose of verifying the presence of various organic

and inorganic species, in addition to OH groups. ZnO, SnO<sub>2</sub>, and Zn:SnO<sub>2</sub> composite nanoparticles'

FTIR spectra were recorded at room temperature using the KBr pellet technique, and the resulting spectra are presented in Figure (4). The wavelength range covered by the spectrum is 4000–500 cm-1. The O–H antisymmetric stretching vibration of water molecules on the surface of ZnO, SnO<sub>2</sub>, and composite is the cause of the absorption band that can be seen at 3439,3440, and 3435 cm-1 respectively. The band that is centered at 677 cm-1 is attributable to the vibrations of tin oxide [18,19].

The band that is found at 1636,1637 cm-1 is due to the bending vibration of water molecules [15-17]. The stretching vibrations of ZnO nano particles are shown by the peak at 674 cm-1, which may be seen in composite samples, where it is noted that the major bonds do not change and that there is no appearance of a new bond. The results of the XRD experiment can be connected with the IR bands' findings, which show that ZnO and SnO<sub>2</sub> Nanoparticles have formed [20,21].

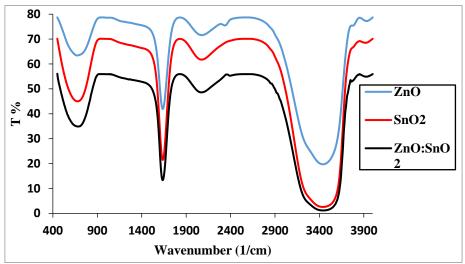


Figure 4: FT-IR spectra of ZnO,SnO2 and ZnO:SnO2 composite.

Table 2: summary of FTIR spectra of ZnO,SnO2 and ZnO:SnO2 nano-composite.				
Samples	wavenumber (cm <sup>-1</sup> )	Type of bond		
ZnO	3439.07	O-H		
	2074.97	C-N		
	1636.96	O-H		
	674.08	Zn-O		
SnO₂	3440.07	O-H		
	2073.72	C-N		
	1637.36	O-H		
	677.34	Sn-O-Sn		
ZnO: SnO₂ Composite	3435.94	O-H		
	2070.07	C-N		
	1636.20	O-H		
	688.00	Sn-O-Sn Zn-O		

The UV-Visible near IR absorption spectrum was used to explore the optical characteristics of ZnO, SnO<sub>2</sub>, and ZnO: SnO<sub>2</sub> that were synthesized by plus laser ablation. The wavelength range for this investigation was 200-1100 nm. The UV-visible absorbance spectra of ZnO, SnO, and Zn: SnO<sub>2</sub> are depicted in figure 5.It was noticed that the absorbance decreased at wavelengths greater than 250 nm; hence, all of the samples are transparent in this region, which is where they can be used in a variety of applications involving semiconductors. Plasmon resonance is a phenomena that is found to take place when there is a modest peak at a wavelength of about 250 nanometers, which indicates the production of particles on the nanoscale. The fact that the peak in the composite sample was split into two smaller peaks suggests the existence of distinct particles (ZnO and SnO<sub>2</sub>,

specifically). It is anticipated that the absorbance will be influenced by a number of parameters including the band gap, the oxygen shortage, and the surface roughness. It is anticipated that small particle size will result in quantum confinement effects, which can be observed as a blue shift of the optical absorption edge due to a widening of the band gap in the ultraviolet range. The Tauc's relation, which was utilized in the process of calculating the bandgap for ZnO, SnO<sub>2</sub>, and Zn: SnO<sub>2</sub> samples, is depicted in Figure (6a-c). The optical energy gap can be found by determining where the tangential line intersects with the h axis. It takes 4.8 and 4.9 eV to bridge the energy gap between ZnO, SnO, and the ZnO: SnO<sub>2</sub> composite. This broad band-gap range is owing to the small size of the nanoparticles, which is why the method results in a significantly greater band gap (the quantum size

effect)[22,23]. The research that has been done on this topic makes it abundantly clear that a smaller particle size is correlated with a larger band gap. There is a good chance that the energy levels of the Nano-particles are influenced by additional factors one of which is the lattice strain [21].

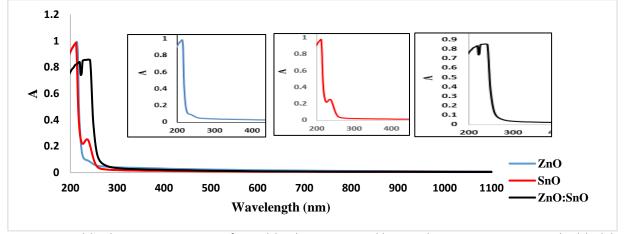
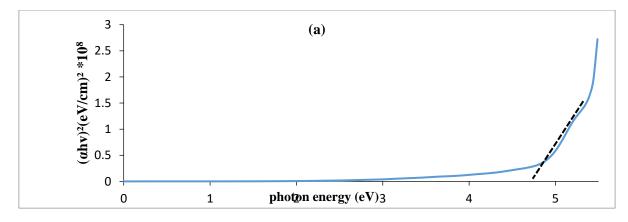
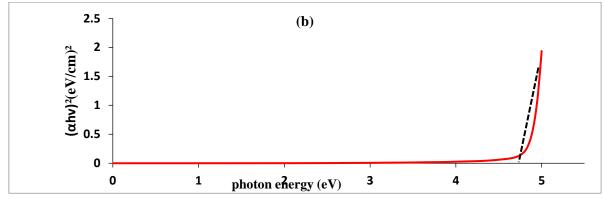


Figure 5: UV-visible absorption spectrum of ZnO (blue line), SnO2 (red line) and ZnO: SnO2 nano-particles(black line).





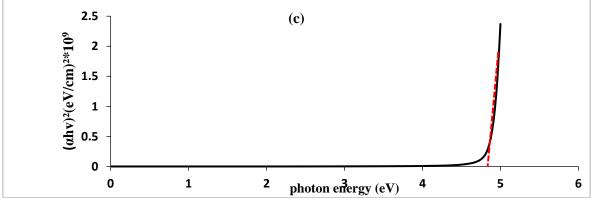


Figure 6: Graph showing the energy band gap of (a)-ZnO,(b)- SnO2NPs and(c)- ZnO: SnO2 composite.

Table 3: the values of energy gap of samples.				
E <sub>g</sub> of ZnO	E <sub>g</sub> of SnO2	E <sub>g</sub> of ZnO: SnO2		
4.8 eV	4.8eV	4.9eV		

In most cases, bacteria may be recognized by the fact that the cells that make up their bodies contain cytoplasm, a cell wall, and a cell membrane. The great majority of the cell wall can be located on the surface of the cell that is not covered by the cell membrane. This particular portion of the cell wall is a layer of homogenous peptidoglycan that is made up of amino acids and sugars. The osmotic pressure that is found within the cytoplasm is due to the fact that the cell wall is responsible for both the maintenance of the characteristic shape of the cell as well as the presence of the cell wall. Gram-positive bacteria possess a single cytoplasmic membrane that is made up of numerous layers of peptidoglycan polymer and a cell wall that ranges in thickness from 20 to 80 nanometers. Additionally, these bacteria have an outside membrane that is constructed of peptidoglycan polymer. Gramnegative bacteria, on the other hand, have a cell wall that is made up of two cell membranes: an outer membrane and a plasma membrane that has a thin coating of peptidoglycan that is between 7 and 8 nanometers thick. These membranes are separated by a peptidoglycan layer that is between 7 and 8 nanometers thick. These size ranges of NPs are easily able to penetrate through the peptidoglycan, which results in severe harm being done to the cell. The cytoplasm is a fluid that has a viscosity similar to jelly and contains all of the components of a cell with the exception of the nucleus. Cytoplasm may be found inside of every cell in the body. This organelle is responsible for carrying out the processes of replication and growth in addition to its role in metabolism. Because of this, the cytoplasm is almost entirely composed of water (about 80% of its overall composition), as well as salts, ions, proteins, carbohydrates, and nucleic acids. This composition makes a contribution toward the improvement of the cellular structure's electrical conductivity [24], which is a positive outcome. The bacterial cell membranes found on the outside of the cell have a net negative charge. Figure 7 is a representation of the cellular architecture that bacteria possess. According to The American Heritage Medical, the process by which bacterial multiplication is stopped or hindered is referred to as anti-bacterial activity. You may also consider it in terms of the overall amount of surface area that is in contact with the bacteria. . Anti-bacterial pharmaceuticals are medications with a specific concentration that, despite being able to hurt or limit the development of bacteria, are safe for the host and do not pose any risk to them in any way. Anti-bacterial pharmaceuticals are an example of this type of drug. These chemicals have the potential to be employed as chemotherapeutic drugs, meaning that they can either treat bacterial infections or prevent them from occurring. The ability of an anti-bacterial agent to either kill bacteria or stop their growth is what determines whether or not the agent is bactericidal or bacteriostatic. Bactericidal agents kill bacteria, whereas bacteriostatic agents prevent germs from growing. The anti-bacterial and antifungal activity of ZnO, SnO<sub>2</sub> nanoparticles, and ZnO: SnO<sub>2</sub> nano-composite on the microorganism gram negative and gram positive as well as one strain of fungus (candida) was tested and

analyzed (Figures 8-10). The results showed that ZnO and SnO2 Nano-particles inhibited the growth of the microorganisms. As can be seen in figures 8-10, all of the nanomaterials that were produced by the laser ablation method were proved effective against grampositive and gram-negative bacteria, as well as fungus. This was deduced from the presence of inhibitory zones. Gram-negative bacteria cultures show a lower amount of growth inhibition when exposed to ZnO, SnO2 nanoparticles, and ZnO: SnO2 nano-composite. This is likely due to the more complex cell walls that gramnegative bacteria cultures have. Gram-negative bacteria cultures distinguished by this from their gram-positive counterparts. The anti-bacterial activity of the ZnO: SnO<sub>2</sub> composite material improved as a direct result of an increase in the concentration of Nano-particles in the material. Because of this, a higher concentration of Nano-particles is required for an action that is relevant in terms of its bactericidal effects. SnO<sub>2</sub>NPs were found to be more effective than ZnONPs and the ZnO: SnO<sub>2</sub> nano-composite while the test was being conducted in the fungal inhibitory zone. The results are summarized in table (2) below. According to some reports, Nanoparticles have the ability to kill bacteria in two distinct ways: first, by disintegrating and producing reactive oxygen species, as demonstrated in figure (11), and second, by electrostatically interacting with the cell walls of bacteria. Because of these interactions between bacterial cells and nanostructures, zones of inhibition (ZOI) are produced in the region surrounding the nanomaterials. The magnitude of the zone of inhibition (ZOI) is directly proportional to the bactericidal activity of the Nano-particles [25-29].

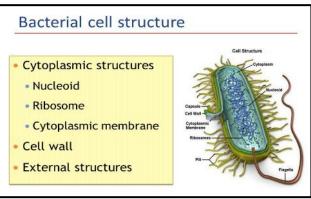


Figure 7: shows bacterial cell structure.

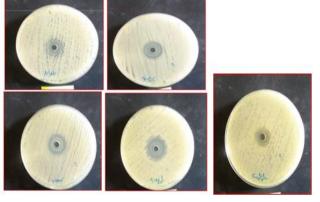


Figure8: shows the inhibition zone of bacterial and fungi for ZnONPs

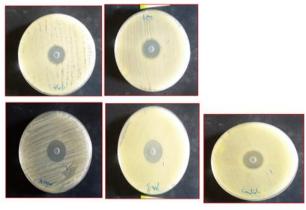


Figure9: shows the inhibition zone of bacterial and fungi for SnO2NPs



Figure 10: shows the inhibition zone of bacterial and fungi for ZnO:SnO2NP-composite.

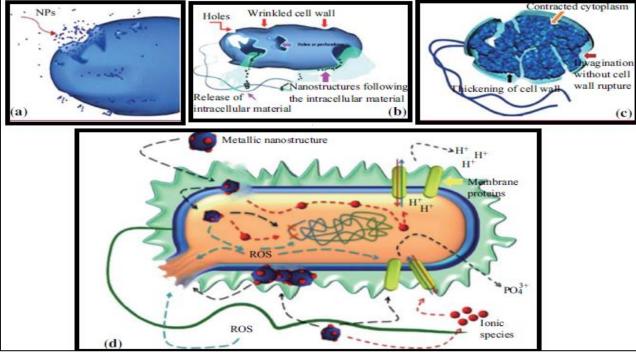


Figure 11: Schematic diagram showing possible mechanism of anti-bacterial activity.

Table 4: Diameter of inhibition zone					
Types	SnO2NPs	ZnONPs	ZnO: SnO2 nano-		
	(mm)	(mm)	composite(mm)		
Klebsiella sp.	18	16	17		
E-Coli	19	20	19		
Stap. aur.	22	20	23		
Stap. empid.	21	21	23		
Candida	20	15	17		

### 4. Conclusion

The different morphologies of NPs have a substantial impact on the level of toxicity they exhibit. It has been shown that the shape of ZnO and SnO2 nanostructures can have an effect on their process of internalization [30,31]. For example, rods and wires are more able to penetrate the cell walls of bacteria than spherical structures. ZnO and SnO2 are both able to highly absorb UV light [32], and ZnO has a better response to UV light than SnO2 does. As a result, its conductivity dramatically

improves, and this property significantly stimulates the contact that ZnO has with bacteria. This results in an increase in the production of ROS since the energy gap is quite substantial. also Surface imperfections have a significant impact on the toxicity of both ZnO and snO2. For instance, the anti-bacterial action of ZnO-NPs or SnO2 is owing to the membrane injury induced by defects such as edges and corners, which results from the abrasive surface of ZnO or SnO2. This injury causes ZnO-NPs or SnO2 to have an anti-bacterial effect.

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