

Synthesis SnO₂ Nanoparticles by Different Plasma Technique and using it as Antibacterial

Saif E.Muslim¹ and Ahmed K. Abbas²

^{1,2} College of Science ,Wasit University, Wasit,Iraq

Email: saife@uowasit.edu.iq

Email: aalzubaidi@uowasit.edu.iq

Cite this paper as: Saif E.Muslim and Ahmed K. Abbas (2024) Synthesis SnO₂ Nanoparticles by Different Plasma Technique and using it as Antibacterial. *Frontiers in Health Informatics*, 13 (4), 564-573

Abstract

In this study, a good comparison was made regarding the nanoparticles prepared by different plasma methods, as the SnO₂ nanoparticles were obtained by the techniques of and APPJ also PLA. In a plasma jet system, a noble gas such as argon is used, One of the electrodes is connected to the material to be deposited, which is immersed in water, In PLA, the material is vaporized by laser ablation , causing the ablated material to form nanoparticles that dissolve in solutions. The samples were thoroughly characterized using different advanced technique, including X-ray diffraction (XRD) for phase identification and crystallographic structure analysis, (FESEM) for surface morphology examination, (TEM) for detailed nanostructure visualization. Nanoparticles have been utilized in the biological field, with those prepared by both techniques demonstrating effectiveness as bacterial inhibitors.

Keywords: Pulsed Laser Ablation (PLA), Atmospheric Pressure Plasma Jet (APPJ).SnO₂ nanoparticles, XRD.FESEM, Antibacterial.

Introduction

Metal oxide nanoparticles (NPs) synthesized using simple techniques have gained significant importance over the past years [1,2]. The metal oxide nanoparticles with diverse properties contributes to improvement of the devices to get new applications. Recently, the use of these particles has gained increasing importance in areas such as optoelectronics, sensors, antibacterial applications and photo catalysis. [3].

Tin oxide (SnO₂) has 3.6 MeV band gap and it is an n-type semiconductor , making it suitable for more applications of potential . [4] SnO₂ is an ideal choice for applications like, lithium-ion batteries, gas sensors , and catalysts for the oxidation of organic compounds, as well as electrodes in solid state ion device . SnO₂ is characterized by its chemical stability, mechanical rigidity, and heat resistance. [5,6,7,8]. Its effectiveness in these applications is based on a crystalline nanostructure with homogeneous pores [9 ,10].

Metal oxide nanoparticles have been found to be effective inhibitors of bacterial strains. The antimicrobial effectiveness of these particles is influenced by several factors, including size of particle, the light presence, and The contents of the medium of aqueous used in the tests . Nanoparticles attach to bacteria through electrostatic interactions, disrupt the integrity of the bacterial membrane of cell, and release toxic free radicals that induce oxidative stress within the bacterial cells. [11-12]. Employing biomolecules as templates in the synthesis of inorganic nanoparticles is an efficient approach to produce functional materials with specific structures and dimensions. DNA stands out as an ideal biological template due to its physical and chemical stability and unique structure[13,14,15].

Non-thermal plasma is utilized in nanoparticle synthesis due to its capability to facilitate chemical reactions at low temperatures.. This technology enables the production of stable nanoparticles with precise sizes without the need for high temperatures, thus preserving the properties of nanomaterials and making them useful for a wide range of application .

Plasma reactions generate plasma either at the surface or in liquids, with reactive species like ions and electrons dissolving at the liquid-plasma interfaces. These reactive species can be used to develop a many applications in medicine and nanotechnology[16,17]. Before ten years, plasma reactions have emerged as an effective approach for synthesizing both non-metallic and metallic nanoparticles at atmospheric pressure. [18,19]. The liquid plasma process is characterized by the production of nanoparticles with small size and lower energy consumption at room temperature, as the dissolved reactive species directly catalyze chemical reactions, which distinguishes it from conventional methods.

Pulsed Laser Ablation (PLA) is a precise method for removing material from solid surfaces using short, high-energy laser pulses. The laser energy causes rapid heating, melting, and vaporization of the target material, resulting in the ejection of atoms, ions, and molecules. PLA is widely used in various applications encompassing thin film deposition, nanomaterial fabrication, and surface modification techniques. The process offers precise control over the material removal and can be conducted in various environments, such as vacuum, gas, or liquid, making it highly versatile for both research and industrial purposes.[20]

1. Experimental details

2.1 Preparation nanoparticles

In the Atmospheric Pressure Plasma Jet (APPJ) technique, plasma is generated by passing argon gas at a flow rate of 3 L/min through a nozzle connected to one of the electrodes, which is powered. The second electrode is in contact with a metal piece measuring 1 cm x 4 cm, from which nanoparticles are to be formed. As illustrated in the figure below, the metal piece is immersed in 3 ml of distilled water, and an electrical potential difference of 15 kV is applied. The distance between the metal and the plasma jet is maintained at 2 cm through 10 min[21].

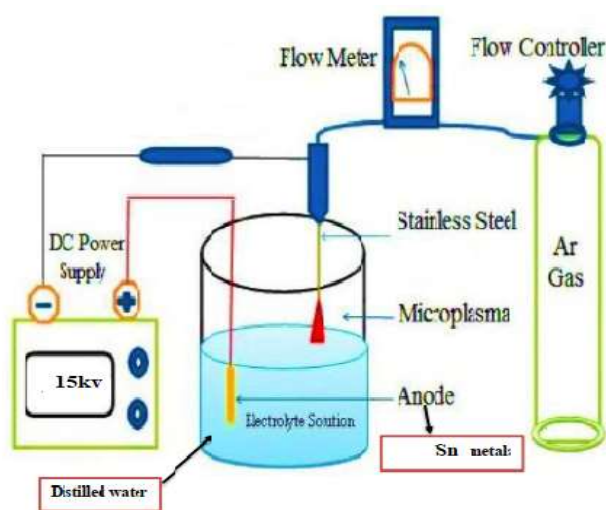


figure1: APPJ system

Furthermore, during operation, the nanoparticles are formed as oxides due to the synthesis process being carried out in distilled water.

On the other hand, nanoparticles are synthesized using laser ablation (PLA). In this process, a 1 cm x 1 cm metal piece is placed in a flask and immersed in 3 ml of distilled water. The Nd-Yag laser is set to 6 Hz frequency, 1064 nm wavelength, with 400 mJ laser energy, and delivers 300 pulses. The laser is positioned perpendicularly above the sample, at an angle of 180 degrees. The separation between the sample and the laser nozzle is approximately 10 cm, figure 2 shows PLA system. Similar to the previous technique, the synthesis in water results in the formation of metal oxides[22].

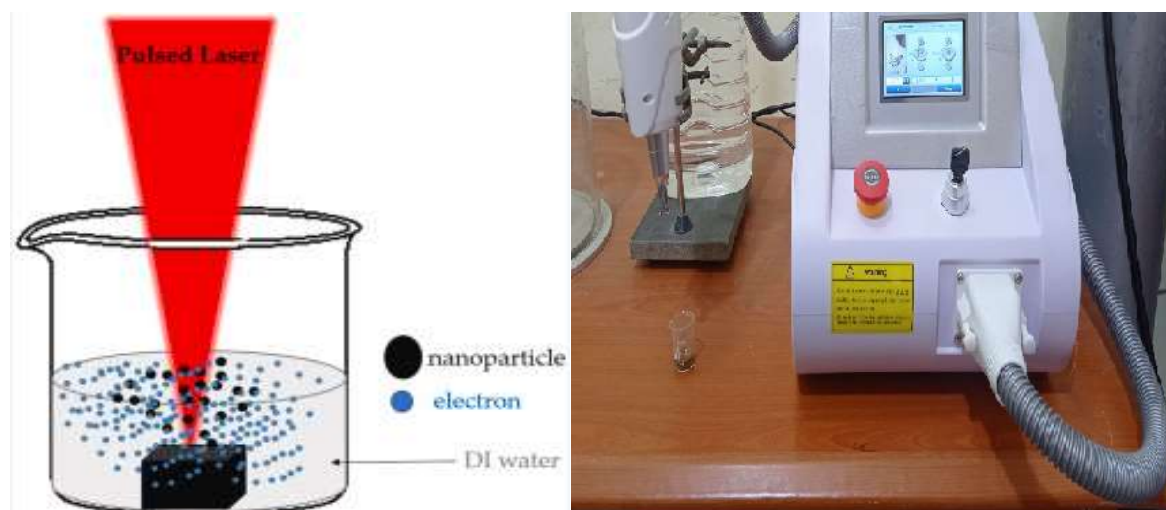


Figure 2 pulsed laser ablation system(PLA)

2.2 Characterization of nanoparticles

The samples were prepared using Atmospheric Pressure Plasma Jet (APPJ) and Pulsed Laser Ablation (PLA) techniques, both involving solutions containing nanomaterials. A portion of these solutions was deposited on a substrate using a hot plate for further testing, including (XRD) and (FESEM). To investigate the crystal structure was analyzed using a SHIMADZU 6000 X-ray diffractometer system. And also Field Scanning Electron Microscope (FE-SEM) Measurements It is used to obtain atomic-scale photographs of materials and is an important tool in nanotechnology. The (TEM) test, was one of the important tests that were carried out for nanoparticles prepared from elements using the (APPJ) and (PLA) method, in order to learn more details about the material, such as the grain size and shape of the formed particles in distilled water.

2.3 Antibacterial tests

2.3.1 preparation of concentration (dilution)

After preparing the NPs of SnO_2 , the initial concentrations were calculated for each specimen by (AAS) and by unit (ppm) a dilution process has used to obtain different concentrations to measure the effect and effectiveness of each concentration on the selected bacteria (where four concentrations were selected for each sample).

2.3.2 Prepare of Mueller Hinton agar

Muller-Hinton (M-H) agar is prepared by adding 38 grams of the powder to 1 liter of distilled water, followed by heating on a burner with continuous stirring until fully dissolved. For 15 minutes, sterilize the M-H solution by autoclaving at 121°C . After that, the solution allowed to be 50°C before being poured into petri dishes and left for about 15 minutes to solidify. Once solidified, the plates are flipped upside down and kept in at 4°C .

2.3.3 Antibacterial Activity

The antibacterial activity of the fabricated samples (SnO_2 NPs produced via Atmospheric Pressure Plasma Jet (APPJ) and Pulsed Laser Ablation (PLA)) was evaluated against 1g-negative and 1g-positive bacterial strains utilizing the agar well diffusion technique. Approximately 20 mL of Mueller-Hinton (MH) agar was aseptically allocated into sterile Petri dishes. By using a sterile wire loop, bacterial strains were obtained from their corresponding stock cultures. Subsequent to the culturing procedure, wells with a diameter of 6 mm were formed in the agar plates using a sterile tip. Various concentrations of the samples (SnO_2 synthesized via (APPJ) and SnO_2 produced by (PLA) methods) were then introduced into the wells. The plates cultured with the

samples and test organisms were incubated overnight at 37°C. Afterward, the mean diameters of the inhibition zones were assessed and recorded.

3.Resulte and discussion

The sample that prepared by APPJ technique showed crystal structure of peak position at(26.50°, 33.70°, 37.50°, 52.80°), indicating coefficient for (110), (101), (200),(211), directions respectively which matched with the SnO₂ reference . Also found in the figure (3) below, The sample prepared using the PLA technique exhibited a crystalline structure with peak positions at 26.55°, 33.85°, 52.80°, and°, corresponding to the (110), (101), and (211) planes, respectively.

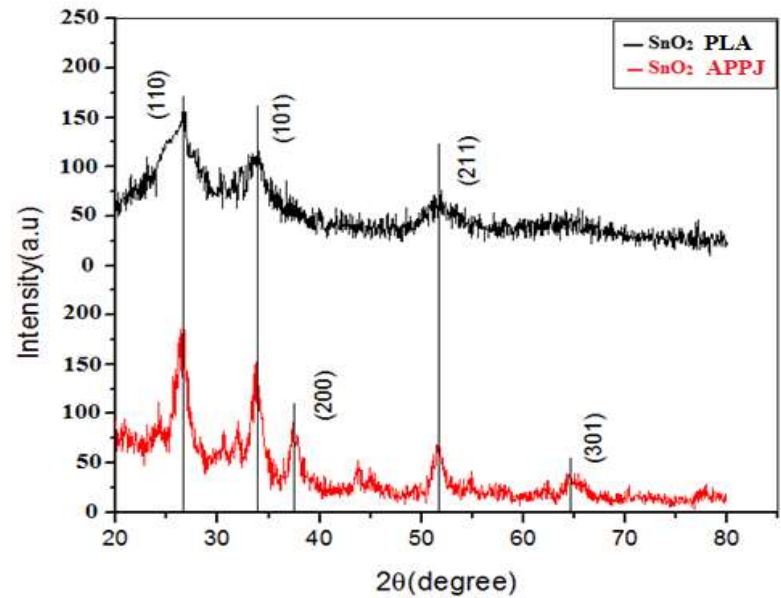


Figure3:XRD patterns of SnO₂ prepared by PLA and APPJ.

The difference in X-ray diffraction (XRD) results between samples prepared by PLA and APPJ lies primarily in the crystal size and structural quality. Samples synthesized using the APPJ method generally exhibit sharper diffraction peaks, indicating larger and more well-defined crystalline structures . In contrast, samples produced via PLA tend to show smaller particle sizes, table 1 as shown ,and potential distortions in the crystal lattice , likely due to the rapid cooling process associated with laser ablation, which can introduce internal stresses and defects[28].

Table 1: Structural parameters of SnO₂ Nano oxide between two methods.

Method	hkl	2θ (Deg.)	FWHM (Deg.)	d _{hkl} Exp.(Å)	C.S (nm)
PLA SnO ₂	(110)	26.55	4.70	3.35	1.74
	(101)	33.85	3.23	2.65	2.57
	(211)	52.25	2.28	1.75	3.88
APPJ SnO ₂	(110)	26.50	1.68	3.36	4.86
	(101)	33.70	1.35	2.66	6.15
	(200)	37.50	1.06	2.40	7.91
	(211)	43.80	0.28	2.07	30.58
	(301)	65.40	1.37	1.43	6.89

The FESEM image of SnO_2 nanoparticles prepared by PLA technology with 400 mJ laser in a liquid medium shows in figure it is clear that these nanoparticles have a regular spherical shape and a homogeneous size. The measured particle diameters were in the range of (22.94–30.71) nm. And The other sample of the same oxide, prepared using the APPJ method, exhibited an almost spherical shape with non-homogeneous nanoparticles, having diameters ranging between 24.51 and 31.77 nanometers.

It is clear that the nanoparticles prepared using the APPJ technique have larger diameters. This is mainly due to the interaction of the plasma with the material, which leads to the agglomeration of the particles or their generation in a larger size[29], While the agglomeration is less in PLA[30].

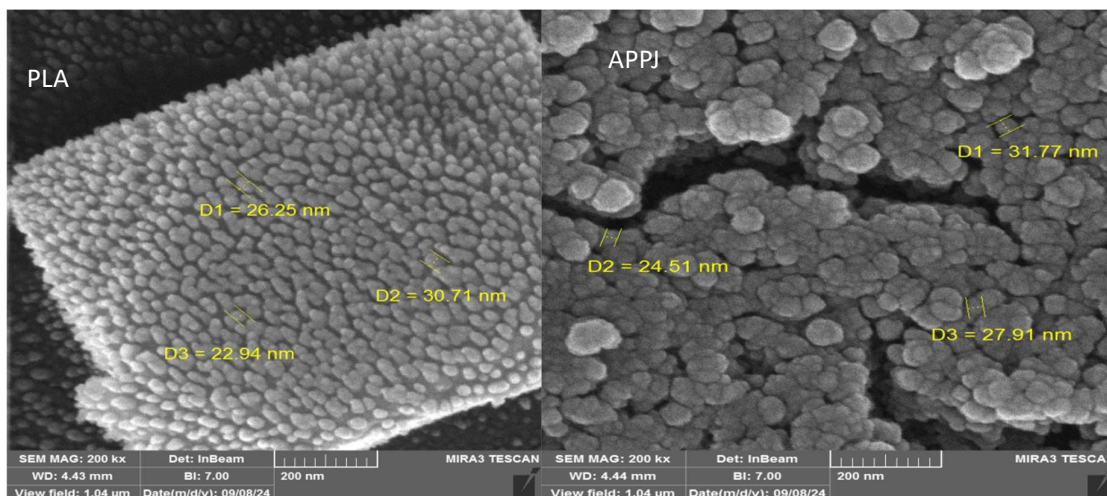


Figure 4: FESEM images for SnO_2 Prepared by PLA and APPJ techniques

TEM was utilized to characterize the shape and size of the SnO_2 NPs (produced via (APPJ) (PLA)) synthesized in distilled water, as illustrated in Figures 5 and 6.

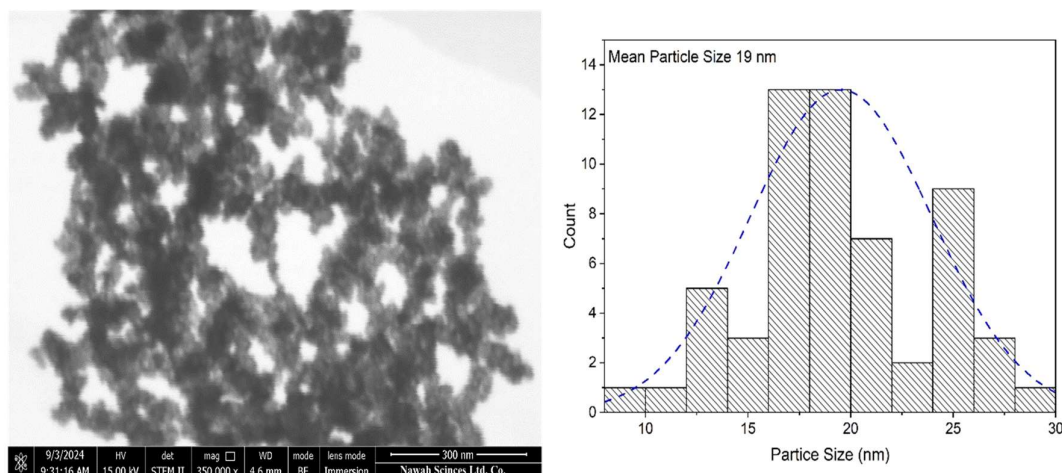


Figure5: TEM and histogram of (PLA SnO_2)

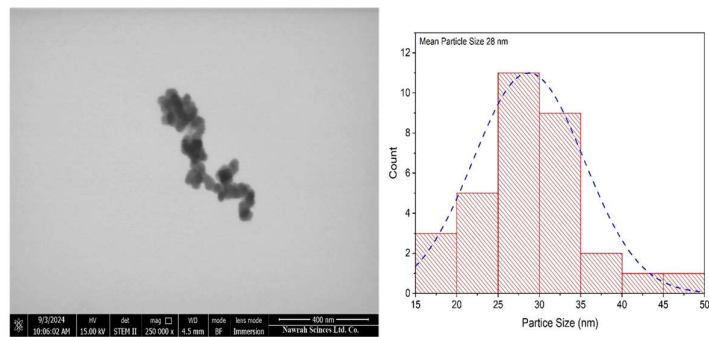


Figure6: TEM and histogram of (APPJ SnO₂)

TEM images of samples prepared using APPJ and PLA techniques of the prepared of SnO₂ showed information related to shape and size, as well as clusters and agglomerations of particles of different shapes, but the distinct particles showed quasi-spherical shapes with nanoscale sizes[31][32].

The AAS analysis was carried . Table (1) shows the concentrations for nanoparticles prepared in distil water by APPJ and PLA techniques for SnO₂,

Table 2 The concentration of samples prepared by APPJ and PLA

sample	Concentration ppm
SnO ₂ (PLA)	2.3
SnO ₂ (APPJ)	26.6

It is clear that the concentration of particles produced by the APPJ method is much higher than that of those produced by the PLA method. This is due to Plasma energy or electrical discharge intensity increases the concentration of nanoparticles, providing more energy to break up the target material and stimulate chemical reactions. as well as the larger area exposed to the reaction[33].

Figures (7) and (8) shows the degree of bacterial inhibition, where within the four diluted concentrations (12.5, 25, 50, 100) ppm of (SnO₂) samples, (E.Coli) bacteria show an inhibition zone.

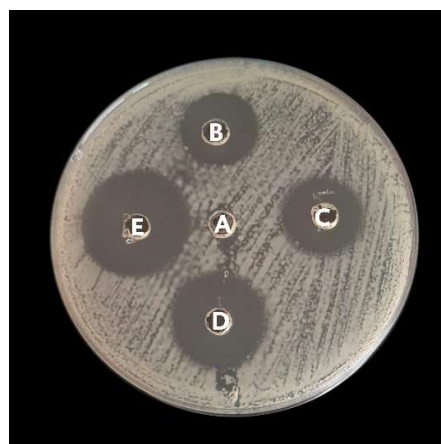
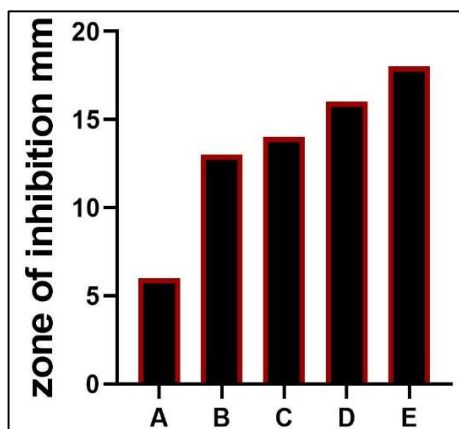


Figure7: Antibacterial activity of (SnO₂ PLA) against *E.coli*. A, Control. B, 12.5 %. C, 25 %. D, 50 %. E, 100 %.

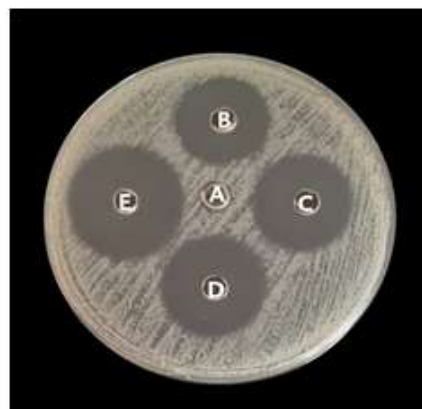
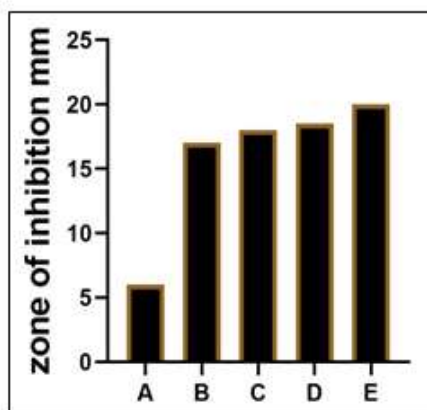


Figure8: Antibacterial activity of (SnO₂ APPJ) against *E.coli*. A, Control. B, 12.5 %. C, 25 %. D, 50 %. E, 100 %.

It is evident from Table 3 below that the bacterial inhibition rate of the sample prepared using the APPJ technique is higher than that of the sample prepared using the PLA technique. This can be attributed to the difference in nanoparticle concentrations, as confirmed by analysis AAS. The results indicate that inhibition increases with increases nanoparticle concentrations[34].

Table (3) Explain the antibacterial activity of nanoparticles

sample		A	B	C	D	E
<i>E.coli</i>	SnO ₂ PLA	6	13	14	16	18
	SnO ₂ APPJ	6	17	18	18.5	20

4.Conclusions

It is concluded that the nanoparticles synthesized using the Atmospheric Pressure Plasma Jet (APPJ) technique exhibit a slightly larger size compared to those produced via Pulsed Laser Ablation (PLA). This difference in size is primarily due to the aggregation phenomena that occur during the plasma interaction, which generates solutions with a higher concentration of nanoparticles in contrast to those synthesized by PLA. The enhanced energy delivered by the plasma and the extensive interaction area are significant contributing factors

to this outcome. Furthermore, the present work indicate that the antibacterial efficacy is concentration-dependent; specifically, an increase in nanoparticle concentration correlates with an increasing in bacterial inhibition.

References

- [1] Brillson L, Cox J, Gao H, Foster G, Ruane W, Jarjour A, Allen M, Look D, von Wenckstern H, Grundmann M. Native point defect measurement and manipulation in ZnO nanostructures. *Materials*. 2019 Jul 12;12(14):2242.
- [2] Abdullayeva N, Altaf CT, Mintas M, Ozer A, Sankir M, Kurt H, Sankir ND. Investigation of strain effects on photoelectrochemical performance of flexible ZnO electrodes. *Scientific Reports*. 2019 Jul 29;9(1):11006.
- [3] Albert Manoharan A, Chandramohan R, Arun Kumar KD, Valanarasu S, Ganesh V, Shkir M, Algarni H, AlFaify S. Transition metal (Mn) and rare earth (Nd) di-doped novel ZnO nanoparticles: a facile sol-gel synthesis and characterization. *Journal of Materials Science: Materials in Electronics*. 2018 Aug;29:13077-86. and characterization, *J Mater Sci*. 2018; 29(15): 13077–13086.
- [4] Grosse P, Schmitte FJ, Frank G, Köstlin H. Preparation and growth of SnO₂ thin films and their optical and electrical properties. *Thin Solid Films*. 1982 Apr 23;90(3):309-15.
- [5] Vidhu VK, Philip D. Biogenic synthesis of SnO₂ nanoparticles: evaluation of antibacterial and antioxidant activities. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 2015 Jan 5;134:372-9.
- [6] He YS, Campbell JC, Murphy RC, Arendt MF, Swinnea JS. Electrical and optical characterization of Sb: SnO₂. *Journal of Materials Research*. 1993 Dec;8(12):3131-4.
- [7] Vidhu VK, Philip D. Biogenic synthesis of SnO₂ nanoparticles: evaluation of antibacterial and antioxidant activities. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 2015 Jan 5;134:372-9.
- [8] D.E. Williams, P.T. Moseley, B.C. Tofield (Eds.), *Solid State Gas Sensors*, Adam Hilger, Bristol, 1987, p. 71
- [9] Qi L, Ma J, Cheng H, Zhao Z. Synthesis and characterization of mesostructured tin oxide with crystalline walls. *Langmuir*. 1998 Mar 31;14(9):2579-81.
- [10] Vidhu, V. K., and Daizy Philip. "Biogenic synthesis of SnO₂ nanoparticles: evaluation of antibacterial and antioxidant activities." *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 134 (2015): 372-379.
- [11] Sharmila PP, Sagar S, Tharayil NJ. Effect of annealing on optical and antimicrobial properties of zinc oxide nanoparticles. *Nanoscience and Nanotechnology*. 2014;8(8):313-9.
- [12] Bhattacharjee A, Ahmaruzzaman M. A novel and green process for the production of tin oxide quantum dots and its application as a photocatalyst for the degradation of dyes from aqueous phase. *Journal of Colloid and Interface Science*. 2015 Jun 15;448:130-9.
- [13] Amininezhad SM, Rezvani A, Amouheidari M, Amininejad SM, Rakhshani S. The antibacterial activity of SnO₂ nanoparticles against *Escherichia coli* and *Staphylococcus aureus*. *Zahedan Journal of Research in Medical Sciences*. 2015;17(9).
- [14] Sharmila PP, Tharayil NJ. DNA assisted synthesis, characterization and optical properties of zinc oxide nanoparticles. *international journal of materials science and engineering*. 2014;2(2):147-51.
- [15] John N, Somaraj M, Tharayil NJ. Synthesis, characterization and anti-bacterial activities of SnO₂ nanoparticles using biological molecule. *INOP Conference Series: Materials Science and Engineering* 2018 Oct 23 (Vol. 360, p. 012007). IOP Publishing.
- [16] Fridman G, Friedman G, Gutsol A, Shekhter AB, Vasilets VN, Fridman A. Applied plasma medicine. *Plasma processes and polymers*. 2008 Aug 15;5(6):503-33.

- [17] Rumbach P, Witzke M, Sankaran RM, Go DB. Decoupling interfacial reactions between plasmas and liquids: Charge transfer vs plasma neutral reactions. *Journal of the American Chemical Society*. 2013 Nov 6;135(44):16264-7.
- [18] Huang X, Li Y, Zhong X, Rider AE, Ostrikov K. Fast microplasma synthesis of blue luminescent carbon quantum dots at ambient conditions. *Plasma Processes and Polymers*. 2015 Jan;12(1):59-65.
- [19] LIEM NV, LE HONG MA, PHAM HONG MI, NGUYEN T, THUY T, HOA NM, VAN PHU NG. Facile synthesis of carbon quantum dots by plasma-liquid interaction method. *Communications in Physics*. 2017;27(4):311-6.
- [20] Stafe M, Marcu A, Puscas NN. Pulsed laser ablation of solids. Springer, Berlin. 2014;10:978-3.
- [21] Jang HJ, Jung EY, Parsons T, Tae HS, Park CS. A review of plasma synthesis methods for polymer films and nanoparticles under atmospheric pressure conditions. *Polymers*. 2021 Jul 10;13(14):2267.
- [22] Fazio E, Gökce B, De Giacomo A, Meneghetti M, Compagnini G, Tommasini M, Waag F, Lucotti A, Zanchi CG, Ossi PM, Dell'Aglia M. Nanoparticles engineering by pulsed laser ablation in liquids: Concepts and applications. *Nanomaterials*. 2020 Nov 23;10(11):2317.
- [23] Bahjat HH, Ismail RA, Sulaiman GM, Jabir MS. Magnetic field-assisted laser ablation of titanium dioxide nanoparticles in water for anti-bacterial applications. *Journal of Inorganic and Organometallic Polymers and Materials*. 2021 Sep;31(9):3649-56.
- [24] Khashan KS, Abdulameer FA, Jabir MS, Hadi AA, Sulaiman GM. Anticancer activity and toxicity of carbon nanoparticles produced by pulsed laser ablation of graphite in water. *Advances in Natural Sciences: Nanoscience and Nanotechnology*. 2020 Jul 13;11(3):035010.
- [25] Khashan KS, Badr BA, Sulaiman GM, Jabir MS, Hussain SA. Antibacterial activity of Zinc Oxide nanostructured materials synthesis by laser ablation method. *InJournal of physics: conference series* 2021 Mar 1 (Vol. 1795, No. 1, p. 012040). IOP Publishing.
- [26] Jihad MA, Noori FT, Jabir MS, Albukhaty S, AlMalki FA, Alyamani AA. Polyethylene glycol functionalized graphene oxide nanoparticles loaded with nigella sativa extract: a smart antibacterial therapeutic drug delivery system. *Molecules*. 2021 May 21;26(11):3067.
- [27] Mohammed MK, Mohammad MR, Jabir MS, Ahmed DS. Functionalization, characterization, and antibacterial activity of single wall and multi wall carbon nanotubes. *InIOP Conference Series: Materials Science and Engineering* 2020 Mar 1 (Vol. 757, No. 1, p. 012028). IOP Publishing.
- [28] Wang Y, Wei X, Liu JH, Wu CX, Zhang X, Chen ML, Wang JH. Cryogenic laser ablation in a rapid cooling chamber ensures excellent elemental imaging in fresh biological tissues. *Analytical Chemistry*. 2022 Jun 2;94(23):8547-53.
- [29] Prime G, Brenčič K, Mozetič M, Gorjanc M. Recent advances in the plasma-assisted synthesis of zinc oxide nanoparticles. *Nanomaterials*. 2021 Apr 30;11(5):1191.
- [30] Tarasenko N. Pulsed laser ablation synthesis and modification of composite nanoparticles in liquids. *Laser Ablation in Liquids: Principles and Applications in the Preparation of Nanomaterials*. 2012:709-68.
- [31] Ramanathan G, Murali KR. Photocatalytic activity of SnO₂ nanoparticles. *Journal of Applied Electrochemistry*. 2022 May;52(5):849-59.
- [32] Al Baroot A, Elsayed KA, Haladu SA, Magami SM, Alheshibri M, Ercan F, Çevik E, Akhtar S, Manda AA, Kayed TS, Altamimi NA. One-pot synthesis of SnO₂ nanoparticles decorated multi-walled carbon nanotubes using pulsed laser ablation for photocatalytic applications. *Optics & Laser Technology*. 2023 Jan 1;157:108734.

[33] Habib T, Ceroni L, Patelli A, Caiut JM, Caillier B. Impact of Micropulse and Radio Frequency Coupling in an Atmospheric Pressure Plasma Jet on the Synthesis of Gold Nanoparticles. *Plasma*. 2023 Oct 13;6(4):623-36.

[34] Kadhum SA. The Effect of two types of nano-particles (ZnO and SiO₂) on different types of bacterial growth. *Biomedical & Pharmacology Journal*. 2017;10(4):1701.