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Properties Enhancement Of TiO_2/AgO/ZnO Nanoheterostructures Prepared by PLAL Technique for biological application"

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تعزيز خصائص التراكيب النانوية $(TiO_2/AgO/ZnO)$ المحضرة بتقنية PLAL للتطبيقات البايولوجية

رسالة مقدمة الى
مجلس كلية العلوم – جامعة ديالى وهي جزء من متطلبات نيل درجة الماجستير في علوم الفيزياء

من قبل

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Abstract

In this research , Titanium Dioxide (TiO_2), Silver (AgO), Zinc Oxid (ZnO), hybrid Titanium Dioxide and Silver oxide (TiO_2/AgO) nanoparticles and hybrid Titanium Dioxide / Silveroxide/Zinc Oxide (TiO_2/AgO/ZnO) nanoparticles were prepared using pulsed laser ablation in liquids (PLAL) technique. The study examined how different pulse numbers (550, 650, and 800) affected the structural and optical properties of nanoparticles produced in distilled water. A Q-Switched Nd-YAG laser, operating at a wavelength of 1064 nm, and with an ablation energy of 610 mJ, as well as a repetition rate of 1 Hz, was used for the synthesis. The experimental setup the diameter of the laser beams at the focal center (2 mm), and the distance between the subject and the lens (7 cm). The hybridization of the ((TiO_2, AgO, ZnO) NPs, (TiO_2/Ag) ,(TiO_2/AgO/ZnO NPs) was achieved using the volumetric method. The structural features of (TiO_2, AgO, ZnO)hybrid (TiO_2/AgO) and hybrid (TiO_2/AgO/ZnO) were examined using X-ray diffraction. An analysis of silver oxide nanoparticles deposited on glass, conducted with the assistance of Field Emission Scanning Electron Microscopy and Energy-dispersive X-ray spectroscopy, demonstrated a cubic and polycrystalline crystal system, . X-ray diffraction a of a solution containing titanium dioxide nanoparticles on a glass slide indicated the formatted of a crystal system with a quadrangular shape. It was determined that the titanium dioxide particles exist in the rutile form. The analysis also identified that the zinc oxide metal possesses a polycrystalline composition and exhibits a hexagonal shape. Furthermore, . In the state of the (TiO_2/ AgO \ZnO) Nps, a distinct phase for cubic oxide (AgO) is observed, aligning with elevated concentrations of silver oxide content.

The results of (FE-SEM) for samples prepared with Distilled Water (D.W) indicated that the particle sizes of silver oxide nanoparticles (AgO) were 39.1, 62.4, and 23.8 nm, while those of titanium dioxide nanoparticles (TiO_2) were 34.26, 49.04, and 32.1 nm. The particle sizes for zinc oxide nanoparticles (ZnO) were measured at 36.54, 37.86, and 30.54 nm. In the case of hybrid (TiO_2/AgO) nanoparticles, the particle sizes were found to be 44.17, 33.73, and 42.91 nm, while for hybrid (TiO_2/AgO/ZnO) nanoparticles, the particle sizes were reported as 53.58 and 45.15 nm. The EDX results showed the primary components and chemical elements present in the (TiO_2, AgO, ZnO)(TiO_2 / AgO, TiO**2** / AgO/ZnO)nanoparticles.

The FTIR results indicated that the silver oxide nanoparticles consisted of pure functional groups with distinct positions and absorption beam density (AgO NPs). It was found that the absorption peak at the wave number of 468.77 cm-1 resulted from the vibration coupling (Ag-O). Analysis of titanium dioxide nanoparticles indicates that the absorption peak near the wave number of 478.3463 cm-1 is attributed to the vibration coupling (Ti-O), and the absorption peak at around 3450 cm-1

Chapter One

General Introduction & Literature Review

1-1 Introduction

Development of nanoparticles and their unique properties have enabled their wide utilization in both physical and biological applications. This chapter will provide an overview of nanophysics, highlighting these specific properties.

Nanotechnology is an expanding area of research where we use to deal with the materials in Nano-dimension. [1] The field of nanoscience has blossomed over the last twenty years and the need for nanotechnology will only increase as miniaturization becomes more important in areas such as computing, sensors, and biomedical applications. Advances in this field largely depend on the ability to synthesize nanoparticles of various materials, sizes, and shapes, as well as to efficiently assemble them into complex architectures. The synthesis of nanoparticles, however, is a fairly established field as particles of submicron or nanosized dimensions have been synthesized for centuries. [2]

Nanoparticles fall into two categories: mainly organic and inorganic nanoparticles. Organic nanoparticles may include carbon nanoparticles (fullerenes) in other hand, inorganic nanoparticles may include magnetic nanoparticles, noble metal nanoparticles (like gold and silver) and semiconductor nanoparticles (like titanium dioxide and zinc oxide). There is a growing interest in inorganic nanoparticles as they provide superior material properties with functional versatility, have been examined as potential tools for medical imaging as well as for treating diseases due to their size features and advantages over available in chemical imaging drugs agents and drugs. When mesoporous silica combined with molecular machines prove to be excellent imaging and drug releasing systems. Gold nanoparticles have been used extensively in imaging, as drug carriers and in thermo therapy of biological targets [3].

Apart from novel applicability of AgNPs researchers still in search of advance methods to synthesize eco-friendly and coast effective tools to develop AgNPs. As silver posse's broad spectrum potential against bacterial and microbial species which specially utilized in industries it has key role in healthcare systems. Nitrate group of silver potentially responsible for its broad spectrum antibacterial potential and as it convert in to AgNPs surface area is drastically increased which improve microbial exposure time and area . Different techniques are available to synthesize

AgNPs such as physical, chemical and biological. Though chemical method is rapid it utilizes capping agents for synthesis which is costly and produces adverse and toxic effects. This demands development of safe, ecofriendly, coast effective tool for synthesis of AgNPs and focused on biological methods such as green synthesis which is nontoxic and developed using plant origin materials and overcomes disadvantages of earlier approaches. Moreover, use of plant extracts also reduces the cost of microorganism's isolation and culture media enhancing the cost competitive feasibility over nanoparticles synthesis by microorganisms [1].

The physical and chemical properties of TiO2 have been of great interest due to the potential application in photocatalytic, photovoltaic, lithium-ion battery and dye-sensitized solar cell systems. Especially, its characteristic properties in optical and electronic properties, nontoxicity, chemical inertness, and high melting temperatures have drawn extensive research on the ability of semiconductor photocatalyst to promote the photodegradation of various pollutants.4,5 Anatase, brookite, and rutile are the major crystalline structures of TiO2, of which rutile phase is most stable; whereas anatase and brookite phases are metastable and easily transformed to rutile phase when heated above about 600- 800 C^0 .As demonstrated in other experimental studies, the anatase form of TiO_2 has shown much higher photoactivity than that of rutile [4].

Zinc oxide is a wide bandgap semiconductor of about 3.37 eV, use in different fields such as industrial and medical. Because of the strong UV absorption properties of ZnO, they are increasingly used in personal care products, such as cosmetics and sunscreen. In addition, ZnO NPs have superior antibacterial, antimicrobial, and excellent UV-blocking properties. Therefore, in the textile industry, the finished fabrics by adding ZnO NPs exhibited the attractive functions of ultraviolet and visible light resistance, antibacterial and deodorant. laser ablation of materials was a nearly new technique first invented in 1993 by Fojtik et al has proven merits as the common efficient procedure for getting nanoparticles. This is the chosen method is characterized by its ease, efficiency, and does not require complicated situations or specific conditions to obtain a nanoscale solution . This promising method can control the size and concentration of fabricated nanometers via changing the laser parameters, therefore, it processes as much attention as a novel NPs manufacture way . In this manuscript, we have studied the effect of the laser pulse on the concentration of NPs prepared by laser ablation for a zinc-bulk in distilled water. The effect of changing the laser pulse at fixed energy on the concentration and size distribution studied experimentally and the morphology of nanoparticles is investigated [5].

Due to the non-toxic, safe inorganic antibacterial agent of silver nanoparticles being used for centuries and is capable of killing about 650 microorganisms that cause diseases . Silver has been described as being „oligodynamic‟, that is, its ions are capable of causing a bacteriostatic (growth inhibition) or even a bactericidal (antibacterial) impact. Therefore, it has the ability to exert a bactericidal effect at minute concentration. It has a significant potential for a wide range of biological application such as antibacterial agents for antibiotic resistant bacteria, preventing infections, healing wounds and anti-inflammatory. Nano oxide and its compounds are highly toxic to microorganism exhibiting strong biocidal effect on many species of bacteria but have a low toxicity towards animal cells. Bactericidal behavior of nanoparticles is attributed to the presence of electronic effects that are brought about as a result of change in local electronic structure of the surface due to smaller sizes. The effects are considered to be contributing towards enhancement of reactivity of nanoparticles surface[3].

1-2 Literature Review

1-2-1Titanium Dioxide:

- In 2014,**Khashan et al**., prepared colloidal liquid from **titanium dioxide** nanoparticles by laser ablation of titanium metal immersed in deionized water. The properties of the suspended nanoparticles were studied using UV-Visible spectroscopy, Fourier transform infrared (FTIR). By using (FTIR), the researchers demonstrated the formation of titanium dioxide particles. and the researchers used the prepared nanoparticles as an antibacterial against (Staphylococcus aureus) and (Escherichia Coli). Titanium dioxide nanoparticles showed inhibitory activity in bacteria **[**6**].**

- In 2015 **Zimbone et al.,** synthesized titanium particles by laser ablation in water and the activity of the prepared **titanium dioxide** particles was studied as a photocatalyst and antibacterial, the average diameter of the prepared nanoparticles was about (34 nm). The researchers showed that the prepared nanoparticles have good stability and high purity in addition to their activity as a high photocatalyst by (staining with methylene blue dye under UV rays) and as antibacterials when tested on Escherichia Coli [7].

 In 2022,**Blazeka et al.,** studied concentration quantification of **Ti nanoparticles** synthesized by laser ablation of a Ti target in water. After synthesis, a colloidal solution was analyzed using UV-Visible spectroscopy. At the same time, the craters that remained on the Ti target after ablation were evaluated with an optical microscope to determine the volume of the ablated material. SEM microscopy was used to determine the TiO2 NPs size distribution. It was found that synthesized TiO2 NPs followed a Log-Normal diameter distribution with a maximum at about (64 nm). From the volume of ablated material and NPs size distribution, under the assumption that most of the ablated material is consumed to form nanoparticles, a concentration of nanoparticles can be determined. The proposed method is verified by comparing the calculated concentrations to the values obtained from the Beer-Lambert law using the Mie scattering theory for the NPs cross-section calculation [8].

In 2022, **Israa at el**., were prepared **Titanium dioxide** nanoparticles in this work by laser ablation of a high purity titanium objective immersed in distilled water. Optical and structural properties of the obtained (TiO2 NPs) using a Qswitched (Nd:YAG) laser of 1064nm wavelength with different laser energy (80, 100, 120, 140, and 160 mJ) at 100 pulses was studied. The produce (TiO2 NPs) were characterized employing (UV-VIS) Spectrophotometer, X-ray diffraction, and scanning electron microscopy (SEM). The obtained (TiO2NPs) showed a decrease in transmittance in the region of the UV spectrum and an increase in the visible spectrum region. The estimated optical band gap of the (TiO2 NPs) was (3.89eV, 3.8eV, and 3.70eV) at (80, 120 and 160 mJ) laser energy,respectively. The as produced (TiO2NPs) appear to be a Brookite crystalline phase with the preferential orientation along (200) direction. The scanning electron microscopy assays showed that the (TiO2 NPs)have a cauliflower shape. Results show that with increasing the energy of laser pulse, the size of nanoparticles was increased noticeably. Where the particle size and its morphology are affected by laser energy.[9]

1-2-2 Sliver Oxide :

 In 2014,**Al-Ogaili et al**., prepared **silver NPs** via pulsed laser ablation technique in liquid and studied the optical and antibacterial activity of prepared NPs against four types of bacteria: Staphylococcus, Proteus, Streptococcus, Streptococcus and Enterobacter by disc diffusion agar method. The findings evidenced that the laser parameters effect on the optical properties of the produced NPs and the silver NPs have effective antimicrobial properties [10]

 In 2014,**Baiee et al**., produced **silver nanoparticles** with an average size of (5 ± 2.4 nm) maximum nanoparticles up to (10 nm) in size using laser ablation, and a silver plate immersed in dilute sodium borohydride. Diode- pumped Nd:YAG laser at the second harmonic wavelength (532 nm) with a pulse duration of (7 ns) was used to generate Ag nanoparticles. It has been proven that concentrating sodium borohydride and reducing the increased laser flux leads to a reducing the average and maximum sizes of silver nanoparticles. The most powerful antibacterial the activity of Ag NPs generated against Gram-negative bacteria E. coli was found to be compared with nanoparticles generated in deionized water without sodium borohydride [11].

 In 2020,**Abu-Bakr et al**., used ice water as a medium to produce **silver nanoparticles** (Ag NPs) by pulsed laser ablation. A nanosecond laser with a wavelength of (532 nm) was used to produce silver nanoparticles in ice water. The results showed that the average size of the nanoparticles was (16nm), ranging from a few nanometers to (40nm). For comparison, nanoparticles were produced in deionized water under the same laser beam parameters where the average size of nanoparticles was (31 nm). From this it could be concluded that the ice environment has a significant effect on reducing the size of Ag NPs [12].

 In 2021,**Al-Maher et al**., studied the effect of gamma ray on **silver nanoparticles** prepared by pulse laser ablation in liquid technique (PLAL) at two energies (540 and 700) mJ and the count of pulses were (100,200,300 and 400) pulse. The prepared samples were divided into three groups: the first group of the samples were kept as they are without any irradiation but the second and third groups were irradiated by Co-60 source with two amount of doses (7.5 and 11) KGy respectively. A series of measurements and studies were done, The gamma irradiation effect was studied through its effect on the optical properties of the nanoparticles at different preparation conditions, represented by a change in the pulses and the energy of the laser used. The results showed that there was an increase the absorbance peaks when increasing the irradiated dose [13].

 In 2022,**Rashid et al**., prepared **silver nanoparticles** (AgNPs) using Nd:YAG laser with a wavelength (355 nm) and (532 nm) at the energies (500 mJ) and (600 mJ) respectively with the number of pulses (500, 600, 700, 800, 900 pulses) each wave length. The properties of the prepared nanoparticles were investigated by UV-VIS, XRD and SEM using EDX, the FTIR analysis then tested the antibacterial activity against two types of gram-positive bacteria (Staphylococcus aureus, Streptococcus mutans) and two Gram-negative bacteria (Escherichia coli, Pseudomonas aeruginosa) isolated from the mouth cavity. The results showed that the Ag NPs generated by the PLAL technique have antibacterial activity and can be used to kill pathogenic bacteria [14].

1-2-3 Zinc Oxide:

 In 2014, **Evan and Hala** prepared the **zinc** particles by pulsed laser ablation method with a wavelength (1064 nm), frequency (1 HZ) and pulse duration (9 ns), the effect of changing laser pulses on zinc nanoparticles, structural and optical properties was studied. The results of the atomic force microscopy showed that with the increase in the number of laser pulses, the grain size decreased. It is characteristic of shifting towards the blue color with increasing pulses. As well as the increase in the intensity of the absorption peak by increasing the number of laser pulses.[15]

 In 2015**, Faten and Iman**, was able to work on the target of **zinc** metal by the method of pulsed laser ablation in the middle of isopronal The effect of laser energies during the ablation process on the optical properties was studied (UV-Vis), (EDX) where It was observed towards short wavelengths that the grain size increased with increasing laser power as well as the surface roughness. The use of isopropanol as a solvent led to the production of spherical nanoparticles of (30-60 nm).[16]

 In 2016, **Solati et al**., used a Nd: YAG laser to irradiate a high purity **zinc** plate in distilled water at different temperatures (0, 20, 40, 60 ċ) and the nanoparticles were diagnosed by UV-Vis spectroscopy as well as (XRD) The results showed that with increasing temperature the size of nanoparticles decreases.[17]

 In 2019**, Suha et al**., prepared **zinc** oxide nanoparticles using a pulsed laser ablation process of a sapphire laser with wavelength (800 nm), pulse repetition rate (1 KHz), and pulse duration (130 fs) using three values of pulse energies. (0.05, 1.11, and 1.15 mJ), which means smaller sizes of the prepared nanoparticles, are associated with lower laser power. (FTIR) analysis was used to confirm the formation of zinc oxide nanoparticles represented by the absorbance values at (435-445 Cm-1). The formation of ZnO nanoparticles was characterized by scanning electron microscopy (SEM).[18]

 In 2021**, Ghufran et al.,** were able to prepare particles of **zinc** oxide from zinc metal by the method of pulsed laser ablation immersed in deionized water. At energy (600 mJ) and number of pulses (100, 150, and 200 pulse). The results were collected and checked (XRD, SEM). The colloidal result revealed the spherical shape and homogeneous composition of (ZnO NPs). The result confirmed the presence of (ZnO) with a hexagonal structure corresponding to the plane (100). The mass concentration increases with the increase in the number of laser pulses . [19]

1-3 Aim of the Work

Present work aims to accomplish the following.

1- Low-cost synthesis (Laser ablation) was used for preparing AgO nanoparticles, TiO2 nanoparticles, ZnO nanoparticles individually.
2- Preparation hybrid nanoparticles(TiO2/ AgO) of unique composition by laser ablation.
3- Preparation TiO2/AgO/ZnO heterostructues are used in Antibacterial applications.
4- TiO2/AgO/ZnO heteronanostructures Improving Optical Characteristics.