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The factors affecting anticancer, antibacterial, and photocatalytic applications of ZnO nanocomposite synthesized by PLAL: A mini review

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HIGHLIGHTS

- ZnO NPs synthesized by PLAL showed higher photodegradation efficiency than those made via chemical routes
- E.coli's lipopolysaccharide-rich outer membrane made it more resistant to ZnO NPs than gram-positive bacteria
- Modifying ZnO NP surface charge enabled targeting specific intracellular sites for improved anticancer effects

Keywords:

Azo dyes; Cytotoxicity; Gram-negative; Gram-positive; Photocatalyst; Laser ablation

ABSTRACT

Fresh water is essential for life to continue on Earth. The accelerated growth of industrialization and globalization is to blame for the current apex of environmental problems. Heavy metals and organic pollutants discharged from industrial waste are extremely harmful at relatively minimal concentrations when tolerance levels are exceeded. They will lead to several diseases in humans. One method for treating wastewater is semiconductor photocatalysis. It depends mainly on the oxidation-reduction mechanism by holes and electrons, respectively, that are generated by the exposure of the semiconductor oxide into a source of photons. Pulsed laser ablation in liquid (PLAL) has attracted significant attention. Controlling the laser parameters is considered a green, competitive, and simple method to synthesize well-separated nanoparticles with a clean surface, small sizes, and numerous defects. ZnO semiconductor is considered cheap, not toxic, and more efficient at absorbing a large portion of the solar radiation spectrum with E_g =3.37 eV. These features give ZnO remarkable significance when used in biological and engineering applications. This short review article aims to know the advantages and challenges of using the PLAL technique in synthesizing ZnO and how to enhance the efficiency of inhibiting bacterial strains, cancer growth, and degradation of dyes using this material. We have found from this review that the size, shape, and zeta potential value govern the success of using ZnO nanomaterial in different applications. We also found an optimum value for ZnO's pulse duration and ablation time that can achieve the highest degradation efficiency.

1. Introduction

Recently, much attention has been focused on pulsed laser ablation in liquid (PLAL) because novel nanostructures can be formed by extreme synthesis conditions [1]. When comparing laser ablation with conventional chemical methods, laser ablation is considered a green, competitive, and simple method to synthesize well-separated nanoparticles with a clean surface, small size, and numerous defects by controlling the laser parameters [2-9]. These defect sites are exposed and readily accessible to reactants [10,11]. Different nanomaterials such as metals, semiconductors, and ceramics are produced using this efficient technique from bulk materials [12,13]. Some special nanomaterials that cannot be obtained by conventional methods can be formed by PLAL [1, 11]. These nanomaterials are chemically, biologically, and photocatalytically active [4,14].

ZnO is considered cheap, biodegradable, not toxic, and more photo-catalytically efficient at absorbing a large portion of the solar radiation spectrum than TiO_2 with E_g=3.37 eV [15,16]. ZnO nanoparticles have shown excellent antibacterial properties. Due to its properties, ZnO has been used in many applications, such as food preservation, medicine making, implanting orthopedic ceramics, and wound healing dresses [14]. Based on its low toxicity both in vitro and in vivo, several researchers have performed cytotoxic studies using ZnO (nano and micro) structures [16,17]. Antibiotic-resistant bacteria such as E.coli, Streptococci, Gonococcus, Pseudomonas aeruginosa, and Pneumococcus can cause various kinds of pyo-inflammatory diseases in different locations [14]. The increase in bacterial resistance and mutations is due to the increased

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usage of antibiotics [18]. To suppress bacterial infections, new generations of antibiotics must be developed. Nanoparticles (NPs), such as silver, zinc, copper, etc., have been developed as attractive and reliable antibacterial agents. In particular, ZnO possesses a high surface energy that can generate different reactive oxygen species (ROS), which makes it an excellent bacterial inhibitor for biomedical applications [11], ZnO is discovered to be biocompatible with lower toxicity to human cells.

The antibacterial activity of the NPs depends on their size, phase composition, degree of crystallinity, concentration in the culture media, surface functionalization, shape and defects, and the type of bacteria (Gram-positive or Gram-negative species) [18,19]. When the size of the NPs is nearly the size of the biomolecules, this will facilitate their mobility and entry through the cell membranes [19]. In biomedicine, metal oxide nanoparticles are efficient in cell imaging, biosensing, and drug delivery. Recently, ZnO NPs have been used as an anticancer agent against different types of cancer. Cancer has been considered as one of the most dangerous diseases. The fiercely of cancer cells is due to their ability to promote the normal cells quickly to out-of-control cells that can spread and influence other cells [20,17]. A huge amount of scientific literature discusses the potential ability of nanomaterials to treat cancer cells both in Vivo and in Vitro [21]. Iraq has reported high incidence rates of breast, bladder, and lung cancer, besides the increased incidence rates of other cancers.

Fresh water is essential for life to continue on Earth. Water shortage has been a primary concern for humankind [22]. The accelerated growth of industrialization and globalization is to blame for the current apex of environmental problems. Over the last few decades, researchers have concentrated increasingly on eradicating dangerous untreated compounds such as pharmaceutical byproducts, organic dyes, pesticides, and fertilizers from aquatic environments [12]. Heavy metals and organic pollutants discharged from industrial waste are extremely harmful at relatively minimal concentrations when tolerance levels are exceeded. They will lead to several diseases in humans [4]. The United Nations expects that by 2030, 47% of the world's population will be in areas suffering from water stress [23]. One method for treating wastewater, air filtration, and sterilizing uses semiconductor photocatalysis, where environmental organic pollutants can be removed with semiconductor materials by photocatalysis [13]. In which sunlight can be converted into chemical energy, [10, 24]. The semiconductor Photocatalytic activity is affected by many factors, such as the bandgap energy of the semiconductor, the synthesis method, and the crystallinity.

Many researchers have studied the different applications of ZnO as an antibacterial agent, anticancer agent, photocatalyst, antiviral, antifungal, UV skin protection, and plant growth [15, 25, 26]. This review aims to understand the advantages and challenges of using the PLAL technique to synthesize ZnO-based nanocomposite and its application as an anticancer, antibacterial, and photocatalyst agent.

2. Mechanism of PLAL

Laser ablation in Liquid (LAL) is based on the ablation of the material by irradiating a laser pulse on a solid target submerged in a liquid to produce nanostructures [27]. Generally, there are two main mechanisms for the formation of NP using PLAL [28, 27]. The first one is by the generation of plasma and vapor when the metal target is hit by the laser beam, followed by the formation of the NP via the nucleation and growth steps as a result of an interaction of the laser beam with the liquid medium, this is called the thermal evaporation process. The explosive ejection process is considered the second major mechanism of formation. Where NPs are directly formed by the ejection of small hot droplets in micro and nano sizes with solid fragments from the target. The laser parameters govern the mechanism of formation of the NPs. As an example, when a high energy density laser with a short pulse (e.g., a nanosecond pulsed laser with a power density of 108-109 W/cm^2, pulse duration of several nanoseconds) is concentrated on a metal target, plasma, and vapor are mainly generated. While using a millisecond laser (low-power density laser), the essential and immediate product is the nanodroplets/fragments [29], as shown in Figure 1.

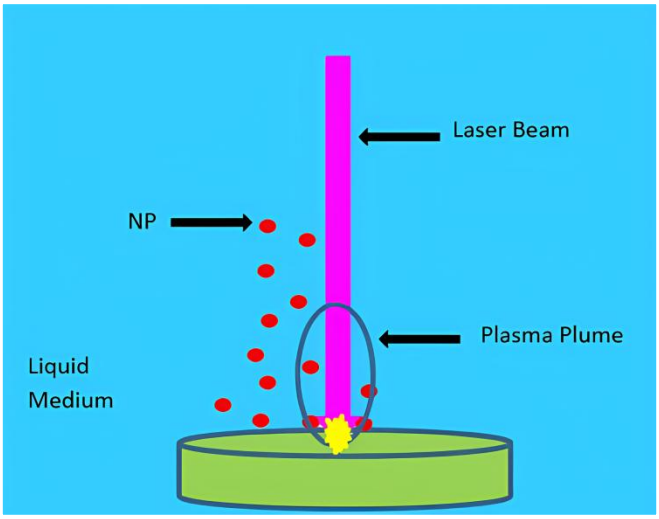

Figure 1: NP formation by PLAL

3. Antibacterial activity of ZnO

Two types of bacteria are investigated in this review article. Gram-negative Escherichia coli (E.coli) and Gram-positive Staphylococcus aureus (S.aureus) bacterial strains after being exposed to different concentrations up to 1000 µg/ml of ZnO NPs, 24 hrs incubation at 37 ºC. The typical wavelength used to monitor the optical density (OD) for cells is 600 nm, and a growth curve is obtained between the OD and the monitoring time in hours [26]. It was observed that the ZnO nanoparticles and nanorods with the highest specific area (more active sites) decreased the bacterial number of these two strains at low concentrations, which can be helpful in food packaging. Moreover, for the ZnO NPs, the Staphylococcus aureus strains were more sensitive than E.coli strains to the antimicrobial activity of ZnO, and concentration dependence was discovered [19]. The production of reactive oxygen species (ROS) due to oxidative stress of the metal nanoparticles is a proposed mechanism for the antimicrobial effect of ZnO NPs. A DCFH-DA assay is deployed to measure the intracellular ROS. It is based on oxidizing the non-fluorescent DCFH-DA to a green-fluorescent dichlorofluorescein due to ROS. The ZnO-treated cells are compared with H_2O_2 as positive and untreated negative control cells. It was found that the Staphylococcus aureus bacterial strains have the highest intensity when compared to E.coli, indicating that it is more sensitive to ZnO NPs than E.coli, especially for ZnO-doped samples, which have achieved a 37% zone of inhibition higher than that of undoped ZnO nanostructures [19, 26]. It was suggested that as the particle size of the ZnO NPs decreases, its antibacterial activity increases due to the increase in the surface area to volume ratio [30,31]. ZnO NPs are known to be nearly water-insoluble; due to the high polarity of water, they aggregate immediately during the synthesis process. So, several researchers have considered adding various stabilizers during the synthesis process that have no significant antibacterial activity, such as Polyvinyl alcohol (PVA), Polyvinyl pyrrolidone (PVP), and Polyglutamic acid (PGA). These stabilizers have enhanced the size and morphology of ZnO NPs as an antibacterial agent [26].

4. Anticancer activity of ZnO

Anticancer activity of ZnO NPs has been studied extensively against many types of cancers, including (MCF7) human breast cancer cells, (AGS) gastric cancer cells, (Hela) human cervical cancer cells, (HCT-116) human colon cancer cells, (Caco-2) human colorectal adenocarcinoma cells and (HepG2) human liver cancer cell, etc. [16]. Examining previous studies done by researchers [17, 32] the anticancer activity of ZnO after an incubation time of 24 hrs has proved to be concentration dependent, with no effect at lower concentrations such as 1-5 µg/ml. The results from the quantitative real-time PCR are used to analyze the levels of apoptotic markers of mRNA of the cancer cells after exposure to ZnO NPs. These results have proved that the up and down-regulation of these markers results in permeabilization of the mitochondrial outer membrane; this will promote caspase activation due to the release of soluble proteins into the cytosol from the intermembrane space [17]. One of the proposed mechanisms for the cytotoxic effect of ZnO NPs is that the NPs first attack the outer membrane of the cells, and then these NPs penetrate the outer layer of these cells. The NPs below 10 nm can easily enter into the inner membrane due to the presence of small pores. The cell organelles, e.g., DNA, RNA, mitochondria, and neoplastic reticulum, can be destroyed due to the agglomeration of the high density of the small NPs in the liquid system [17]. The antioxidant capacity production of the cancer cells is reduced due to the ROS generated by the interaction of ZnO NPs with cancer cells [33].

Table 1: The mechanism and effect of ZnO-based nanocomposites applied to different cancer types based on their size and shape

Cancer Type	Shape and average size of the nano ZnO	Mechanism and effect	Ref.
Hela	Spherical, 348 nm	At a 100 µg/ml concentration, cell viability decreased to 35.98% due to increased ROS.	[34]
A431 skin carcinoma	Microtubule-like morphology with aspect ratio (L/D)=52.5	Concentration of 25 µM, cell viability decreased to 5.56% ± 0.93% due to ROS	[35]
(EAC) Ehrlich ascites carcinoma	20 nm, Irregular semi-spherical ZnO NPs 19-23 nm, spherical ZnO/DOX 22-41 nm, spherical ZnO/DOX/FA	IC_{50} at 10.8 µg/ml for ZnO NPs IC_{50} at 20.8 8 µg/ml for ZnO/DOX IC_{50} at 8.3 µg/ml for ZnO/FA IC_{50} at 38.8 µg/ml for ZnO/DOX/FA due to necrosis	[36]
MCF-7 Human breast cancer WRL68 Human hepatic	18-25 nm, Flower-like structure	IC50 at 136 µg/ml against MCF-7 IC50 at 14.07 µg/ml against WRL68 The toxicity is due to the release of Zn^{+2} that inhibits the enzymes	[37]
(MDA-MB-231) Human breast cancer	50-60 nm, spherical	The concentration of 17.5 µg/ml, viability 20% due to cell necrosis and chromatin fragmentation or condensation, ROS production that leads to apoptosis and inhibiting of cell migration	[38]
MCF-7 (Breast cancer) and A549 (Lung Cancer)	16-19 nm, nanospheres	Concentration of 31.2 µg/ml, cell viability decreased by 54.2% for (A549) 50.8% for (MCF-7) with no study for the proposed mechanism	[39]
HepG2 (Liver Cancer)	5±2 nm, QDots	At a concentration of 10 µg/ml, cell viability was 14% due to the destruction of cell organelles and the extreme generation of ROS.	[17]

These ROS are responsible for generating free radicals, which can enter the inner wall of the membrane by penetrating the outer wall of these cells [16]. A study reported that ZnO NPs could target different cell types of cancer, cancer stem cells, cancer cells, and macrophages and perform several key functions simultaneously, including cancer proliferation inhibition, cancer recurrence, and metastasis prevention, cancer immune-surveillance resuscitation and drug-resistant cancer sensitization [16]. The zinc ion released from the ZnO NPs after directly interacting with the biological macromolecules in the cell culture medium might have a potential cytotoxic effect on cancer cells [33, 32]. Many researchers have studied the anticancer activity of ZnO-based nanocomposites against different cancer types. Table 1 illustrates the mechanism and effect of ZnO-based nanocomposites applied to different cancer types. While the mechanism responsible for ZnO was proposed by Tabrez et al. [38], as shown in Figure 2:

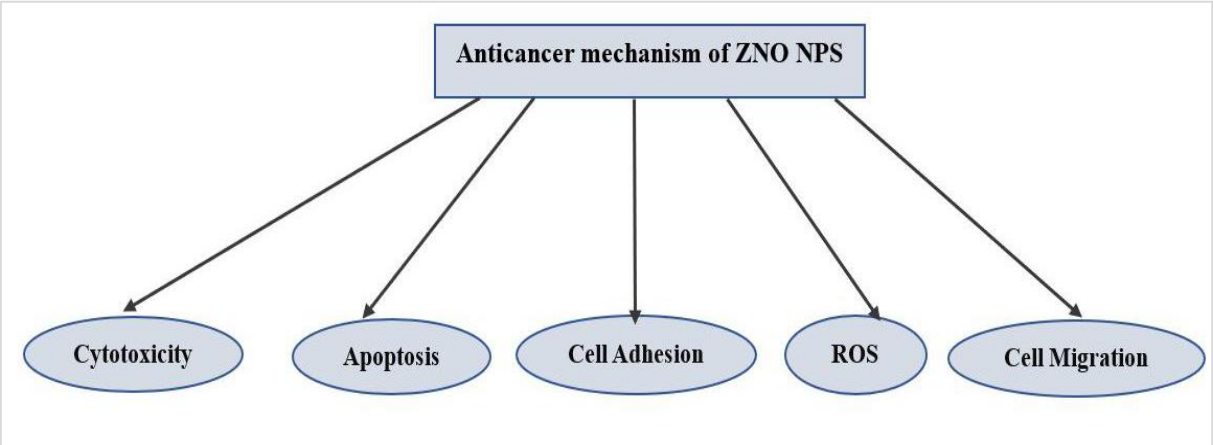

Figure 2: The mechanism responsible for the ZnO anticancer activity

5. Zeta potential

The zeta potential is considered an vital measurement to characterize the electric properties of the bacterial and cancer cells, which will be discussed in detail below [40].

5.1 Bacterial cells

Researchers have found that for different bacterial strains, including E. coli and S. aureus, the zeta potential of the bacterial cell walls has a negative value [26,41]. These values were found to be more negative for Gram-negative bacteria than for Gram-positive bacteria because Gram-negative bacteria have an extra negatively charged layer of lipopolysaccharide (LPS) [42,43]. A study by Arakha et al. revealed that the zeta potential of dead cells is less negative than that of living cells [40,41]. Arakha et al. investigated the zeta potential role of synthesized ZnO NPs (positively and negatively charged) by co-precipitation method on three randomly chosen bacteria (Gram positive and Gram negative). They found that the ZnO NPs (particle size 25-35 nm) with positive potential (+12.9 mV) showed higher antimicrobial activity for both Gram-positive and Gram-negative bacteria when compared to negative potential ZnO NPs (particle size of 35-45 nm and -12.9 mV) [42]. They also found that the ROS production for the same concentration of positively charged ZnO NPs is higher than that of negatively charged ZnO NPs when incubated with the Gram-negative (E.coli) and gram-positive (S. aureus) bacteria, respectively. This was attributed to the neutralization of the potential that occurred was higher in E. coli than in S. aureus, i.e., more attachment (strong attraction force) for the positively charged ZnO NPs on the membrane of E. coli than that of S. aureus. The study found that the minimum inhibitory concentration (MIC) is two and a half-fold higher for negatively charged ZnO NPs (250 µg/ml) than that of positively charged ZnO NPs (100 µg/ml) against the same bacteria. Abdelsattar et al. [44], studied the antibacterial effect of biosynthesized propolis-mediated ZnO, Ag@ZnO, and Au@ZnO NPs against Gram-positive Staphylococcus sciuri (S. sciuri) (MW415886) and Gram-negative Pseudomonas aeruginosa (P. aeruginosa) (OL375153) and Salmonella enterica (NCTC 13,348) bacteria. They found that (S. sciuri) was intensively affected by the treatment with Ag@ZnO NPs because zeta potentials for the Ag@ZnO, Au@ZnO, and ZnO NPs were 23.9, 13.6, and 11.4 mV, respectively and this will result in a strong attraction force between (S. sciuri) and Ag@ZnO NPs with (MIC of 75 µg/ml).

Eren et al. [45], investigated the antimicrobial activity of synthesized p-ZnO nanocrystals (NC) positively charged (10 mV, < 100 nm) and negatively charged n-ZnO (-11.2 mV, 100-500 nm). They found that the MIC of p-ZnO and n-ZnO against S. aureus were 26 and 25 µg/ml with no effect against E.coli. They suggested that E.coli (gram-negative bacteria) has an outer membrane that is lipopolysaccharides rich, which can form a barrier against antibacterial agents, making it more complex than gram-positive bacteria [43]. Jiang et al. [46], listed the mechanism responsible for the antibacterial activity of ZnO NPs against different bacterial species from the literature shown in Figure 3. It was stated that the antibacterial mechanism is either governed by ROS production, Zn+2 ion release, or direct interaction of the cell membrane with ZnO NPs [26, 43].

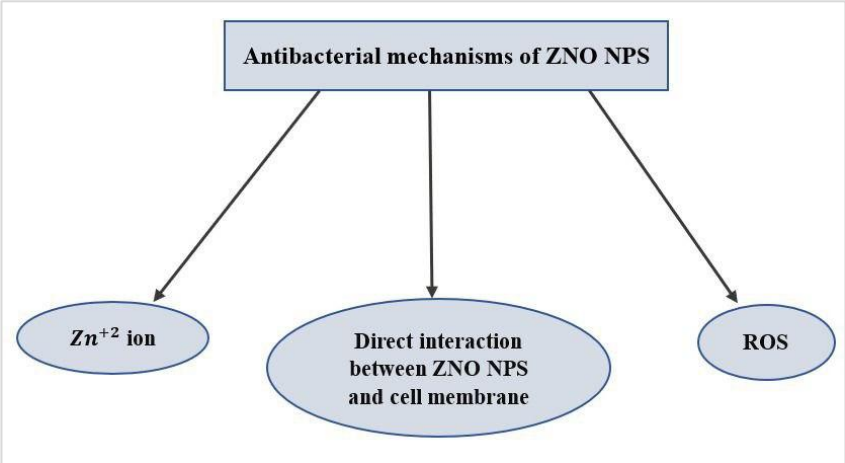

Figure 3: The antibacterial activity mechanisms of ZnO NPs

5.2 Cancer cells

For cancer cells, zeta potential is investigated by many researchers to highlight the cellular interaction with charged molecules or ions. It is well known that a less negative value of the measured zeta potential compared to healthy cells indicates tumor cell proliferation. In a study, Zhang and his colleagues [49], reported the zeta potential for normal epithelial cell line MCF 10A and cancerous epithelial call line MCF-7 [41]. They found that the value of the zeta potential for the MCF 10A was more negative (-31 mV) than MCF-7 (-20 mV). They discovered that incubating MCF-7 results in a significant decrease in the value of zeta potential, while for MCF 10A, the value slightly increased as shown in Table 2. Altankov et al. [47], found that the surface zeta potential of the cells is decreased by incubating negatively charged ions or molecules and increased with positively charged ions or molecules incubation.

Physicochemical properties of the particles, such as the size, shape, and surface charge, govern the cellular uptake of nanoparticles, [25]. One of the processes responsible for cellular uptake of nanoparticles is the nanoparticle binding on the cell membrane. This attachment is mostly affected by the particle's surface charge. So, higher cellular uptake happens due to the strong binding of the higher surface charge nanoparticles (cationic) with the cell membrane (anionic). Patil et al. [48], concluded that modifying the surface charge of the nanoparticles can localize them to specific intracellular targets (lysosomes, mitochondria, cytoplasm, etc.). They figured in their study that Adenocarcinoma lung cancer (A549) possesses a zeta potential of -10.2 mV ± 19.7 mV. This means the cell membrane possesses a few cationic sites to adsorb negatively charged nanoparticles. The large negatively charged portions of the cell surface exert a repulsive force on the negatively charged nanoparticles, forming clusters from these nanoparticles that bind at the cationic membrane sites, [48,49]. Cellular uptake favors endocytosis due to the electrostatic interaction between the positively charged sites and the negatively charged nanoparticles, resulting in a localized neutralization leading to membrane bending.

Table 2: The zeta potential of some types of Bacteria and cell lines [41, 49]

Type	A549 Adenocarcinoma lung cancer	E.coli and S.aureus (dead)	MCF-7 breast cancer	MCF 10A healthy breast	S.aueus (live)	E.coli (live)
Zeta potential value (mV)	-10.2 ± 19.7	~ -20	-20.3	-31.2	-31.7	-49

Many researchers have studied the relationship between nanoparticle size and toxicity against cancer cell lines [50]. They found that nanoparticles with the smallest size do not necessarily have the highest toxicity.

6. Photocatalysis (fundamentals and mechanism)

ZnO possesses special properties such as a direct broad energy gap of (3.37 eV), a high value for the excitation of the binding energy of (60 meV), deep broad UV/violet absorption at room temperature, low resistivity, [15,51]. Due to its outstanding electrical, mechanical, and optical properties. These properties have inspired scientists to use it as a catalyst in various applications. As a result of these advantages, it has been extensively used alone or in heterogeneous catalysis [52]. The oxidation steps of heterogeneous photocatalysis can be explained as follows (see Figure 4): [15, 53]

1) Diffusion of the organic toxins from the liquid phase to the ZnO photocatalyst surface.
2) The organic toxins are adsorbed on the ZnO surface.
3) Occurance of the oxidation-reduction in the adsorbed phase.
4) The results from the reaction are desorbed.
5) The product is removed from the interface region.

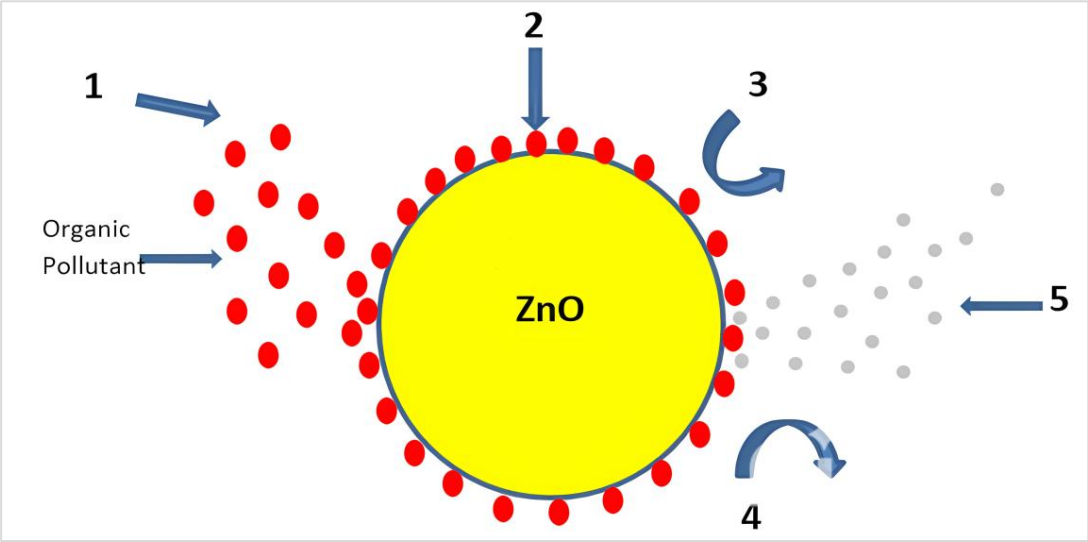

Figure 4: Oxidation steps of heterogeneous photocatalysis

When ZnO is exposed to solar radiation with a value of the energy greater or equal to the energy band gap of ZnO (E_g), an e-h pair is generated due to the transition of e^- from the valence band (VB) to the conduction band (CB). The generated pairs of electron-hole can be involved in the redox reaction by migration to the ZnO surface. Hydroxyl radicals and superoxide radical anions are produced due to the interaction of the h^+ with water and hydroxide ions and the interaction of e^- with the oxygen, respectively. Hydroxyl radicals are formed from the reaction of the superoxide radicals with the hydrogen peroxide. Then, intermediate products are formed rapidly due to the attack of the hydroxyl radicals with the pollutants adsorbed on the surface of ZnO. These intermediate products are then turned into eco-friendly compounds such as CO_2 and H_2O [15, 52].

When ZnO is compared to TiO_2, ZnO, in terms of absorption efficiency, is higher than TiO_2 across a larger portion of the solar radiation. The catalyst photoactivity is determined by its capability to produce photoinduced electron-hole pairs. The major drawback of ZnO as a photocatalyst is that the electron-hole pairs recombine rapidly, decreasing quantum efficiency and energy loss. The optical absorption ability of ZnO governs its solar energy conversion performance due to its large band gap energy. Thus, intensive efforts are being made to enhance the optical properties of ZnO by preventing the electron-hole recombination generated by photo absorption and reducing the energy band gap to harness light in the visible spectrum [52]. So, a detailed discussion of the method of preparation of ZnO and the performance improvement of ZnO in photocatalysis, e.g., doping with metals or non-metals and coupling with other semiconductors, will be given below.

7. Classification of ZnO nanomaterial

ZnO nanostructures can be divided into zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) [54-57]. Figure 5 shows the different morphological dimensions of zinc oxides. It was concluded that the ZnO nanoparticles or nanorods possess the highest specific surface area and narrow pore diameter size distribution. In contrast, ZnO bulk materials like tetrapods and hierarchical structures possess low specific surface area and broader diameter distribution of the pores, [19]. The specific surface area of the photocatalyst highly affects its photocatalytic activity. A superior candidate for photocatalysis is ZnO nanosheets due to their large specific area and polar faces [15]. The thinner the ZnO nanosheets, the more the percentage of the dye degraded [58]. Nanoparticles with high surface areas are frequently used in solar photocatalysis because more organic pollutants may be readily adsorbed with a faster degradation rate [15, 58, 15] found that the photocatalytic activity decreases as the crystallization of the nanoflower and nanorod increases. This may be because the defects (such as surface and oxygen defects) have attached hydroxyl groups, which encourage the entrapment of photogenerated electron-hole pairs. So this improves their separation [58,59].

The variation of the morphology, size, and crystallinity governs the physical and chemical properties of the nanomaterials. Additionally, it is well known that photocatalytic interactions mostly occur at the interface between organic pollutants and the surface of the photocatalyst. So, any size, morphology, and crystallinity change can alter the surface chemistry, affecting the reaction rate [60]. One of the parameters responsible for the photocatalysis of ZnO is the pH of the solution. The zero-point charge for ZnO determines that the surface charge is between 7.0 and 8.0. At values less than 7.0, the catalyst surface has a positive charge. So, it can attract negatively charged dyes like Rhodamine B (RhB), Methylene orange (MO), and 4-nitrophenole. Meanwhile, for pH values higher than 7.0, the ZnO surface becomes negatively charged. So it will attract cationic dyes like Methylene Blue (MB) [61, 62].

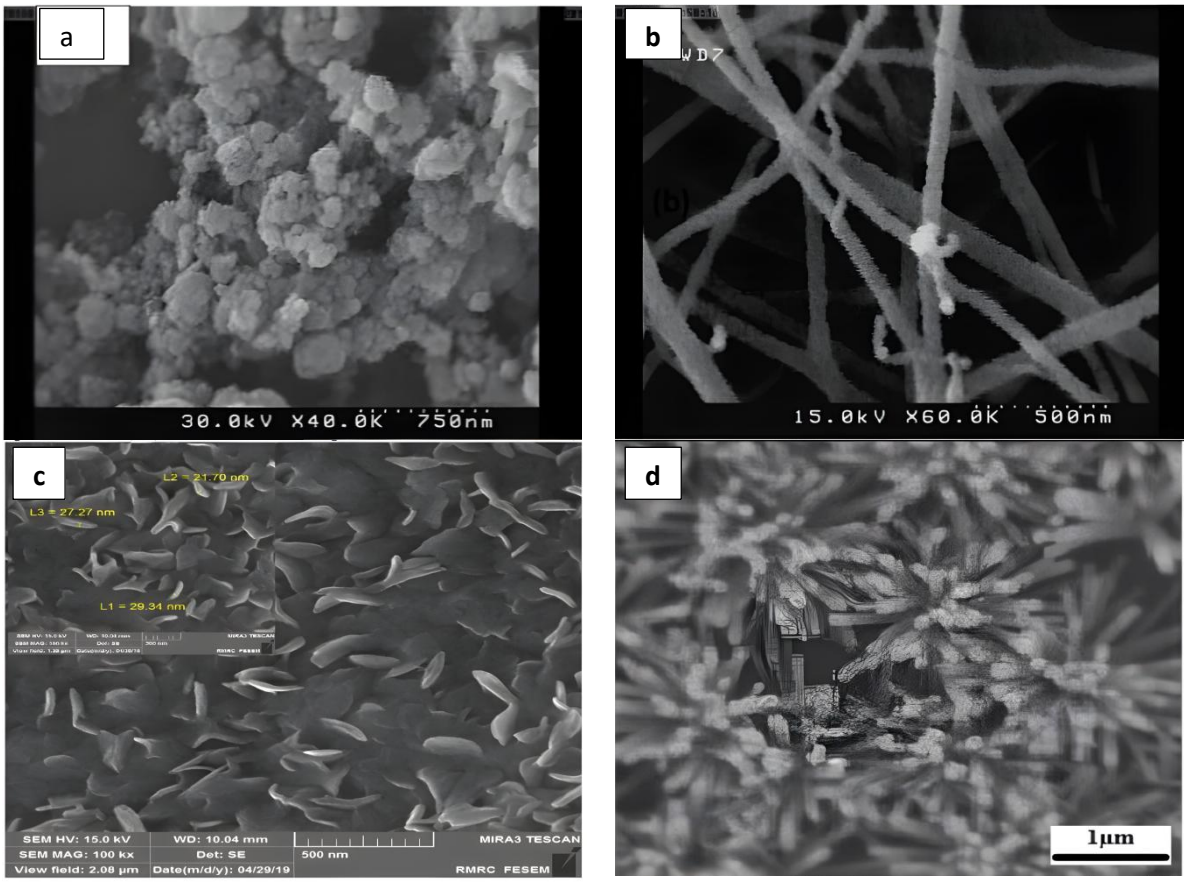

Figure 5: The FESEM images of (a) 0D, (b) 1D, (c) 2D and (d) 3D ZnO

8. Laser parameters affecting the synthesis of ZnO

Different laser parameters affect the synthesis of ZnO, resulting in different morphological shapes of ZnO, like the ablation energy, pulse duration, and repetition rate.

8.1 Pulse duration

A longer pulse duration results in more oxygen defects. For example, a nanosecond pulsed laser synthesizes ZnO with higher photocatalytic activity than that synthesized by a millisecond laser for 1064 nm, in which the defects in the nanocrystals promote the photocatalytic activity. The defects enhance the e-h separation, facilitating the interactions with carriers generated photonically [63]. Figure 6 depicts the change in the pulse duration versus the photodegradation efficiency of Methylene Blue (MB). From this figure, we can see that the efficiency of degradation increases with increasing pulse duration, then reaches a maximum value, and after that value, it starts to decrease again.

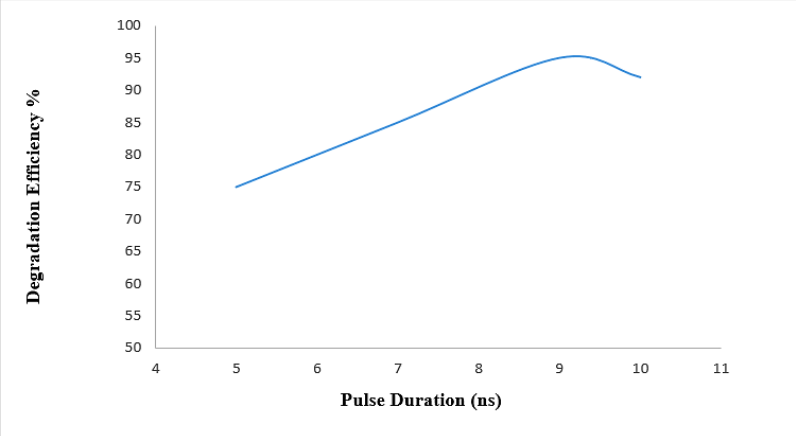

Figure 6: The relation between the photodegradation efficiency of MB using ZnO as a photocatalyst with the ablation time of the laser [64-68]

8.2 Ablation time

As the ablation time increases, the material will be ablated from the metal plate [68]. Stated that by preparing ZnO/CNT, as the ZnO concentration on the surface of the CNT goes up, the photodegradation process increases, and then it reaches a critical value. After this value, it will start to decrease because the CNT mechanical properties will change as the functionalization increases to an extreme value, resulting in a blockage of the active sites [68]. There is not enough data about the laser wavelength or pulse energy used to synthesize ZnO as a photocatalyst, but articles confirm their effect on the ablation rate [27]. Figure 6 shows that the maximum efficiency for ZnO as a photocatalyst can be obtained when the ablation time of the ZnO target is around 30 min.

9. The advantages and challenges of PLAL

What is different in PLAL over wet chemical routes because composition, particle size, crystallinity orientation, crystallographic phases, density defects, and the related electronic, optical, thermal, mechanical, and catalytic properties of the produced nanomaterials can be independently controlled. There is no need for surfactants during the production of nanomaterials. These surfactant molecules can hinder the catalytic active sites by lighting the surface atoms of the nanoparticles, and the absence of these capping agents is an advantage in PLAL compared to chemical routes [69]. Based on the laser repetition rate, PLAL is rapid, and the preparation of NP takes approximately 1 hour or less [70,71], stated that increasing the No. of laser pulses (ablation time) results in a linear increase in the ablated mass in micrograms. In the wet chemical method, hazardous materials are used to synthesize ZnO and adjust the pH value, while no byproducts or toxic chemicals are used for PLAL. Table 3 highlights the difference between PLAL and wet chemicals in the photodegradation of organic dyes.

Table 3: Comparison between the photodegradation efficiency of ZnO (metallic / non-metallic) doping synthesized by PLAL and wet chemical method

Type of material	ZnO nano-morphology	Method of preparation	Type of pollutant	Photodegradation efficiency	Ref.
ZnO/CNT	Spheres	PLAL (1.06 μm)	MB	85%	[68]
ZnO	Sheets	Wet chemicals	MB	82%	[72]
ZO/TiO_2-rGO		PLAL	MB	98.5%	
Au@ZnO	Core/Shell	PLAL	R6G	90%	[73]
Au@ZnO	Core/Shell flower like	PLAL	MB	100%	[74]
ZnO	Rodlike	Wet chemicals	MB+R6G	100%	[75]

Challenges are represented by the following points [69]:

1) Size cannot be controlled easily.
2) The elements ratio in a chemical compound cannot be controlled as more than one phase of the chemical material can be obtained. Muller and his coworkers discovered that the product composition can be determined by the nature of the dissolved anions in the liquid medium [76].
3) The nanomaterial production on a gram scale is still limited [77].
4) During the ablation, solvent cooling is required to prevent solvent evaporation.

10. Conclusion

A short review was presented to find the relation between PLAL anticancer, antibacterial, and photocatalysis of ZnO-based nanocomposites. PLAL is considered a facile method that does not require complicated equipment. It is also considered a green method of synthesis, in which inorganic NPs coated by organic material can be obtained. It is considered a clean method of synthesis as there is no byproduct from this technique. From this review, we have concluded that the ZnO NPs synthesized by PLAL has achieved a material with more photodegradation efficiency compared to their counterparts synthesized by chemical route. For the antibacterial effect of ZnO NPs, the E.coli (gram-negative bacteria) has an outer membrane that is lipopolysaccharides rich, which can form a barrier against antibacterial agents, making it more complex than gram-positive bacteria. For the anticancer effect, it was found that by modifying the surface charge of the nanoparticles, ZnO NPs can be localized to specific intracellular targets. The challenges in producing NPs using the PLAL method can be summarized by controlling the size, the crystallinity phase, and the lack of large-scale production. According to the above, ZnO NPs is a promising, safe material that can be used in antibacterial, anticancer, and photocatalysis applications.

Author contributions

Conceptualization, **H. Al-attar**, **M. Mohammad.** and **B. Bedair.**; data curation, **H. Al-attar.**; formal analysis, X.X.; investigation, **H. Al-attar.** and **M. Mohammad.**; methodology, **H. Al-attar.**; project administration, **M. Mohammad. and B. Bedair**.; resources, **H. Al-attar.**; software, **B. Bedair.**; supervision, **H. Al-attar**. and **M. Mohammad.**; validation, **H. Al-attar.** and **B. Bedair.**; visualization, **B. Bedair.**; writing—original draft preparation, **H. Al-attar.**; writing—review and editing, **H. Al-attar**, **M. Mohammad.** and **B. Bedair**. All authors have read and agreed to the published version of the manuscript.

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The data that support the findings of this study are available on request from the corresponding author.

Conflicts of interest

The authors declare that there is no conflict of interest.

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