


Original Article

Photodynamic therapy in cancer treatment: properties and applications in nanoparticles

Terapia fotodinâmica no tratamento de câncer: propriedades e aplicações em nanopartículas

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Abstract

Most of the treatment strategies for tumors and other disorders is photodynamic therapy (PDT). For several years, increasing the efficiency of nanostructured treatment devices, including light therapy, has been considered in different treatment methods. Light Dynamics The use of nanomaterial in this method's production and progress. The use of nanoparticles as carriers is a promising accomplishment, since all the criteria for an ideal photodynamic therapy agent can be given with these nanomaterials. The kinds of nanoparticles that have recently been used in photodynamic therapy are mentioned in this article. Latest advancements are being explored in the use of inorganic nanoparticles and biodegradable polymer-based nanomaterial as carriers of photosynthetic agents. Photosynthetic nanoparticles, self-propagating nanoparticles, and conversion nanoparticles are among the successful photodynamic therapy nanoparticles addressed in this report.

Keywords: photodynamic therapy, nanostructured, photosensitizer, photosynthesis, polymer.

Resumo

A maioria das estratégias de tratamento para tumores e outros distúrbios consiste na terapia fotodinâmica (PDT). Por vários anos, observou-se o aumento da eficiência de dispositivos de tratamento nanoestruturados, incluindo terapia de luz, que tem sido considerada em diferentes métodos de tratamento. Desse modo, este trabalho visa analisar a utilização de nanomateriais na produção e evolução deste método. A utilização de nanopartículas como carreadores é uma conquista promissora, pois todos os critérios para um agente de terapia fotodinâmica ideal podem ser obtidos com esses nanomateriais. Os categorias de nanopartículas que têm sido utilizados recentemente na terapia fotodinâmica são mencionados neste artigo. Os últimos avanços estão sendo explorados na utilização de nanopartículas inorgânicas e nanomateriais à base de polímeros biodegradáveis como portadores de agentes fotossintéticos. Nanopartículas fotossintéticas, nanopartículas autopropagantes e nanopartículas de conversão estão entre as nanopartículas de terapia fotodinâmica bem-sucedidas abordadas neste trabalho.

Palavras-chave: terapia fotodinâmica, nanoestruturada, fotossensibilizador, fotossíntese, polímero.

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Received: October 23, 2022 – Accepted: April 06, 2023



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1. Introduction

Light therapy has been a non-invasive, effective and modern treatment for about two decades that has opened its place in the treatment of some cancer and non-cancer diseases (Yoo et al., 2016; Ling and Hyeon, 2013; Nie et al., 2013; Yamada et al., 2014; Meisen and Kathrein, 2000). This method is based on the interaction of two factors, the first factor is sensitive to Light (Ps) which has two basic properties (Yavuz et al., 2006; Lee et al., 2015a; Wang et al., 2007). The first characteristic is the ability to selectively absorb in atypical cancer cells (tumor tissue), while in adjacent healthy cells, absorption is almost non-existent (or so low that it is not considered) and the second characteristic is the formation of photo biochemical interactions due to long-term radiation (Jun et al., 2005; Huber, 2005; Ozel and Kockar, 2015). A specific wave (depending on the type of substance Ps) of radiation (mainly laser) is the basis of occupational therapy. In this way, with irradiating light with appropriate wavelength (as a second factor) to Ps, the light molecule absorbs and is excited and then returns to the ground state to emit radiation, but most Ps have a weak fluorescence, so with an electron spin conversion to triple and this causes the transfer of energy to oxygen or surrounding molecules that later react with oxygen (Butler and Banerjee, 1975; Leslie-Pelecky and Rieke, 1996; Kim et al., 2009; Ma et al., 2004; Iida et al., 2007). These reactions lead to the formation of free radicals or radical ions (Santoyo Salazar et al., 2011; Upadhyay et al., 2016; Lee et al., 2015a; Noh et al., 2012). These substances then react with molecular oxygen at the ground state to produce the superoxide anion radicals of hydrogen peroxide and hydroxyl (Yoo et al., 2016). Interactions mentioned that this element is naturally present in body tissue conditions (Figure 1).

Non-toxicity, selective harvesting and maintenance with tumor tissue, adequate production of oxygen free radicals with absorbing wavelengths that can easily pass through the tissue, are the most important properties of the ideal photosensitizer (Sun and Zeng, 2002; Baumgartner et al., 2013; Klokkenburg et al., 2004). Reactive oxygen species (ROS) have a half-life of 3.5 microseconds and only have a motility of 0.01 to 0.02 micrometers (Goya et al., 2003), so damage occurs depending on where ROS is produced. The nucleus usually remains intact and DNA damage is rare (Caruntu et al., 2007; Kovalenko et al., 2007; Kandasamy and Maity, 2015).

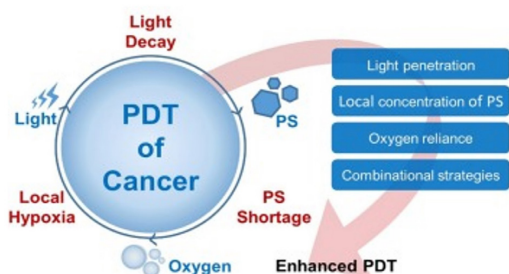


Figure 1. Photodynamic therapy process.

Hematoporphyrin derivative photosensitizer - HPD American-Canadian drug Photofrin (PF) was first used in bladder, esophageal, and lung cancers (Néel, 1947; Herzer, 1996). This is the first-generation Ps of a mixture of multicopying, which due to the limited selective accumulation in the tumor tissue, the ratio of its accumulation in the target tissue to healthy tissue is negligible (Ogi et al., 2016, 2017; Kartikowati et al., 2016a). It is a relatively long time (one month) after treatment that the patient is forced to endure a certain light regimen, something that is significantly reduced in second-generation drugs (chlorines) with 48-hour urination (Ogi et al., 2016; Suhendi et al., 2015). Bio nanotechnology has opened up new avenues for photodynamic therapy. Photodynamic therapy is the use of a light-sensitive drug (a photosensitizer), along with light at visible wavelengths, to destroy target cells (Kreibig and Vollmer, 1995; Mie, 1908). Therapeutic photodynamics, or PDT, is now recognized as the hallmark of clinical treatment for various diseases, such as cancer, and especially for the treatment of superficial tumors. Because the efficiency of PDT is attributed to the amount of unique 1O_2 production, two different nanoparticle utilization strategies can be pursued. One of these two strategies is biodegradable nanoparticles, from which the photosensitizer is released (Lee and El-Sayed, 2005; Gans, 1915; Her et al., 2017; Gomez et al., 2014). They are free. Another remaining limitation of PDT is the limited penetration of light into tissues. The absorption of two photons raises hopes for light penetration, as this allows two photons of laser energy to be used to generate excitation. Selected studies of localized cancer or precancerous disorders are shown in Table 1.

2. Treatment Mechanism with Photodynamic Therapy

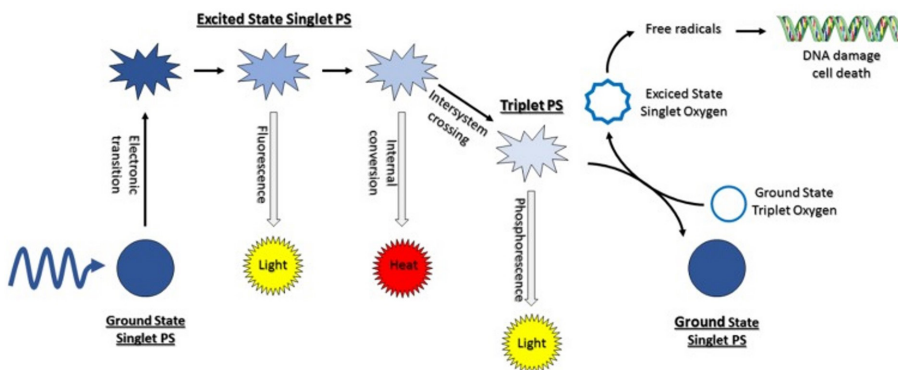
Photodynamic therapy's molecular mechanism is based on the three non-toxic components that achieve the desired effects inside pathological tissues only with reciprocal interactions between (Petryayeva and Krull, 2011; El-Sayed, 2001; Link and El-Sayed, 1999; Pérez-Juste et al., 2005):

- Photosensitizer (PS);
- Light with the required wavelength;
- Oxygen dissolved in cells.

The photodynamic reaction has two major pathways. Both are closely dependent within cells on oxygen molecules (Liu et al., 2014; Chen et al., 2008; Pitsillides et al., 2003). There is a common first step to both processes. After entering the cell, a photosensitizer is irradiated with a light wavelength coinciding with the spectrum of PS absorption and is transformed from the singlet specific energy state S_1 due to the absorption of the photon into the excited singlet state S^1 (Karakoçak et al., 2016; Pan et al., 2007; Misawa and Takahashi, 2011). Part of the energy is radiated in the form of a fluorescence quantum, and the remaining energy is guided to the excited triplet state T^1 with a photosensitizer molecule - the proper therapeutic form of the compound (Figure 2).

Table 1. Trials selected for localized cancer or precancerous conditions.

Condition	Photosensitisers	Treatment	Trial type	Patients
Carcinoma of the lip	Temoporfin	Temoporfin (0.15 mg/kg) 96 h before 20 J/cm ² light (652 nm)	Non-randomised phase II trial	25
Barrett's oesophagus	Aminolevulinic acid	30 mg/kg oral aminolevulinic acid or placebo 4 h before laser Endoscopy. Total light dose 60 J/cm ² (514 nm)	Randomised, double blind placebo controlled trial	36
Barrett's oesophagus	Porfimer sodium	2 mg/kg porfimer sodium 48–72 h before laser treatment (630 nm)	Multicentre, partially blinded randomised study	208
Cervical intraepithelial neoplasia	Aminolevulinic acid	Topical application of 3% aminolevulinic acid gel to cervix for 3 h, followed with 100 J/cm ² 635 nm laser light	Randomised, double blind placebo controlled trial	25

**Figure 2.** The Photodynamic reaction mechanism.

2.1. Form I of photodynamic reaction mechanism

The photosensitizer will transfer energy to the biomolecules from its surroundings in the excited triplet state T^1 (Chithrani et al., 2006; Fang et al., 2011; Paciotti et al., 2006; Choi et al., 2003). A hydrogen or electron is exchanged between the photosensitizer in the T^1 state and the cancerous tissue (substrate), which contributes to the creation of the photosensitizer and substrate free radicals and anion radicals (Chen et al., 2015; Patra et al., 2010; Kim et al., 2017). Electrons interact with molecules of oxygen that stay in their underlying energetic state. This approach leads to the development of reactive oxygen species (ROS) - initially in the form of anion radical superoxide ($O_2^{\cdot-}$), which produces more ROS generation within the cells. The initiated cascade of reactions leads to the death of cancer cells with oxidative stress (Smaisim et al., 2022a; Isola et al., 2022; Salimi et al., 2017b; Kianfar et al., 2018a).

2.2. Form II of photodynamic reaction mechanism

Energy is passed directly to the oxygen molecule in the simple energetic state as a result of the photosensitizer's transition into the excited triplet state (the basic triplet

state). Since they have the same spins, direct energy transfers between molecules ($PS \times O_2$) is possible. This creates excited particles of oxygen, so-called singlet oxygen, characterized with exceptionally high oxidizing properties.

The bulk of organic compounds are in the simple state of singlet. However, their triplet state (as the basis) and excitation into the singlet describe oxygen molecules. Because of this, excited photosensitizer particles do not affect the structures of organic cells and only react with oxygen molecules dissolved in the cytoplasm (Salimi et al., 2017a).

The most important method for conditioning the performance of PDT is believed to be the type II system. However, the contribution ratio of both pathways depends on several factors, including: the concentration of oxygen, the dielectric constant of the tissue and the composition of pH and photosensitizer. The first type of process starts to prevail when the oxygen runs out.

In the photosensitized area, highly reactive oxygen species cause photographic damage to proteins, fats and other molecules. In the apoptosis and/or necrosis process, this leads to the direct death of tumor cells (Kianfar et al., 2020a; Liu and Kianfar, 2020). The reciprocal contribution of multiple cell death forms is based on the photosensitizer's intracellular position. Mitochondrial damage can lead to

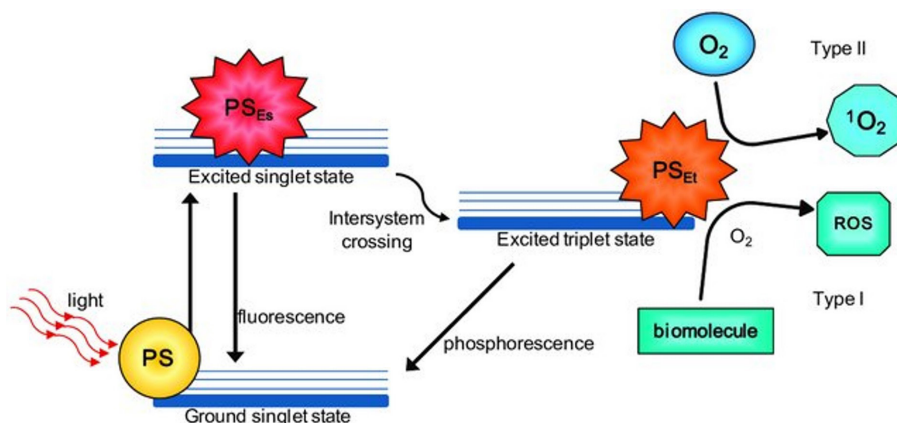


Figure 3. Photodynamic Reaction mechanism.

apoptosis, necrosis can be triggered with cell membrane degradation and loss of integrity, and autophagy can be caused with lysosome or endoplasmic reticulum damage (Figure 3).

3. Superiority of PDT Method

Due to the selective absorption of Ps substance, malignant lesion destruction is selective and healthy tissue adjacent to the irradiated tumor is not damaged (Kianfar et al., 2018a, b). In addition, with using the adjunctive method of PDD diagnosis, which is based on spectrophotometry (spectroscopy). The PS is absorbed into the tissue, it is possible to objectively and accurately identify the border of cancerous and healthy tissue and irradiate only the cancerous part (similar to what surgeons do during such biopsies, with removing a margin from healthy tissue and is a relative and inaccurate method. Figure 4 shows the general principles and stages of photodynamic therapy.

- The treatment is very simple and almost non-invasive (Kianfar et al., 2020b).
- Compared to other treatment methods, this group of patients, namely surgery, chemotherapy and radiotherapy, has much fewer side effects.
- It is more economical for both the general treatment system and the patient.

3.1. Benefits photodynamic therapy cancer

- ✓ Selectivity (Kianfar et al., 2017).
- ✓ Little to no scar following regeneration.
- ✓ Lower prices relative to other treatments.
- ✓ Impossible for new technologies to treat metastatic cancers.

4. Nanotechnology for Photodynamic Therapy

In order for PDT to be both efficient and protected, it is important that PS be administered to target cells (such as tumor cells) at therapeutic amounts, whilst at the same time being consumed with non-target cells in

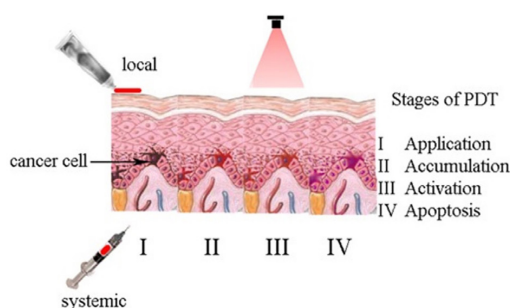


Figure 4. General principles and stages of photodynamic therapy.

only limited amounts, there with mitigating adverse side effects in healthy tissues (Chen et al., 2023; Kianfar et al., 2020a, b). To achieve this goal, there are two major hurdles. Second, most PSs have expanded π -conjugation structures that make the molecules highly planar, although the molecules appear to be highly hydrophobic, so most PSs stack up in an aqueous atmosphere to form aggregates (Kianfar et al., 2020a). This process of aggregation decreases the PSs' performance, which must be highly photoactive in monomeric form. Second, the PSs tested so far generally do not have a high tumor cell specificity or a pronounced tumor-localizing effect, rendering it difficult to target only the diseased tissue when PDT is applied (Faghieh and Kianfar, 2018). Therefore, several attempts have been aimed at developing delivery mechanisms that can integrate PS in monomeric form without limiting its operation and without having any in vivo adverse effects. The ability of Nano-carriers to target tumors is also of great importance in PDT using nanoparticles due to the improved permeability and retention (EPR) effect. Figure 5 illustrates how the PDT effects can be potentiated with encapsulation of PS in nanoparticles. Many various lipid and detergent nanostructures are used in these Nano-delivery systems (liposomes and micelles). In fact, before nanotechnology became a distinct and rapidly growing field of specialization, these Nano carriers were routinely used in PDT. (Kianfar, 2019; Kianfar, 2021). In the other side, before

the nanoparticles have a chance to aggregate in the tumor, the PS may be released prematurely in the serum, which is hypothesized to occur with the improved permeability and retention impact (Kianfar, 2021). If biodegradable, the structure of the substance may be limited to lipids or such polymers, while no degradable nanoparticles may stay in the body for long periods of time, and this may contribute to questions about the toxicity caused with the delivery vehicle rather than the drug (Syah et al., 2021).

4.1. Photosynthesis (PS) for cancer

A crucial factor is known to be the photosensitizer. The excessive photosensitization of the skin following systematic administration of photosensitizer and the need for patient avoidance of sunlight for many weeks are a significant drawback of PDT. However, light avoidance is tolerable for the majority of cancer patients (Abdelbasset et al., 2022). Nonetheless, there is also a need to investigate drug delivery methods for localized tumors to administer photosensitizer locally, while enhancing clinical effectiveness, shortening therapy time, and finally removing skin photosensitization (Jasim et al., 2022; Kianfar et al., 2022a). Progress in injection techniques, particularly in endoscopic needle injection, can be anticipated to reinvigorate interest in the advancement

of fully localized interstitial PDT procedures (Kianfar et al., 2022a; Ansari et al., 2022; Hachem et al., 2022; Smaisim et al., 2022b). the mixture of the injection of medications with light irradiation. The 2nd generation photosensitizers are called porphyrin derivatives or synthetics of established chemical structures made since the late 1980s. The light avoidance length of certain photosensitizers of the 2nd generation has been substantially decreased (e.g.<2 weeks). Photosensitizers of the third generation typically apply to improvements such as biological conjugates (e.g. antibody conjugate, liposome conjugate) and built-in capabilities for photo quenching or bleaching (Kianfar, 2022; Salahdin et al., 2022; Kianfar et al., 2022b; Isola et al., 2022; Fattah et al., 2023).The target-specific PDT uses photosensitizers that combine the sensitivity of an over-expressed cell marker with the phototoxic properties of the conjugated PDT photosensitizer with the antibody-or antisense-conjugated photosensitizers (Kadhim et al., 2023; Al-Awsi et al., 2023). A quick analysis of the advantages and deficiencies of each is worthwhile (Table 2).

In general, the optimal photosensitizer for solid tumor PDT should fulfill at least some of the following criteria (Abderrahmane et al., 2023; Wang et al., 2022; Xiao and Smaisim, 2022):

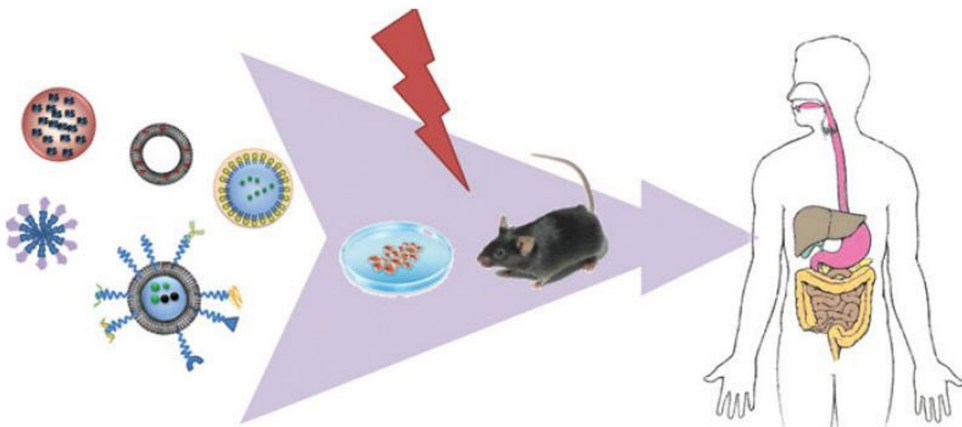


Figure 5. From in vitro trials, nanotechnology could hasten the advancement of PDT science, moving on to in vivo tests, and eventually to clinical applications.

Table 2. Photosensitizers in Photodynamic Pulmonary Therapy.

Name	Wavelength	Dose	Dra to illumination Interval, hr
	nm	Mg/kg	
Photofrin	630	2.0	48
ALA	630	30.0	48
Foscan	660	0.15	96
MACE	664	3.0	6
Fotosens	675	1.0	24

- ✓ A pure chemical which is commercially available,
- ✓ Low toxicity of darkness, but high photocytotoxicity
- ✓ Excellent selectivity against tumor cells,
- ✓ A longer wavelength enables greater penetration of light,
- ✓ Rapid removal from the body, as well as
- ✓ Many routes for administration (oral, intravenous, intratumoral or inhalational).

These requirements include a general reference guide. Although all or any of these requirements are fulfilled with some photosensitizers, there are currently only a few PDT photosensitizers that have earned official clearance around the world. Those may, but are not restricted to (Mourad et al., 2022; Smaism et al., 2022a; Abderrahmane et al., 2022; Tan et al., 2022; Mir et al., 2023; Ruhani et al., 2022; Cai et al., 2022; Moarrefzadeh et al., 2022):

- ✓ Photofrin-like (630 nm, Axcan Pharma, Inc.)
- ✓ Levulan (predrug of protoporphyrin IX; 630 nm, DUSA Pharmaceuticals, Inc.)
- ✓ Metvixa (predrug of protoporphyrin IX; 630 nm, PhotoCure ASA.)
- ✓ Foscan-Foscan (652 nm, Biolitec AG)
- ✓ Laserphyrine (664 nm, Meiji Seika Kaisha, Ltd.)
- ✓ Visudyne's (693 nm, Novartis Pharmaceuticals)

4.3. Properties of NPT for delivery of light sensitizers

Different nanoparticles each have their own characteristics in terms of the type of function, but in general should (Hai et al., 2022; Fadhil Smaism et al., 2022; Smaism et al., 2022b):

1. Have the ability to functionalize the surface for different chemical and biochemical groups, for example, with peeling (adding to the surface of PEG nanoparticles (polyethylene glycol) can prevent enzymatic degradation and microbial attacks on the sensitizer (Yang et al., 2020).
2. The surface of nanoparticles should have good porosity
3. It has a suitable size to be able to use the enhanced permeability and retention effect (EPR).
4. be non-immunological.
5. be optically transparent.
6. Optically more stable than in-body sensitizers (PS).
7. Have the ability to create a multifunctional system such as multiple therapies or diagnostics.

Since the efficiency of photodynamic therapy depends on the amount of oxygen produced, two strategies for nanoparticles in photodynamic therapy are proposed. (A) Degradable nanoparticles that release Ps into target tissues and then Ps produce unique oxygen. B) Non-degradable nanoparticles in which a single oxygen is produced and then diffused (Jiang et al., 2022; Tian et al., 2022a; Alharbi et al., 2022). Nanoparticles were first defined by Birrenbach and Speiser as nanoparticles and Nano spheres with a diameter of less than 100 nm. Interest in nanoparticles as drug carriers has increased in recent years because they can easily transport hydrophobic drugs into the bloodstream, and their high effective levels can be used to add chemical agents. These substances have a high volume of distribution and are effectively picked up with cells. In addition, they enable controlled drug release and have a variety of synthetic strategies for them (Wu et al., 2022; Tian et al., 2022a, b; Brontowiyono et al.,

2022). Specific and direct localization of sensitizers is also available through active targeting of Ps-containing nanoparticles (conjugating the receptor and other components). Therefore, the combination of these factors reduces the effective dose of light sensitizers for the treatment of PDT (Figure 6).

4.4. Nanoparticles used in PDT

The criteria for nanoparticle classification in PDT are very different. In a review article written by Kumar, nanoparticles are divided into active and inactive types depending on their involvement in the PDT process (Figure 7) (Mozafarifard et al., 2022):

- A) Biodegradable polymer nanoparticles.
- B) Non-destructible nanoparticles are divided like ceramic and metal nanoparticles.

Active nanoparticles according to the activation mechanism in the process of photodynamic therapy into 3 groups:

 - A) Photosynthesizes: Nanoparticles that transfer energy from incident light to ambient oxygen, such as CdSe semiconductor nanoparticles
 - B) Self-illuminating nanoparticles: These nanoparticles are activated with x-ray radiation and activate the light sensitizers attached to them with light fluorescence. Like nanoparticles BafBr: Er +, Mn+.
 - C) Up converting: These nanoparticles convert low energy light into high energy light to sensitively stimulate the attached optical stump, including NaYF4 nanoparticles: Yb, Er / Tm.

5. Inactive nanoparticles in dynamic light therapy

5.1. Biodegradable nanoparticle carriers

However, the results of degradation of these nanoparticles in exogenous conditions have been reported differently from the in vitro conditions (Sharba et al., 2022; Smaism et al., 2022a; AbdulHussein et al., 2022; Ahamad et al., 2022; Doss et al., 2022). The main advantages of this type of nanoparticles are high loading of the drug, the possibility of controlling the release of the drug and the high diversity of particles and their synthesis processes (Lefteh et al., 2022; Al-Madhhachi and Smaism, 2021). As expected, deforming the surface of these nanoparticles with PEG increases their circulation time. In one study, PLGA nanoparticles were used to create a sterile drug delivery system for Vertopporin, a sensitizer suitable for the treatment of several types of cancer, including skin. It is generally accepted that the mean size of nanoparticles can play an important role in drug therapeutic activity (via cell and tissue sampling depending on the size 370 and 167 nm). In this study, it was found that smaller particles have a greater therapeutic effect (Smaism, 2017a, 2017b, 2018 Smaism et al., 2016a). Other light-sensitive compounds studied for PLGA nanoparticles include hypericin and indomethacin green (ICG). ICG is an FDA-approved dye used to create contrast in diagnostic procedures for superficial cancers, including breast and skin (Farahani et al., 2023; Mir et al., 2023; Wang et al., 2023a).

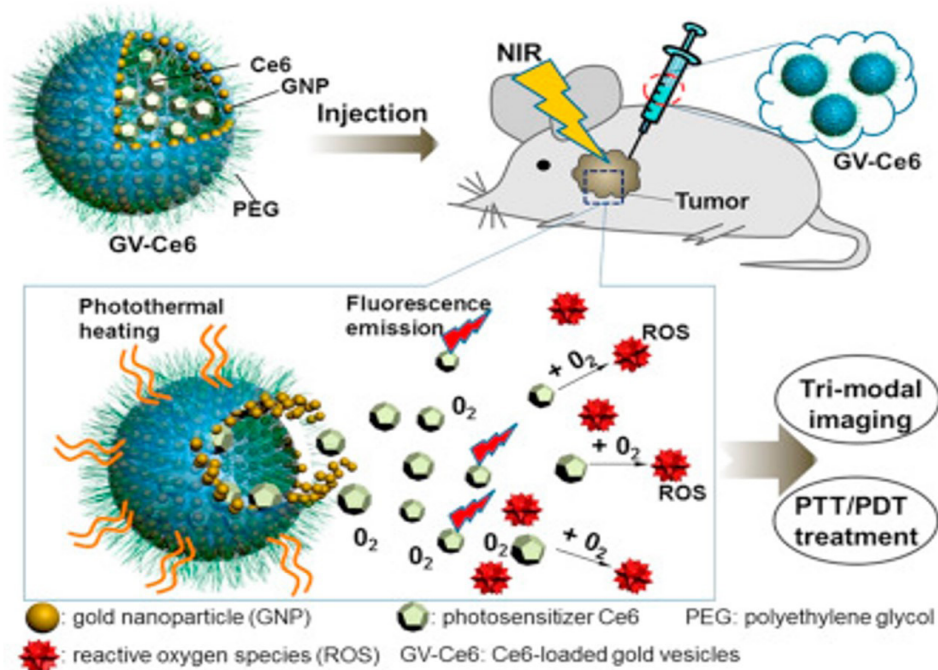


Figure 6. Schematic diagram of fluorescence trimodality/thermal/photoacoustic imaging-guided photo thermal/photodynamic cancer synergistic treatment with photosensitizer (Ce6)-encapsulated plasmonic gold vesicles (GVs).

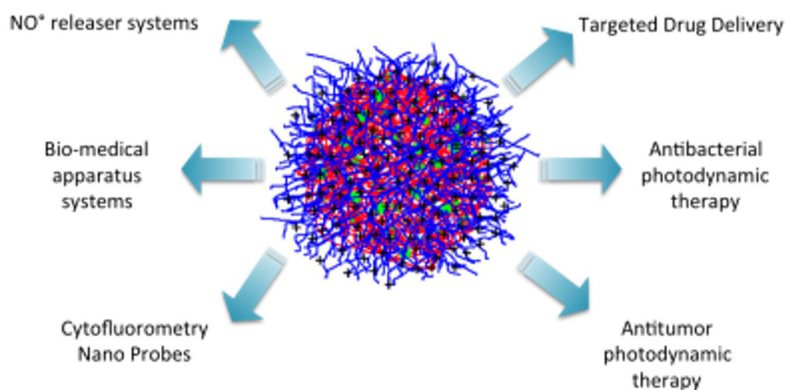


Figure 7. Schematic Polymeric Nanoparticles and Photodynamic Therapy.

Of course, this dye is absorbed in solution at 800 nm and has an emission peak of 820 nm, so it has great potential for photodynamic therapies. Recently, the bio-dispersion of ICG embedded in PLGA nanoparticles (300 nm in diameter and loaded 20%) and free ICG in $C_{57}BL/6$ mice was shown and found that drug-containing nanoparticles were two to eight times more precipitated than free ICG They had a tumor. Therefore, the use of nanoparticles has increased the shelf life of light-sensitive compounds in tumor tissue. Hypersin-containing PLA nanoparticles have been used for photodynamic treatment of ovarian cancer and showed

higher optical activity of hypersin loaded in nanoparticles than free hypersin. However, increasing the drug load on these nanoparticles reduces the optical toxicity at high concentrations (Figure 8).

5.2. Non-Biodegradable nanoparticles carriers

The function of these nanoparticles is different in PDT and they are not usually used for drug delivery because they are not destroyed and therefore cannot release the drug (Figure 9). Therefore, the Ps itself carried in the corn cannot be toxic, but produces toxic products of non-toxic

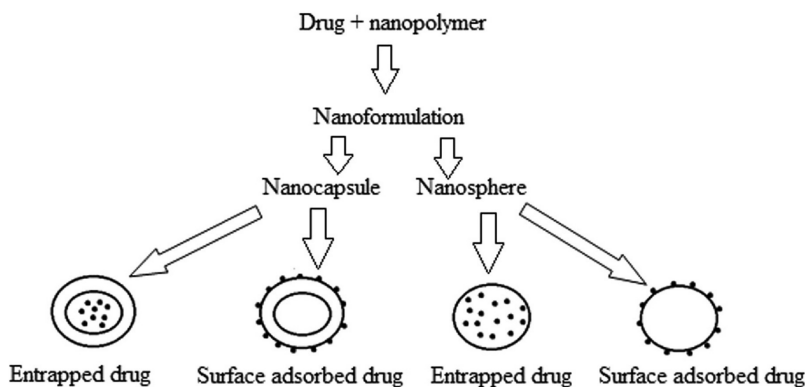


Figure 8. Schematic Biodegradable nanoparticle carriers.

environmental molecular oxygen and acts as a catalyst and can be applied continuously with excitatory light. A small hole (pore) in a ceramic particle with a diameter of 0.1 to 0.5 nm is very small for the drug to leave, but it is very suitable for the entry of O_2 and the exit of 1O_2 . In order to be effective, these nanoparticles must be small in order to have a volume distribution parallel to the drug, and this requires precise size control so that the size is less than 100 nm and preferably less than 50 nm (Wang et al., 2023a; Farahani et al., 2023). Ceramic nanoparticles that hold Ps non-covalently have several advantages over organic polymer particles, including resistance to pH-temperature changes, microbial and enzymatic attacks. Particle size-shape-prosthesis and their particle size distribution index (PDI = Poly dispersity index) can be easily controlled during fabrication. They are produced in ambient temperature conditions. Their surface can be easily changed for selective targeting (Targeting) and these Ps particles protect the environment well. It should be noted that although biodegradable polymer nanoparticles easily release the drug, the efficiency of PDT depends on the production of 1O_2 , so drug release is unnecessary (Mir et al., 2023; Abderrahmane et al., 2023; Wang et al., 2023a; Chen et al., 2023a; Narayanasamy et al., 2023). The half-life of 1O_2 in aqueous medium is in the microsecond range because 1O_2 reacts rapidly. Probably the first paper published on ceramic nanoparticles to encapsulate Ps in PDT was on the use of silica nanoparticles containing the drug HPPH (2-devinyl-2- (1-hexyloxyethyl) pyropheophorbide. This study demonstrates the high potential of ceramic nanoparticles in PDT. HPPH is currently in phases one and two of esophageal cancer clinics (Tahmasebi et al., 2021; Taifur Rahman and Evgeny, 2014; Suryatna et al., 2022).

In 2002, a group showed that pegylated silica (binding of polyethylene glycol polymer (PEG) to the nanoparticle surface) (which increases carrier biocompatibility) with small sizes has wide applications in biology. The team compared the spectroscopic properties between (mTHPC (meta-tetrahydroxyphenylchlorin) prepared with sol-gel method and examined free mTHPC. Among the current topics of interest is the combination of PDT method with other therapeutic and diagnostic methods. Among these studies, we can mention the polymer micelle system for simultaneous

encapsulation of HPPH and Fe_3O_4 nanoparticles. In this paper, a magnetic core is used to guide the carrier to the target cells. Wieder has recently developed drug delivery systems based on gold nanoparticles that have Ps attached to the surface of gold nanoparticles. Phthalocyanine derivatives attached to nanoparticles (phthalocyanine nanoparticles) were created with a diameter of 2 to 4 nm. Phthalocyanine monomer in the form of covalently on the surface of gold nanoparticles with absorbing a wavelength of 685 nm catalytically increases the production of ROS with high efficiency. Incubation of nanoparticles with Hela cells showed good cell harvest and 0.43 more cell death than free phthalocyanine (probably due to a 50% increase in ROS production in phthalocyanine nanoparticles compared to free phthalocyanine). Wieder and colleagues also made a comparison between gold and silica nanoparticles. He expected that the photosensitizer on the surface of gold nanoparticles was more efficient than the photosensitizer inside silica particles (regardless of the 1O_2 emission from the particles) (Bahadoran et al., 2022; Mahmood et al., 2022). Metal nanoparticles smaller in size than silica particles. Can be produced, therefore due to the high active surface, high photosensitizers can bind to them and produce higher cytotoxicity. In a study with Oo, 5-ALA electrostatic bonding was used on the surface of gold nanoparticles (30 nm in diameter) and observed a 50% increase in cell death compared to free 5-ALA. Increased ROS production with this researcher was also observed. It was observed and stated that this is due to the transfer of near field energy from gold nanoparticles to protoporphyrin nanoparticle surface due to the effect of SPR. Also, in a study conducted with our group, in addition to observing the catalytic role of gold nanoparticles in the production of ROS, the optimal conditions for the use of gold nanoparticles in the ALA-PDT process were determined and characterized (Bokov et al., 2022; Mansoor Al Sarraf et al., 2022; Mahmoud et al., 2022a, b; Raya et al., 2022).

5. Two-photon Excitation in PDT

The death of cells is mediated with singlet oxygen in PDT. Owing to its short life span (~3.5 ms in the aqueous environment) and its failure to diffuse longer distances

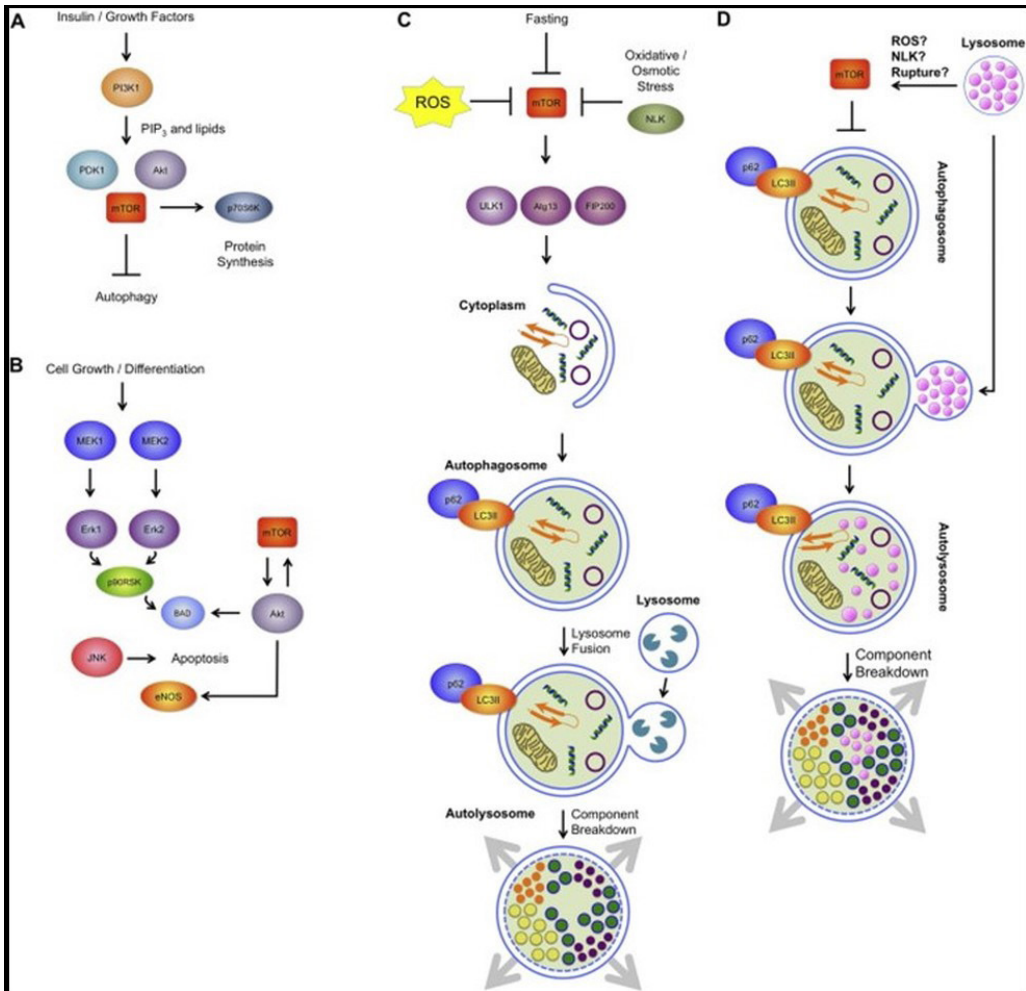


Figure 9. As regulated with hormones and nutrients, and as postulated in reaction to nanoparticles, autophagy pathways. (A) Graphical diagram of the simplified form of control of autophagy. PI3K1 stimulates PDK1, Akt, and mTOR, which in turn prevents autophagy and, for protein synthesis, activates p70S6K. (B) Schematic diagram of the pathway MEK1/Erk and its relations to mTOR and Akt. Poor may be dephosphorylated with Akt and p90RSK, resulting in apoptosis. Akt can also phosphorylate eNOS, resulting in apoptosis. Apoptosis can be caused with phosphorylated JNK. In nanoparticle studies where apoptosis is being studied, these causes are starting to be confirmed. (C) Graphical diagram of the impact on mTOR of fasting, generation of ROS and oxidative/osmotic tension. All three inhibit mTOR and induce autophagy in these situations. This is believed to occur through ULK1, Atg13, and FIP200, but other autophagic pathways that with pass mTOR have been observed. Once activated, autophagy involves the sequestration into organelles called autophagosomes of a subset of the cytoplasm, which can be partly recognized with LC3-II and p62. The autophagosomes combine with lysosomes to form autolysosomes where, with the action of membrane permeases, the contents are degraded and released back into the cytoplasm. (D) Schematic diagram of a lysosome bearing spherical nanoparticles to form an autolysosome combining with an autophagosome. How the existence of nanoparticles in lysosomes modulates the mechanism of autophagy is unclear.

beyond 100 nm in vivo, the region affected with singlet oxygen is spatially limited to a small volume. PDT is thus considered a comparatively safe, targeted modality of non-invasive therapy (Meena et al., 2016; Dhanalekshmi et al., 2019a; Dhanalekshmi et al., 2022). Currently, PDT treatment requires PS excitation through absorption of one photon. The key drawback of one photon excitation, with the excitation of photosensitizer present there, is the potential photodamage of the over and underlying tissues adjacent to the treated area (Dhanalekshmi et al., 2019b, 2021). The new two-photon excitation (TPE) system of

sensitizers overcomes the above-mentioned drawback with specifically controlling the amount of therapy in three dimensions. A closely focused femtosecond laser beam is used to get high fluxes of light as a light source for TPE. In this process, a PS molecule is concurrently excited with the absorption of half the energy of two incident photons or twice the wavelength of one excitation photon. In order to excite a molecule from the ground state to a higher energy electronic state, TPE is the mutual absorption of two photons at equal or separate frequencies. Two-photon absorption at low light intensity is a third-order

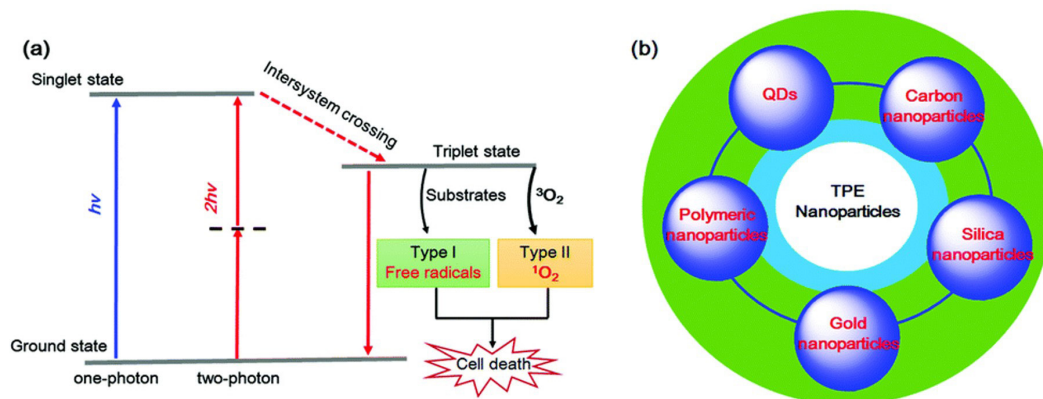


Figure 10. (a) Graphical illustration with type I and type II pathways of one or two-photon excitation mediated PDT. (b) The five distinct forms of PDT cancer TPE nanoparticles that will be presented in this study.

mechanism and several orders of magnitude slower than linear absorption. Without modifying the photophysical and photochemical properties of the photosensitizer, the two photon absorption excites the molecule, meaning that the excited states achieved with one or two photon absorption are similar. Awareness of the cross section value of PS for two photon absorption helps to determine its suitability for biological applications. For PDT applications, high TPA cross-section values are favorable since the ratio of the radiation consumed to the tumor input-energy flux will be high, reducing the potential photodamage to the neighboring normal cells. In 2003, with zinc-imidazolyl coordinations, Kobuke and co-workers reported a self-assembled conjugated porphyrin exhibiting a broad two photon absorption cross-section value ($s^{(2)}$) of 7,600 GM, which was the largest of the reported values calculated using femtosecond pulses. This importance is greater than that of protoporphyrin IX or Photofrin with three or four orders of magnitude. Furthermore, the development of singlet oxygen with high toluene efficiency was found, suggesting a suitable candidate for TPE-PDT. For effective two-photon absorption, Collins and co-workers developed porphyrin dimmers with polar functional groups. They also demonstrated its *in vivo* PDT efficiency. Figure 10 show (a) Graphical illustration with type I and type II pathways of one or two-photon excitation mediated PDT. (b) The five distinct forms of PDT cancer TPE nanoparticles that will be presented in this study.

6. Active Nanoparticles in Photodynamic Therapy (Mir et al., 2023)

6.1. Photosynthetic nanoparticles

Quantum dots have long been considered as a nanoparticle optical probe with high quantum efficiency, high optical stability, and size-dependent fluorescence properties. These nanoparticles can be soluble in water or specific to specific areas and malignancies. Quantum

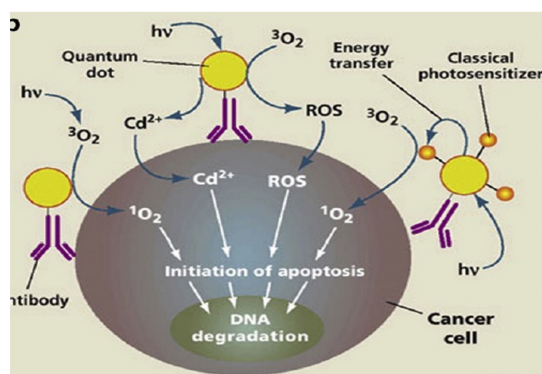


Figure 11. Possible mechanisms of optical light generation in the photodynamic process with quantum dots.

dots can also transfer energy to ambient molecular oxygen and lead to cell death, and recently articles have been published on their potential for Ps (Hameed Mahmood et al., 2022). In a study, two-phase energy transfer of quantum dots of CdSe to Ps attached to these particles is expressed (Huang et al., 2021). The group also predicted the interaction of phospholipid-coated (water-soluble) quantum dots (Figure 11). They hypothesized that the triplet state is the lowest energy level of the CdSe quantum dots and that the triplet energy transfer (TET) is responsible for producing 1O_2 from 3O_2 , but in any case, the 1O_2 production efficiency is about 5% (with 65% efficiency). Quantum fluorescence emission has limited their use (Mir et al., 2023). Many efforts have been made to improve the efficiency of 1O_2 production with quantum dots. These include connecting the covalent Ps to the quantum dots CdSe and ZnS via an organic bridge. These attempts had common problems, including the low solubility of the designed system in water, while the ability of quantum dots to produce toxic oxygen was not used in these cases (Kianfar et al., 2020a).

6.2. Self-lighting nanoparticle

A new method for treating cancer with a combination of radiotherapy and photodynamic therapy has been proposed, called SLPDT = Self lighting photodynamic therapy (Figure 12). In this method, scintillation luminescent nanoparticle nanoparticles with Ps that are covalently attached to their surface (such as porphyrins) have been used for photodynamic treatment *in vivo* (Mir et al., 2023). It should be noted that this system reduces the damage of this beam to healthy tissues around the target tissue with reducing the dose of ionizing radiation. Direct biological applications of this method have not yet been used. Among these nanoparticles, we can mention nanoparticles with the composition (BaFBr: Eu⁺, Mn⁺).

6.3. Up conversion nanoparticle

In general, tri-excitation luminescence materials (called phosphors) emit light with more energy than excitation light through various mechanisms, including up conversion and spontaneous two photon absorption. In two-photon absorption, the transition from the ground state to the excited state takes place with the spontaneous absorption of two photons. Up conversion relies on discontinuous discontinuous adsorption and stepwise luminescence, while at least two unstable components (usually ions) are involved in the process. The first component is used as the excitation store and the second component as the radiation state (Figure 13). Antistox radiation for the up-conversion process is ten to one hundred times kT (temperature (T) multiplied with the Boltzmann constant (k) is a measure of energy at the molecular scale) is greater than excitation energies, both the up-conversion mechanism and TPA because with wavelengths High radiation is generated thus providing the potential for access to tumors and deeper tissues. The role of nanoparticles in these cases becomes nanotransformable. These types of nanoparticles cannot cause the ROS effect, so they need to bind a suitable Ps. Up converting Nanoparticle (UCN) is a nanoscale compound that produces photons with energetic energy with absorbing NIR or IR radiation with metal ions mediated with lanthanides and actinides inside a suitable host. Raises . Sometimes referred to as Up-converting Phosphorus (UCP), they are known as sub-micron ceramic particles containing lanthanides that are visible with IR absorption. Binding of molecules and surface engineering (Kianfar et al., 2020a). Various materials are known as dopants in UCNs, some of which have real or potential applications in biology. Ionic materials are usually rare earth crystals such as lanthanides and actinides that are doped in a suitable crystalline matrix (Kianfar et al., 2020b). One of the common nuclei for biological applications is NaFY4, which has recently been doped with Er³⁺ / Yb³⁺ or TM3⁺ / Yb³⁺ to form micrometer-sized particles Kianfar et al. (2020a). The first report of PDT use with UCNs is the use of NaYF₄: Yb³⁺, Er³⁺ coated with a thin porous silica layer containing PsMerocyanine-370 and tumor-specific agents attached to its surface (Meena et al., 2016; Dhanalekshmi et al., 2019a; Dhanalekshmi et al., 2022). In subsequent studies, NaYF₄ nanocrystals contaminated with Er and Yb elements were coated with polyvinylpyrrolidone (PVP) and polyethylene (PEI =

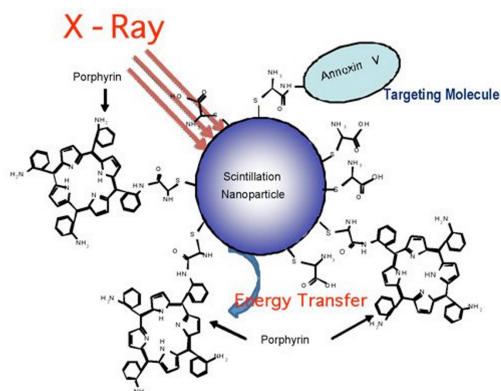


Figure 12. X-ray induced photodynamic therapy for cancer care, a graphical diagram nanoparticle-porphyrin conjugates. Annex in V is a molecule which can attack tumor cells with certain particular antigens.

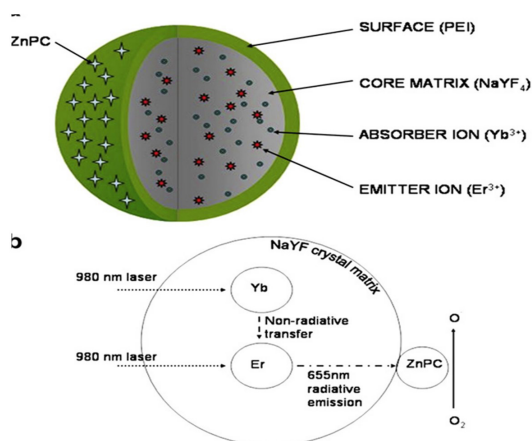


Figure 13. Structure and mechanism design of Upconverting nanoparticles. These nanoparticles absorb high-wavelength light and transmit it to the short-wavelength and appropriate Ps at the nanoparticle surface.

Polyethyleneimine) polymers. The resulting particles were 50 nm in size and had a positive surface charge. For use in photodynamic therapy, a light-sensitive compound ZnPc (phthalocyanine tin) was placed on the surface of these nanoparticles. This nanoparticle system had three very interesting functions; Dissolve non-polar ZnPc, help low-energy radiation to synthesize the energetic energy needed to stimulate ZnPc, and help target ZnPc to target tumor cells (Smaisim, 2017 a).

In general, there are several benefits to using UCNs:

1. Ability to examine deeper tissues with NIR light
2. NIR light cannot cause tissue damage.
3. Nanoparticles tend to deposit in tumor tissues due to the effect of EPR, but this property is intensified with the binding of targeting agents on the surface of the particles.

7. Conclusion

- For nearly two decades, light therapy has been used as a new, non-invasive and beneficial treatment for some cancers and non-cancers. Two factors affect dynamic light therapy: light-sensitive substance (Ps) and light radiation at the right wavelength. Of course, another effective factor can be added to this set, which is the element of oxygen, which is mentioned as a third factor or a condition for such interactions. Additional points of this discussion are given in the introductory section on photo dynamics therapy. In addition, issues such as the mechanism of PDT treatment, the advantages of this method, as well as how nanotechnology relates to the photodynamic therapy, especially nanoparticles used in PDT and their properties in delivering light-sensitive material in cancer, are discussed in this article.
- Despite its relatively long history, Norpooya therapy has not been well used in the clinical phase compared to other methods, but the emergence of nanomaterial's and nanostructures holds great hopes for increasing this treatment. The side of the relevant organizations is the hydrophobicity of Ps and the lack of selective accumulation of sufficient amounts of Ps in the damaged tissues. Nanoparticles can well accommodate hydrophobic drugs and increase the accumulation of Ps in the target tissue with using the effect of Enhanced Permeability and Retention (EPR) or monoclonal antibody binding. Therapeutic or diagnostic methods such as MRI can be used. Degradable nanoparticles cause proper release of Ps in target tissues, while non-degradable nanoparticles act mainly on the target cells with releasing reactive oxygen species, and Ps itself can be used as a catalyst until it leaves the cells. The emergence of active nanoparticles in PDT can increase access to deeper tissues in this method. These nanoparticles are either in the form of Ps or convert X-ray and Near Infra-Red to the appropriate wavelength for Ps attached to nanoparticles. Of course, few clinical studies have been done with these nanoparticles, and there are still questions about the appropriate dosage of the drug and radiation side effects and clinical benefits of these nanoparticles.

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