Al-Nahrain Journal of Science
ANJS, Vol.25 (4), December, 2022, pp. 1-10

Synthesis Methods and Applications of TiO_2 based Nanomaterials

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Article's Information

Received:
05.08.2022
Accepted:
12.08.2022
Published:
31.12.2022

Keywords:
Nanoparticles
Titanium dioxide
Sol-gel
Hydrothermal
Solvothermal
CVD

Abstract

Nanomaterials or nanoparticles (NPs) are nano-size particles with a (1-100) nm dimension, they show unique properties such as magnetic, electronic, optical, and activating effects. That is why NPs have many applications. Titanium dioxide (TiO_2) or Titania based nanoparticals are commonly used NPs due to their medical and industrial applications. TiO_2 NPs are used in photodynamic therapy (SDT) and drug delivery due to their non-toxicity. In this review paper we will show some of the types, synthesis methods, and applications of nano-TiO_2.

DOI: 10.22401/ANJS.25.4.01

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1. Introduction

TiO_2 is an inorganic semiconductor material of great interest because of its unique electronic and structural properties dependent on its phase. TiO_2 has low cost, relatively harmless and chemical stability [1]. titanium particles have different types, the commonly types are Brookite that contains more titanium than other types (90-100)%, the second one is rutile with (95-99)% titanium and finally anatase with (90-95)% [2], at ambient conditions the most stable phase is rutile however, anatase and brookits are metastable phase [1], the less common types are ilmenite, titanite, leucoxene, perovskite and dloparite [2].The crystal phases of TiO_2 anatase, Brookite, and rutile are depicted below in Figure 1.

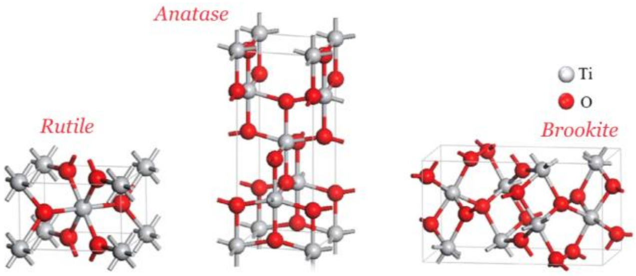

Figure 1. The three crystal structures of TiO_2.

Brookite is rarely studied due to its complicated structure and its difficulty in synthesis in pure form. However, interest in brookite has increased because of its remarkable properties that have been found lately [3]. These phases depend on processing temperature and the preparation method of TiO_2. According to XRD analysis, when TiO_2 production occurs at a temperature < 873K, an analase crystal phase will be obtained. However, anatase shows more stability and transfer to rutile. If two conditions are met, the first one is at a temperature higher than 973 K and the second one is using small TiO_2 NPs (size less than 50nm) [4]. Analase as well as rutile show more stability than analase when the particles size is more than 14 nm [5].

2. Nano-TiO_2 Synthesis Methods

2.1 Sol-gel method:

This method is a common method to synthesize TiO_2 NPs because it is a simple, low-cost, and non-toxic. In this method, TiO_2 NPs are obtained in the crystal phase as shown in the following lines. The sol is produced by the reaction of two compounds; the first compound (hydrolyzed titanium iv isopropoxide) is prepared from dissolved titanium iv isopropoxide (TTIP) in absolute ethanol with a stirrer for 1 hour. Following the addition of the second compound as a hydrolysis catalyst (deionized $H_2O + HNO_3$) drop by drop with a stirrer at 60 °C for 2 hours, the gel is produced by evaporating the solvent from the sol solution by heating it at 100 °C for 1 day, and after annealing for 4 hours at 600 °C, TiO_2 NPs in the crystal phase [6].

The size of NPs that are obtained by the sol-gel method depends on temperature [7]. According to Scanning Electron Microscopy (SEM), when sol annealed at 450 °C, the size of the NPs is 30 nm [8], as shown in Figure 2(a). However, when sol annealing at 600 °C, the size of NPs will be 60 nm, as illustrated in Figure 2(b).

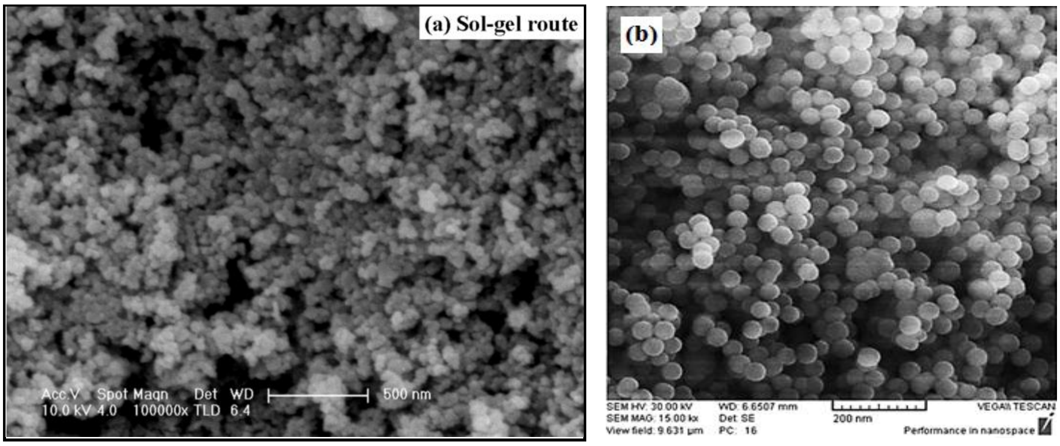

Figure 2. (a) TiO_2 NPs SEM when sol annealing at 450 °C. (b) TiO_2 NPs SEM when sol annealing at 600 °C.

2.2 Hydrothermal method:

This method isn’t commonly used because it requires an autoclave and it is expensive. The term "hydro" means using water as a solvent, and "thermal" means using temperature. This method was used not only to synthesise nanoparticles but also nanotubes. Typically, TiO_2 NPs are prepared by dissolving TTIP in distilled water, followed by the addition of NaOH under stirring until the formation of a white colloidal sol, and then being transferred into an autoclave for 12 hours at 240 °C and drying for 2 hours [8]. TiO_2 nanotubes can also be prepared by the hydrothermal method when dispersing TiO_2 (Degussa P25) into NaOH solution for 2 hours at 30 °C, placing the mixture in the autoclave for 72 hours at 110 °C, followed by redispersing for 3 hours in HCl solution, placing it in the centrifuge, after that, using distilled H_2O in order to stabilise the pH at 6.7, and finally drying the final product at 80 °C in a vacuum oven for 24 hours. Finally, the sample was annealed for 2 hours at 400 °C [9]. According to SEM, the grain size of nano-TiO_2 synthesized by the hydrothermal method is ~100 nm. The SEM of TiO_2 nanotubes and nano-TiO_2 are depicted below in Figure 3 (a) and (b).

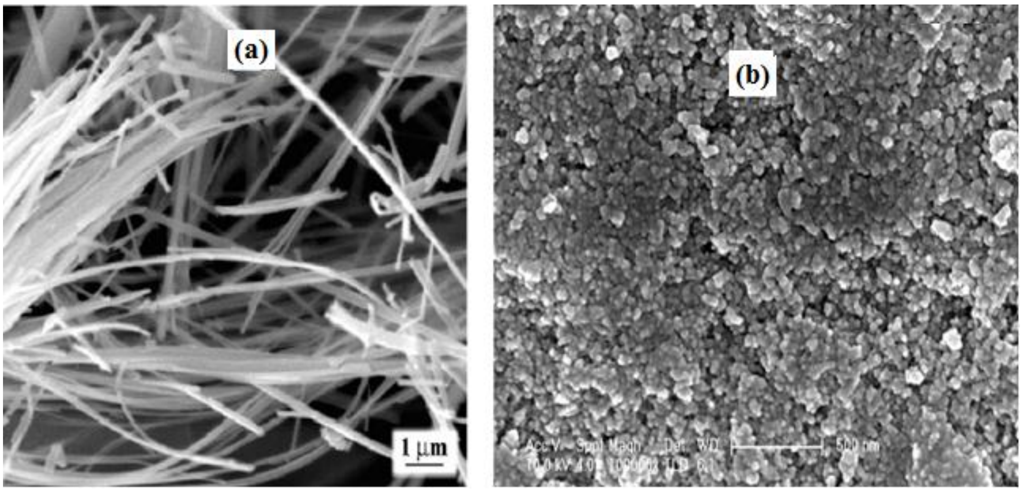

Figure 3. SEM of (a) TiO_2 nanotube, (b) TiO_2 NPs.

NPs synthesized by the sol-gel method have a smaller crystalline size than NPs synthesized by the hydrothermal method, and the NPs produced are highly crystalline [8]. Because the method conditions play an important role in the size of prepared NPs, and in the sol-gel method, there is a possibility to adapt their conditions, so the sol-gel method is more suitable for synthesizing small-sized NPs than the hydrothermal method [11].

2.3 Solvothermal method:

This method is somewhat similar to the hydrothermal method, the difference being that this method requires the use of a non-aqueous solvent. The temperature may rise in this method higher than the temperature in the hydrothermal method due to the ability to use high boiling point organic solvents [12]. The TiO_2 NPs were synthesized by mixing tetrabutyl titanate (TBT) with glycerol in absolute ethanol and stirring for 30 min. The solution was transferred into an autoclave at 140 °C (the temperature may change according to desired results). After 24 hours, the product was washed with absolute ethanol. The precipitate with a white colour was collected and dried at 80 °C in a vacuum overnight. The sample was annealed in a muffle furnace for 2 hours at 500 °C [13]. The SEM for this method is show in Figure 4 at different temperatures.

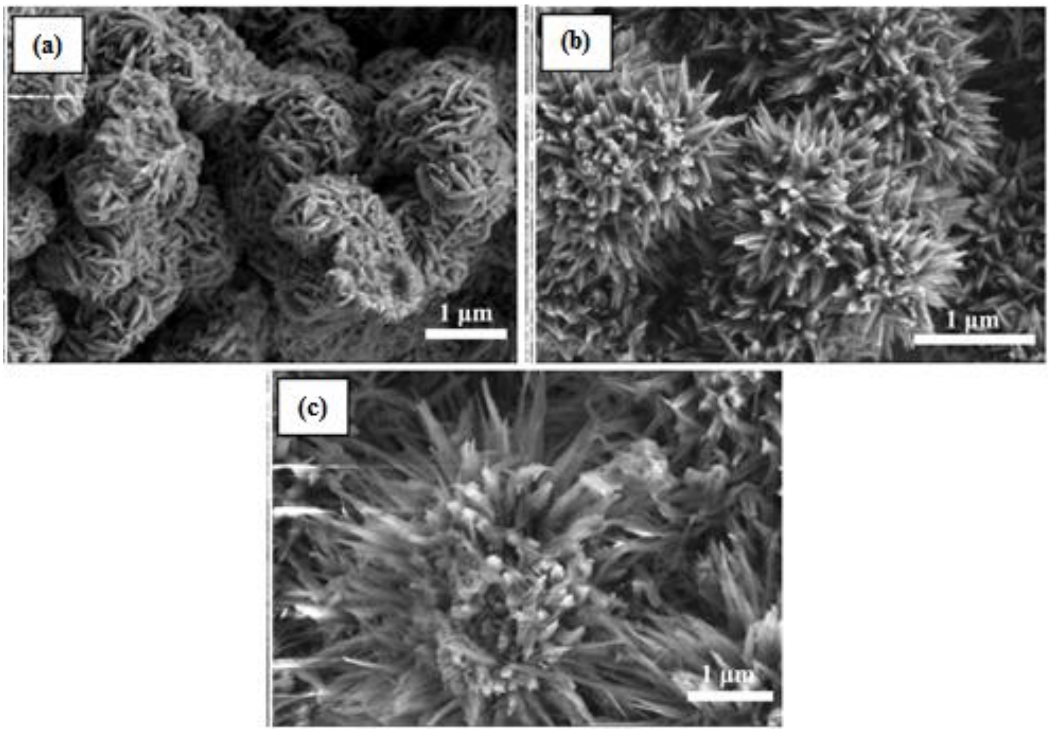

Figure 4. Nano-TiO_2 SEM by solvothermal method at (a) 140 °C, (b)170 °C and (c) 200 °C.

This method provides a higher control of particle shape distribution and particle size of TiO_2 NPs than the hydrothermal method. Because of that, this method can produce NPs with a narrow size distribution [14].

2.4 Direct oxidation method:

TiO_2 nanorods are synthesized by the oxidation method when Ti plate are oxidized by H_2O_2. Typically, Ti plate is placed in an H_2O_2 solution for 72 hours at 353 K to obtain TiO_2 nanorods in the crystal phase [15,16] as shown in Figure 5. The addition of an inorganic salt of NaX, such as NaCl, NaF, or $NaSO_4$ will control the nanorods. If NaF or $NaSO_4$ is used, pure anatase will be produced. If NaCl is used, rutile has the most chance of being produced, Nanotube can be prepared via this method the same way, but H_2O_2 was replaced by NH_4F and malonic acid as an oxidising agent [15].

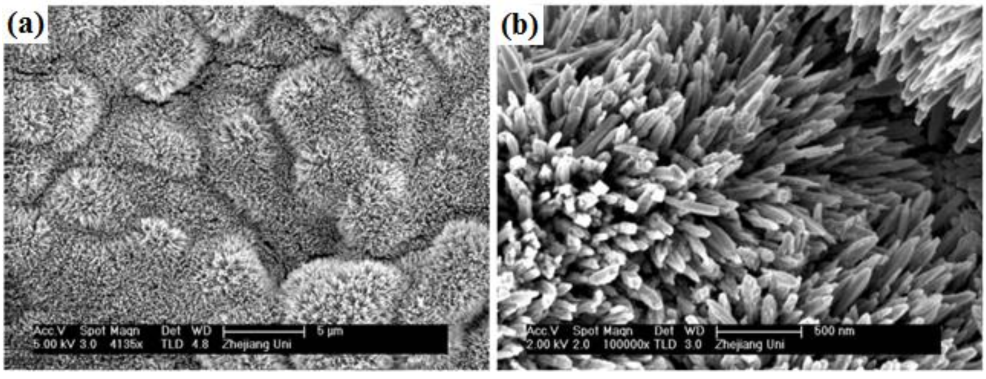

Figure 5. FESEM of the Ti plate surface after soaking in the H_2O_2 solution (a) Low magnification, (b) high magnification image showing rod-like morphology.

The precipitation rate was affected by the anions and TiO_2 nanorods were obtained in the crystal phase. The good thing about this method is its green chemistry, as it produces extremely low residual pollutants [17]. Peng and Chen used acetone as the source of oxygen to obtain TiO_2 nanorods aligned arrays when they oxidised a Ti substrate at 859 °C for 90 min [18]. as shown in Figure 6 (a). The structure of the final product depends on the oxygen source. If pure oxygen is used, crystal grain films will be obtained. However, random non-fibers will be obtained from low oxygen concentrations as shown in Figure 6 (b). These nanofibers grow from TiO_2 grain ledges. The high concentration of oxygen (pure oxygen) causes oxygen diffusion to dominate and an oxidation process to occur when TiO_2 interfaces with Ti metal. As a result, large polycrystalline TiO_2 grains will form [17].

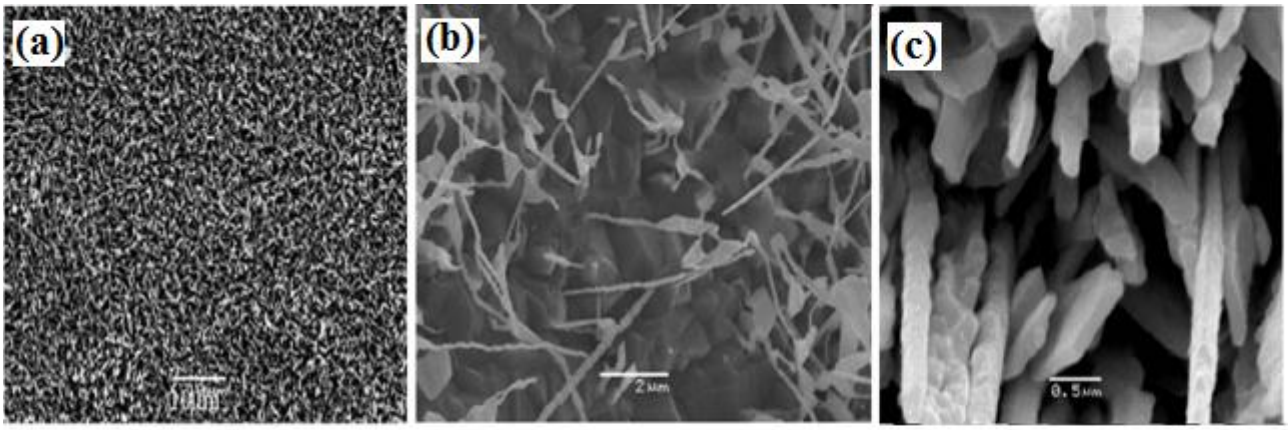

Figure 6. SEM images of (a) low magnification of large-scale nanorod arrays prepared by oxidizing Ti with acetone at 850°C for 90 min, (b) chain-like and ribbon-like Nano fibers, (c) high magnification of column nanorod.

2.5 Sonochemical method:

This method uses ultrasonic techniques for NPs synthesis in a short period of reaction time by using the phenomenon of acoustic cavitation [19]. The major advantages of this method are: short reaction time, simple method, and energy-efficient process [20]. González-Reyes et al. prepared TiO_2 NPs in the anatase phase, and anatase was transferred to rutile because TiO_2 particles and pore kept growth by surface motion in addition to the growth of grain by grain boundary motion. Typically, TTIP is dissolved in a mixture of acetone and ethanol as a pressure-transmitting medium. The solution was subjected to sonochemical treatment in an ultrasonic bath for 50 min at 38 kHz. The prepared solution was evaporated at 150 °C followed by annealing at 400 °C for 2 hours [21]. Figure 8 shows TEM images of the 3 stages of prepared TiO_2 NPs by González-Reyes et al. Anatase was prepared in the first stage, the particles grew in the second stage, and anatase-rutile was shown. Finally, the rutile was completely obtained in the third stage [21]. Hamed Arami et al. TiO_2 NPs in rutile phase were prepared directly by dissolving TiO_2 plates in NaOH solution at room temperature for 2 hours, followed by sonochemical treatment in an ultrasonic bath for 2 hours at 40 kHz, centrifuged, washed several times in deionized water, and annealed at 60 °C for 24 hours [22]. Figure 7 shows TEM and SEM images of the prepared TiO_2 NPs by Hamed Arami et al.

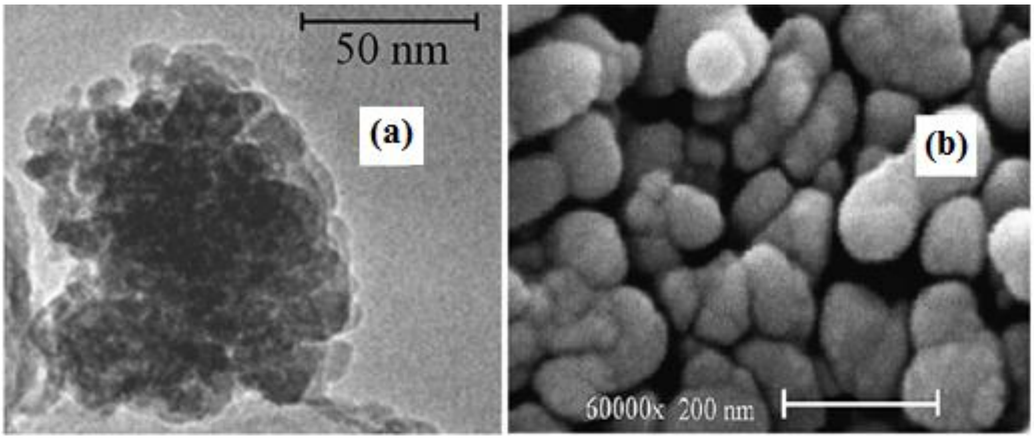

Figure 7. (a) Shown TEM and (b) SEM images of the prepared TiO_2 NPs.

2.6 Chemical vapour deposition method (CVD):

This method is based on heating the substrate until metalorganic or inorganic precursors decompose, or on plasma activation. CVD occurs at low pressure but requires an expensive vacuum system, which is why plasma-enhanced chemical vapour deposition (PECVP) is being developed [23,24]. Heejin Lee et al. TTIP was used as a Ti source and evaporated at 90 °C using argon gas as shown in Figure 9 (a). At 900 °C the mixture was passed through an alumina tube. This tube was connected to a T-junction containing beads of soda lime glass. These beads were pre-treated for 30 min in acetyl alcohol as shown in the sechemate diagram in Fig 8 [25]. Shinde and Bhosale evaporated TTIP at 287-362 °C using oxygen-gas [26], as shown in Figure 9 (b).

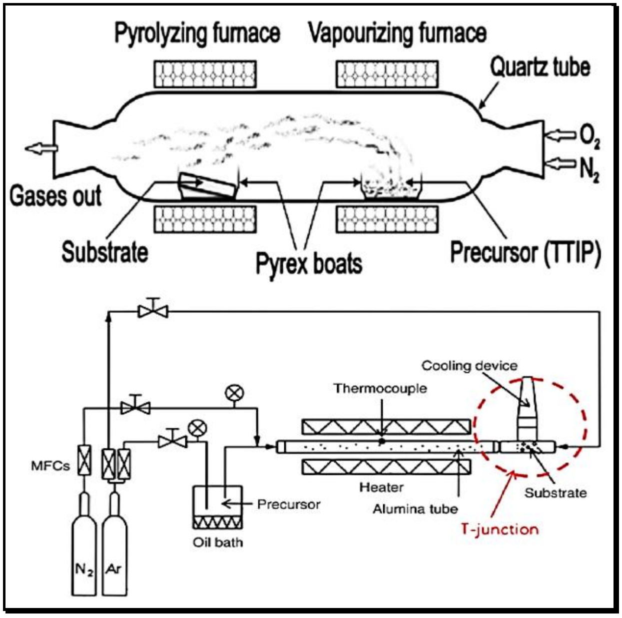

Figure 8. The sechemate diagram of evaporated TTIP in argon gas.

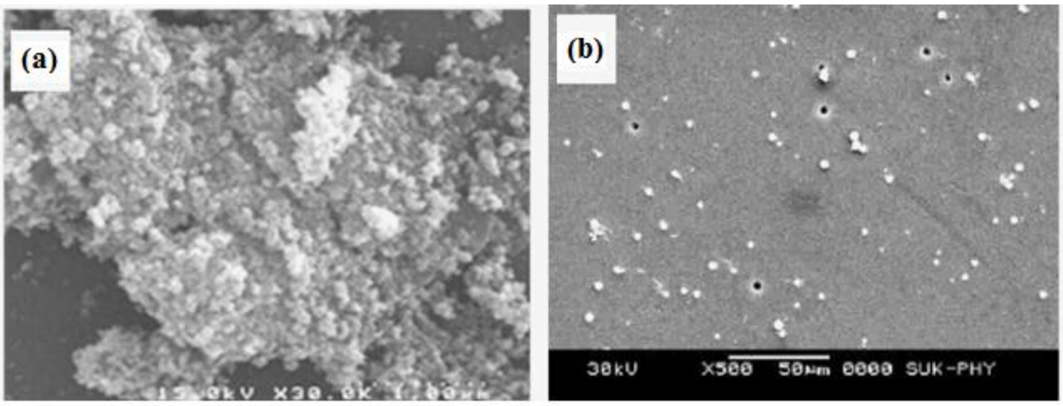

Figure 9. SEM of (a) evaporated TTIP in argon gas and (b) of evaporated TTIP in oxygen gas.

3. Nano-TiO_2 Application

There are many important uses for nano-TiO_2, and this review will summarise the most important uses. In the food industry, nano-TiO_2 is used to improve the white color, flavor, and brightness [27]. As a UV radiation shield, they are frequently used as additives and anti-caking agents in cosmetics and sunscreens [28]. To achieve the performance required for this use, El-Deen et al. show the improvement of TiO_2 electrochemical properties and the requirement for amorphology to prevent particle aggregation during cycling [29]. The use of Nano-TiO_2 as a semiconducting catalyst in the reaction of hydrogen production is recognized as an economical and green method, even in its modified or pure forms [30-32]. The use of Nano-TiO_2 increases the efficiency of the therapy and the selectivity of photosensitizer (PS) [33]. The use of nano-TiO_2 in drug delivery [34] As shown in Figure 10, nano-TiO_2 interacts with drugs to improve their ability to penetrate cell membranes and selectively accumulate in diseased tissues [36,37].

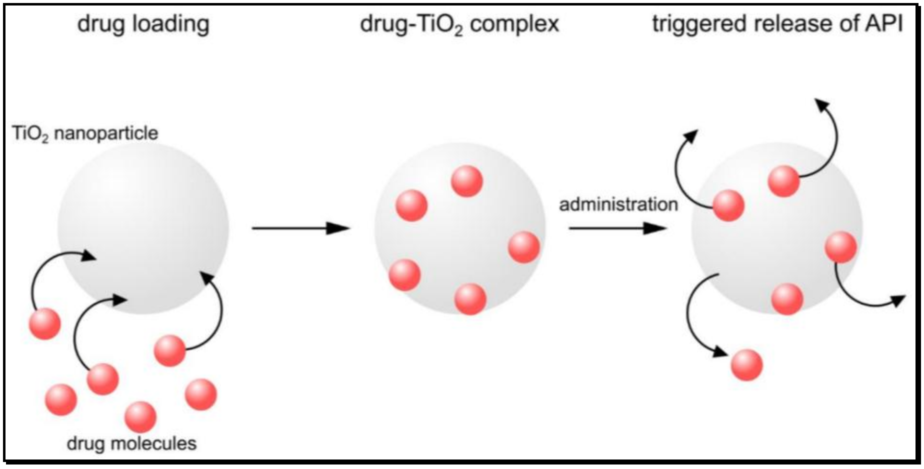

Figure 10. Simplified mechanism of nano-TiO_2 as drug delivery vehicle.

Nano-TiO_2 showed antibacterial activity against E. coli and S. aureus because TiO_2 binds to groups that donate electrons such as amides, hydroxyls, carboxylates, etc. Therefore, it inhibits the activity of DNA and cellular enzymes, which leads to increased permeability due to the formation of little pores in the walls of bacterial cells and leads to cell death [38].

Nano-TiO_2 is used to target antigens or biomarkers which are specific to cancer cells, and shows good results in anti-cancer drug delivery in cancer therapy [39]. For successful cancer therapy, it's important to choose a delivery system that targets the cancer cells without affecting the normal cells, such as TiO_2 NPs [40]. The TiO_2 NPs are radiosensitive; therefore, they can be used in radiotherapy in cancer therapy [41]. This radio sensitivition results from the generation of reactive oxygen species (ROS) and effects on cell killing. ROS is generated from exposing Nano-TiO_2 to light radiation in aqueous solution, hence the energy gap for anatase is 3.23 eV and 3.06 eV for rutile. The molecules pass to an excited state if they absorb a photon with equal or higher energy than the energy gap value of Nano-TiO_2; hence the energy gap for anatase is 3.23 eV. The free negative electrons attack surrounding O_2 and H_2O to form ROS, including H_2O_2 superoxide (O^{2-}) and hydroxyl radical. These three molecules are unstable and react with cell components to cause necrotic or apoptotic cell death [42-44]. Figure 14 shows a simplified mechanism of ROS generation by nano-TiO_2.

Photodynamic therapy is one way to treat cancer by ROS generation from nano-TiO_2 [45-47] as photosensitizer (PS), an active component. PS is administered either topically or intravenously to the body. Exposing nano-TiO_2 to light radiation leads to an excited electron to a higher energy state and the transfer of energy in an oxygenated aqueous solution by sensitizer to surrounding molecules, either O_2 or H_2O, creating ROS, which leads to cell death in surrounding tissue [45]. The other way to treat cancer is through homodynamic therapy (SDT). This way uses nano-TiO_2 as a son-sensitizer to generate ROS [48-50]. Therefore, PDT and SDT cause little or no toxicity and cytotoxicity. Therefore, these methods are strong alternatives to chemotherapy and classical radiotherapy [51]. The schematic view of PDT and SDT is shown in Figure 11.

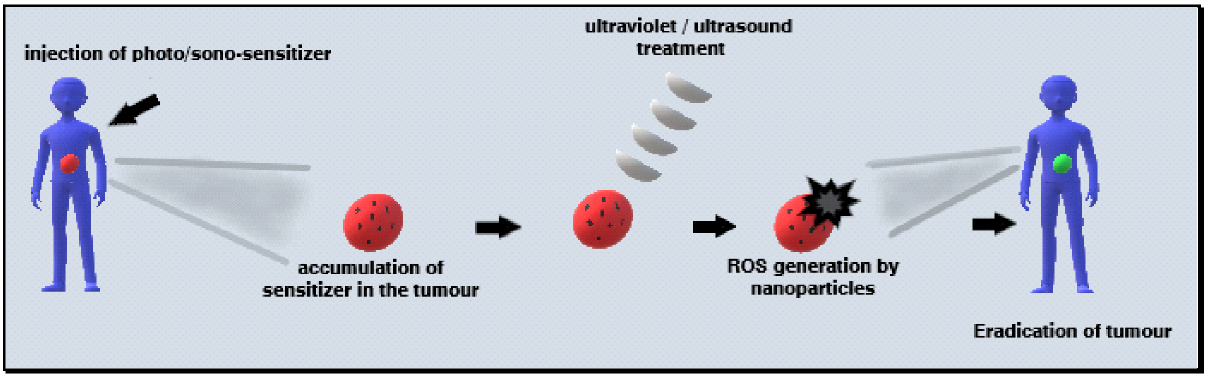

Figure 11. The schematic view of PDT and SDT.

Nano-TiO_2 is used in teeth whitening and tooth personal care because of its photochemical activity [53]. It can eliminate odour by decomposing organic compounds like tobacco and gasoline [56]. Figure 12 shows the photocatalytic effect of TiO_2.

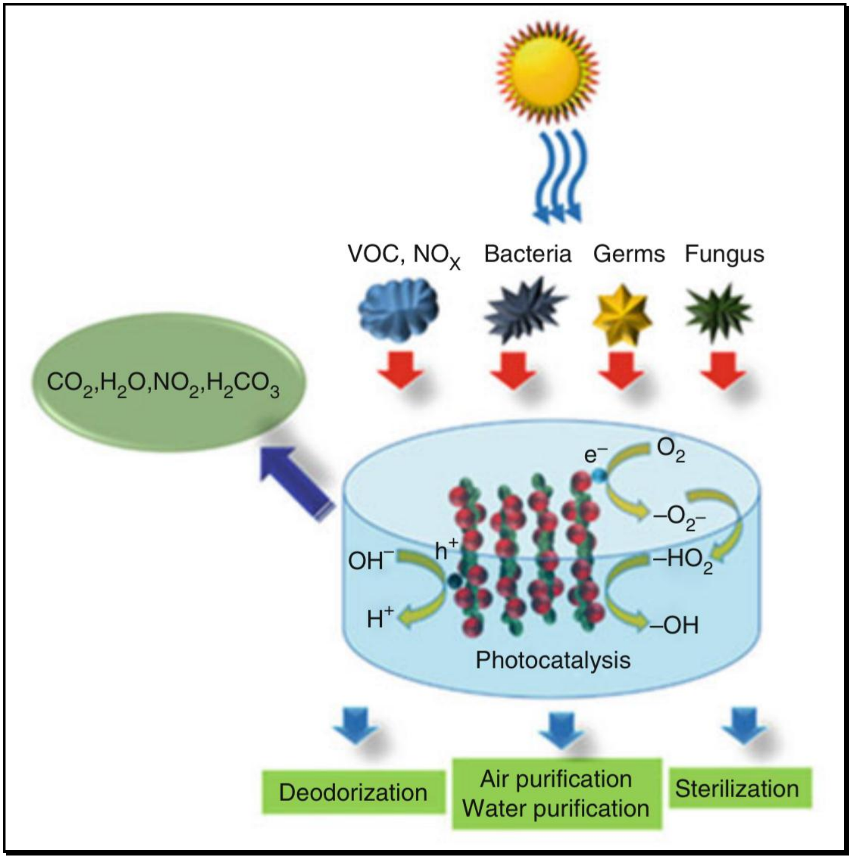

Figure 12. Photo catalytic effect of TiO_2.

Anatase TiO_2 NPs are semiconductors with high bandwidth because of which they're used in dye-sensitized solar cells (DSSCs) [57]. It is used as a coating material to protect it from corrosion because of its adhesion ability and ability to withstand high temperatures due to its high melting point, reaching 1840°C [58]. Because of its band gap values, Nano-TiO_2 can absorb UV rays in the range of 220-400 nm, so it is used as a UV protection material [59].

4. Limitations of Nano-TiO_2

In many studies, TiO_2 is poorly sensitive to visible light as a photocatalyst because of its wide band gap, which is only excited by ultraviolet light as well as the relatively high rate of recombination of electron-hole pairs. This leads to poor efficiency and a low quantum yield of photocatalytic reactions. In many studies, in order to overcome this limitation, they used many processes such as: modifying TiO_2 with non-metal ion or metal ion doping; noble metal addition; anionic and cationic doping; co-doping with two or more ions; and surface fluorination to improve the surface structure, extend the light absorption into the visible region and slow down the rate of recombination of electron-hole [60,61].

The enhancement of nano-TiO_2 activity as a photocatalyst can be increased by transition metal doping, but it causes toxicity of certain metals and thermal instability. Behnajady et al.; modified TiO_2 via doping with magnesium (Mg) to yield Mg-TiO_2. They found that magnesium didn't cause toxicity. It's low cost and easy to prepare, so it is very suitable for industrial applications [62].

Rutile TiO_2 absorbs 4% of the sun's light. This is triggered by absorption into a strong oxidising state, and unwanted reactions occur, reducing the stability of DSSCs [63]. To prevent that, anatase TiO_2 is used in DSSCs [57]. Due to their small size and particle-particle aggregation [64], nano-materials are difficult to handle.

5. Conclusions

Many synthesis methods, medical and industrial applications rely on its unique properties, which include magnetic, electronic, optical, and activating effects, as well as adhesion and heat resistance. This review paper mentioned some of these methods and applications. Regardless of the many applications of nano-TiO_2, it has many limitations that should not be overlooked. These limitations were mentioned in this review as well. In the future, nano-TiO_2 will continue to attract attention, both in commercial applications and in scientific research.

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