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Synthesis, Modification, Applications and Challenges of Titanium Dioxide Nanoparticles

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ABSTRACT

The paper revealed the synthesis and ability of TiO_2 nanoparticles to possess desirable features such as biocompatibility, crystalline and chemical structure stability, as well as optical and electrical properties, which makes it a vital research material in the various area of application. In this paper, it was posited that the use of biological synthetic method is the most eco-friendly preparation method when compared to the physical and chemical synthetic methods which are affected by the demerit of equipment cost and chemical toxicity respectively. Modification techniques such as immobilization, doping and coupling have been reported in this review to be effective in increasing the performance efficiency of TiO_2 nanoparticles and solving the problem of separation difficulty encounter in water and wastewater treatment. It was also reported that TiO_2 nanoparticles has been successfully applied in the various field such as water and wastewater treatment, photovoltaic devices, environmental remediation as well as in biomedical operation and devices. Finally, it was reported in this review that chronic inhalation of TiO_2 nanoparticles may result to health related problems, which may constitute a threat to the ecosystem.

Keywords: *Modification, Nanoparticles, Immobilization, Synthesis, Biomedical, Eco-friendly*

INTRODUCTION

Titanium, which has been reported to be less dense than steel but stronger than it, is a light, strong, silvery and corrosion resistance metal which exist as the ninth most abundant element in the earth's crust, and can be found in nature in the form of various oxides, of which the most common is titanium dioxide (TiO_2) [1-2]. Titanium dioxide, which is also referred to as TiO_2 or titania is a thermally stable, non-inflammable and poorly soluble white solid inorganic substance which can be regarded as a global product due to its wide range of applications. It was first introduced as a commercial product in 1923, and has been used for many years in a vast range of consumers and industrial goods including paints, catalyst systems, medical devices, aerospace and turbines, ceramics, adhesives, sunscreens, ointment, toothpaste, coatings, paper and paper board, coated fabrics and textiles, plastics and rubber, printing inks, cosmetics and pharmaceuticals, food colorants, water treatment agents, floor coverings, roofing materials and in automotive products [2]. TiO_2 is a vital research material due to its biocompatibility, physical optical and electrical properties as well as the stability of its chemical structure, and can exist in the crystalline forms of brookite, rutile and anatase. The common forms are anatase and rutile which has density and band gap of 3.9 g/ml, 3.2eV (corresponding to a UV wavelength absorption of 385nm), and 4.26 g/ml, 3.0 eV (with excitation wavelengths that extend into the visible light range of 410 nm) respectively. However, anatase which is considered as the most preferred and photochemical active phase of TiO_2 is the most stable form by 8-12 KJ mol and can be converted to rutile by heating to a temperature of 700 ºC, while brookite which is the third crystalline form of TiO_2 is uncommon and unstable [3-6]. Due to the impressive and advantageous properties of TiO_2 nanoparticles (NPs), it has receive a wide attention in many fields such as tackling of energy and environmental challenges, improvement in health care, biomedical devices and drug delivery systems [7]. In this review, the physical, chemical and biological synthetic methods for the preparation of TiO_2 NPs have been explained. The modifications, applications and challenges of TiO_2 NPs were also discussed respectively.

SYNTHESIS OF TIO_2 NANOPARTICLES

The synthetic methods for the preparation of TiO_2 NPs can be classified into physical, chemical and biological synthetic methods depending on the nature by which the TiO_2 NPs are synthesized.

Physical Synthesis of Tio_2 NPs

Contrary to the demerit of chemical toxicity which is associated with the chemical synthesis of TiO_2 NPs, physical synthetic methods does not involve the use of toxic chemicals but are usually faster as they are done with the use of specialized instruments. However, it should be noted that physical synthetic method has the demerit of lower quality of products and the use of costly vacuum system or equipments when compared to chemical methods [8-9]. An example of physical method used for the synthesis of TiO_2 NPs is physical vapor deposition.

Vapor Deposition (VD)

VD usually takes place in a vacuum chamber and is concern with the vaporization of the target material by a heat source and then the rapid condensation of the vaporized target material, VD can be subdivided into physical and chemical methods depending on whether chemical reaction occurs during the vaporization-condensation process. If no chemical reaction occurs, it is called physical vapor deposition (PVD); otherwise it is called chemical vapor deposition (CVD) [9-10]. However, it must be emphasized that the use of PVD produces resultant NPs that have the same composition with the target materials, while the use of CVD produces resultants NPs which does not have the same composition with the target materials. This is because of the chemical reaction that occurs between the vapor and the system component during the vaporization-condensation process [9-10]. CVD have been effectively used to synthesized TiO_2 nanostructures directly grown on a substrates by vaporizing titanium acetylacetonate (Ti ($C_{10}H_{14}O_5$)) in a low-temperature zone of a furnace at 200-230 ^{0}C and carried by a N_2/O_2 flow into the high-temperature zone of 500-700 ^{0}C. It has been reported that under a pressure of 5 Torr and temperature 560-630^{0}C, single-crystalline rutile and anatase TiO_2 nanorods were formed respectively, while, anatase TiO_2 nanowalls composed of well-aligned nanorods were formed at a temperature of 535 ^{0}C, under a pressure of 3.6 Torr, this therefore implies that the phase and morphology of TiO_2 nanostructures can be tuned with the reaction conditions [10]. The use of PVD with the aid of Au as a catalyst in the synthesis of TiO_2 nano wires has been reported by utilizing pure titanium metal powder on quartz in a tube furnace which is 0.5 mm away from the substrate at a temperature of 850 ^{0}C and pressure of 300 Torr, when argon gas is made to flow at a rate of 100 sccm and held for 3 h [10].

Arc-Discharge Method / Plasma Based Synthesis

This technique involves the use of an igniter, which is attached to an anode in order to generate a low-voltage, high-current self sustaining arch, it also involve the instigation of an arc by contacting a cathode made of a target material. Plasma based synthesis has the merit of high temperature and high enthalpy to vaporize any material as well as high quench rate which result to homogenous nucleation [11]. It has been reported that typical operating parameters such as arch voltage, arc current, feed rate for metal/hydride powders, gaseous flow rate and torch input power rate are paramount requirements for the plasma based synthesis of TiO_2. However, it should be noted that lower input power to torch lowers the plasma temperature and this leads to an incomplete conversion which indicate a rapid dissociation at high temperature [11].

Chemical Synthesis of TiO2 Nanoparticles

Chemical synthetic method is the most frequently used approach for the synthesis of TiO_2 NPs when compared to other methods. However, it has been associated with the demerit of chemical cost and toxicity. Chemical synthetic method for the preparation of TiO_2 NPs include; photochemical, sol-gel, solvothermal, hydrothermal, sonochemical and electrochemical methods.

Sol-Gel Synthetic Method

This is the most commonly used method for the synthesis of TiO_2 Nanoparticles, and it involves the acid-catalyzed hydrolysis of titanium (IV) alkoxide precursor, which is followed by condensation. The merit of this method includes versatility and the ability to facilitate the synthesis of nano-sized crystallized TiO_2 powder of high purity at relatively low temperature process [6, 11]. The sol-gel synthetic method has been reported to result in the formation of a three dimensional polymeric skeletons with close packed first-order particles resulting from the development of Ti-O-Ti chains, which is

favored by factors such as low water content, low rate of hydrolysis and excess quantity of titanium alkoxide in the reaction mixture. However, under a condition of high rate of hydrolysis, medium water content and large quantity of Ti-OH, sol-gel synthetic method has been reported to result in the formation of $Ti(OH)_4$ which exhibit insufficient development of three dimensional polymeric skeletons with loosely packed first-order particles [10]. Autoclave heating of titanium alkoxide and tetramethyl ammonium hydroxide at 200 ^{0}C or direct heating of alkoxide and tetramethyl ammonium hydroxide in a three-neck flask at 90-100 ^{0}C has been reported to be effective in the sol-gel synthesis of highly crystalline anatase TiO_2 [10].

The application of amines such as triethanolamine, diethylenetriamine, trimethylenediamine and triethylenetetramine has been shown to be effective as surfactants and shape controllers of TiO_2. Secondary amines, such as diethylamine and tertiary amines, such as triethylamine and trimethylamine can act as complexing agents of Ti (IV) ions in order to promote growth of ellipsoidal particles with lower aspect rations [10, 12]. A sol-gel synthesis of TiO_2 nanoparticles prepared by mixing titanium tetraisopropoxide (TTIP) precursor with triethanolamine (TEOA) ([TTIP]/[TEOA]) 1:2), in the presence of water has been reported, It was observed that at a pH value above 11 with (TEAO), the morphology of TiO_2 nanoparticles changes from cuboidal to ellipsoidal. However, TiO_2 NPs shaped evolves into ellipsoidal above pH 9.5 with diethylenetriamine with a higher aspect ratio than with TEOA [10, 13].

Sol Synthetic Method

This is a non hydrolytic sol-gel method which involves the reaction of titanium chloride with molecules such as titanium alkoxide, alcohols and ethers which can act as an oxygen donor.

$$TiX_4 + Ti(OR)_4 \rightarrow 2TiO_2 + 4RX \quad (1)$$

$$TiX_4 + 2ROR \rightarrow TiO_2 + 4RX \quad (2)$$

From the equation above, it can be seen that Ti-O-Ti bridges is formed by the condensation between Ti-X and Ti-OR or R-O-R [10]. Sol synthesis of TiO_2 nanoparticles with nearly uniform size and shape has been reported to be effective by the slow addition of titanium chloride to anhydrous benzyl alcohol under vigorous staring at temperature (40-150 ^{0}C) for 21 days in a reaction vessel. The precipitate was thoroughly washed and calcinated for 5 hours at a temperature of 450 ^{0}C, the TiO_2 NPs size and growth was observed to be strongly dependent on the thermal condition as well as the concentration of titanium chloride and benzyl alcohol [10, 14]. The hydrolysis of titanium butoxide in the presence of acetylacetone and *p*-toluenesulfonic acid at 60 °C has been reported to yield mono-disperse non-aggregated TiO_2 NPs, which could be dispersed in water-alcohol or alcohol solutions at concentrations higher than 1 M without aggregation, which is attributed to the complexation of the surface by acetylacetonato ligands and through an adsorbed hybrid organic-inorganic layer made with acetylacetone, *p*-toluenesulfonic acid, and water [10, 15].

Hydrothermal Synthetic Method

Hydrothermal synthesis of TiO_2 nanoparticles is usually conducted in an aqueous reaction in an autoclave (steel pressure vessel) with or without Teflon liner under a controlled temperature/pressure condition which can be elevated above the boiling point of water, thereby reaching the saturation vapor pressure. This synthetic process is called hydrothermal because water is used as the solvent in the synthesis of nanoparticles [10]. At a temperature of 647.15 K and pressure of 221 bar, water is said to exist as a supercritical fluid which can both act as a liquid and gas, while exhibiting the ability to decrease the surface tension at the interference fluid of solid and dissolves the chemical compounds which are very difficult to dissolve at ambient conditions. The use of supercritical conditions takes the advantages of enhanced solubility and reactivity of metal and it is becoming very popular for the synthesis of NPs because of its short residence time with rapid reaction rates and particle growth as well as other advantages such as simplicity, very low grain size, presence of a single phase and synthesis of high purity nanocrystals with high crystallinity and eco-friendliness nature [16-17].

The addition of 0.5 M isopropanol solution of titanium butoxide into deionized water in the presence of a peptizer (tetraalkylammonium hydroxides), has been reported to be peptized at a temperature of 70 ^{0}C in order to prepare TiO_2 NPs. The obtained powders were washed with deionized water and absolute ethanol and then dried at 60 ^{0}C, after filtration and treatment of the precipitates at 240 ^{0}C for 2 h. It was observed that the concentration of peptizers influences the morphology of the TiO_2 nanoparticles, it was also

noted that under the same concentration of peptizer, the particle size of TiO_2 decreases with an increase in alkyl chain length [10, 18].

The synthesis of anatase TiO_2 NPs phase without secondary structure by the drop wise addition of TTIP into a mixture of ethanol and water at a pH of 0.7 using nitric acid and temperature of 240 ^{0}C for 4 h has been reported to be effective. It was posited that the concentration of the Ti precursor and the composition of the solvent system has an impact on the control of the size of the particles to the range of 7-25 nm [10, 19].

Solvothermal Synthetic Method

Solvothermal method is a versatile method for the synthesis of NPs with narrow size distribution and disperity, this method has been observed to be almost similar to hydrothermal synthetic method except that non aqueous solvents are used for the synthetic process and the temperature can be elevated much higher that hydrothermal synthetic method. Solvothermal method has also been reported to have a better control than hydrothermal method in terms of the size and shape distributions as well as crystallinity of TiO_2 NPs [10].

The solvothermal synthesis of TiO_2 NPs has been reported to be carried out with/without the aid of surfactants. The average particle size of TiO_2 powders synthesized without the aid of a surfactants by mixing TTIP with toluene at the weight ratio of 1-3:10 and kept at 250 ^{0}C for 3 h was reported to increase with a corresponding increase in the composition of TTIP in the range of weight ratio of 1-3: 10, while the pale crystalline phase of TiO_2 was not produced at 1:20 and 2:5 weight ratios [10, 20]. However, the solvothermal synthesis of TiO_2 NPs with the aid of sufficient amount of oleic acid (OA) as a surfactant has been reported to yield long dumb bell-shaped nanorods, when TTIP was dissolved in anhydrous toluene with OA as a surfactant and kept at a temperature of 250 ^{0}C in an autoclave without stirring. It was also reported that at a fixed precursor to surfactant weight ratio of 1:3, the concentration of rods in the nanoparticles assembly increases with an increase in the concentration of the titanium precursor in the solution. The average particle size was noted to be smaller with a narrower size distribution compared to the synthesized TiO_2 NPs without surfactant [10, 21].

Photochemical (Irradiation) Synthetic Method

This deals with the use of electromagnetic radiation such as ultraviolet, microwave, X-ray and γ-ray irradiation in the synthesis of NPs. The application of microwave irradiation (with frequency between 900 to 2450 MHz) in the synthesis of NPs has become popular due to its simplicity, rapid and short reaction time, high yield of products and ease of operation compared to the conventional heating methods [17]. For example, the use of microwave irradiation in the synthesis of a colloidal suspension of TiO_2 NPs was reported to be successfully within 5 min to 1h, while the use of a conventional synthetic method by hydrolysis at 195 ^{0}C was carried out between 1 to 32 h [10, 22].

Electrochemical (Electrolysis) Synthetic Method

This involves the use of electricity as the driving or controlling force in the synthesis of NPs, this synthetic method takes place at the electrolyte-electrode interface in an electrolytic cell by the passage of electric current through two electrodes separated by an electrolyte. The main advantages of this method include low cost, ease of operation and availability of equipment, high flexibility, less contamination and eco-friendly process [17]. The electrochemical synthesis of pure anatase of TiO_2 NPs has been prepared by heating 0.2 M $TiCl_3$ at pH 2 at 500 ^{0}C for 4 h with a pulse electro deposition approach [10, 23].

Sonochemical Synthetic Method

This deal with the enhancement of chemical reactions by the application of powerful ultrasound radiation (10 to 20 MHz) in the synthesis of NPs, the chemical effects of the ultrasound doesn't come from the direct interaction between the molecular species, instead it comes from the acoustic cavitation such as the formation, growth and implosive collapse of bubbles in a liquid, which produces intense local heating (5000 k), high pressures (1000 atm), enormous heating and cooling rates (>10^9 k/s) is responsible for the sonochemical reaction that results in the synthesis of NPs [10, 17]. The application of Sonochemical synthetic method in the preparation of TiO_2 NPs from an aqueous NaOH solution of TiO_2 has been reported to produce arrays of TiO_2 nano whiskers with a diameter of 5 nm and nano tubes with a diameter of 5 nm and a length of 200-300 nm [10, 24].

Biosynthesis of Titanium Dioxide Nanoparticles

The biological synthetic method is affiliated with the use of extracts from living organisms and has been reported to be the most ecological

friendly approach for the preparation of TiO_2 NPs because it does not involve the use of toxic chemicals, neither does it release toxic chemical products to the environment during the synthetic process. A few example of biological synthetic process for the preparation of TiO_2 NPs is briefly reviewed below [25].

Eclipta Prostrate Extract

The aqueous leaf extract of *Eclipta prostrate* obtained as a filtrate from boiling 10 g of the leaves in 100 ml of distilled water at 60 ^{0}C for 10 min has been successfully used in the synthesis of TiO_2 NPs by adding 15 ml of the *E. prostrate* extract to 85 ml of 5 mM TiO_2 at room temperature under stirring condition for 24 hours for the formation of the nano crystals [26].

Nyctanthes Arbor-Tristis

Sundrarajan and Gowri, reported the synthesis of TiO_2 NPs by *Nyctanthes Arbor-Tristis* leaves extract obtained as filtrate by mixing 1g of the dried leaves with 50 ml of ethanol and extracted under reflux condition at 50 ^{0}C for 5 hours. The biosynthesis of TiO_2 NPs was carried out by starring 0.4M of titanium tetraisoproxide in ethanolic leaf extract at a temperature of 50 °C for 4 h. The formed TiO_2 NPs were subjected to centrifugation and calcinate at 500 ^{0}C before analytical characterization was carried out [27].

Vigna Radiata Extract

Chatterjee *et al*., investigated the biosynthesis of TiO_2 NPs with the use of *Vigna Radiata* extracts obtained as filtrate by boiling 10 g of crushed dried sprouted green grams in 100 ml of distilled water for 30 min. The biosynthetic process was conducted by stirring a mixture of 20 ml of *Vigna Radiata* extracts and 80 ml of 1 mM TiO_2 solution at room temperature for 24 hours and the filtrate was calcined to obtain the TiO_2 NPs which was subjected to analytical characterization [28].

Psidium Guajava Extract

A research by Santhoshkumar *et al*., on the synthesis of TiO_2 NPs by using *Psidium guajava* extract obtained as a filtrate from boiling 20 g of freshly amassed leaves of *Psidium guajava* in 250 ml of distilled water at 60 ^{0}C for 15 min has been successfully conducted. The biosynthesis of TiO_2 NPs was done by stirring a mixture of 20 ml of aqueous leaf extract of *Psidium guajava* and 80 ml of $TiO(OH)_2$ in an Erlenmeyer flask for 24 hours showed a colour change to light green, indicating the formation of TiO_2 NPs which was characterized by FTIR, FESEM and XRD [29].

Fusarium Oxporum Extract

Isolated fungi *Fusarium oxporum* has been effectively used in the biosynthesis of TiO_2 NPs by Siva and co-worker, the fungus *Fusarium oxysporum* was grown in 500 ml Erlenmeyer flasks each containing 100 ml of MGYP media at 25-28 °C on a shaker at 200 rpm for 96 h. The mycelial mass was separated from the culture broth by 5000 rpm centrifugation at 10 ^{0}C for 20 min and the settled mycelia were washed three times with sterile distilled water. 20 g of the harvested mycelia mass was added into 500 ml Erlenmeyer flasks containing 20 ml of aqueous 0.025 M TiO_2 solution and kept on a shaker (200 rpm) at 27 ^{0}C for 96 h. After incubation, nanoparticles containing fungal mycelia were filtered under laminar flow through Watman filter paper and subjected to calcinations at 180 ^{0}C for 5 h for crystallization of TiO_2 NPs, which were analysed by FTIR and UV-vis spectrophotometer [30].

Arnicae Anthodium Extract

The biological synthesis of anatase TiO_2 NPs using *Arnicae anthodium* aqueous extract has been successfully investigated. This was done by stirring a mixture of 30 ml of aqueous extract of *A. anthodium* and 30 ml of of 5mM TiO_2 at room temperature for 24 hours. After this period, the solution was heated to heated to 100 °C for the time 30 minutes and filtered by 0.45 µm Milipore membrane filter, followed by 0.2 µm Millipore membrane filter in order to obtained the synthesized TiO_2 NPs which was characterized using uv-visible spectrometer, SEM and FTIR [31].

Curcuma Longa Extract

The use of *Curcuma longa* extracts for the synthesis of TiO_2 NPs has been adequately studied by using two methods. The plant extracts was obtained as a filtrate from heating 15 g of the powder *C.longa* in a soxlet extractor containing 300 ml of distilled at 40 ^{0}C for 3-4 h. In the first method, 50 ml of the filtrate was mixed with 2.5 ml of 50 mg/ml TiO_2 solution on a magnetic steer hot plate at 50 ^{0}C and 1000 rpm for 5 h. The second method involves the mixing of 50 ml of the filtrate with 5 ml of 50 mg/ml TiO_2 solution under the same condition as the first method but for a period of 8 h [32]. It was observed that the first method resulted in the production of TiO_2 in both supernatant (colloidal solution) and precipitate (nanopowder), while the second method resulted in the production of precipitate only. The colloidal solution was kept

for characterization while the precipitate was washed with distilled water and subjected to centrifugation at 15, 000 rpm for 10 min and dried at room temperature for 24 h [32].

Bacillus Mycoides

The use of isolated strain of *Bacillus mycoides* in the synthesis of TiO_2 NPs has been successfully conducted by adding 40 mL of a 25 mM titanyl hydroxide solution to a culture of 200 µL of *B. mycoides* grown overnight (12h). The mixture was incubated at 37 ^{0}C for 24 h with constant shaking. After this time, the solution was incubated at room temperature for 8 h and the appearance of a white precipitate was formed, which indicated the production of TiO_2 NPs. The precipitate was removed from the culture by centrifuging 15 min at 3820 × g. Finally, the biosynthesis product was washed and resuspended by successive centrifugations in Mili-Q ultra pure water [33].

MODIFICATION OF TiO_2 NPS

In order to enhance the effectiveness of TiO_2 NPs in various fields of application, there have been various methods for the modification of TiO_2 NPs. A few of them is summarized below;

Immobilization of TiO_2 NPs

Immobilization of TiO_2 on substrate is an important field of research and the aim of this is to enhance higher surface area, superior adsorption properties, reduce electron-hole recombination and avoid the problem of post separation difficulties associated with TiO_2 NPs [7, 34]. The immobilization of TiO_2 can be done of powder/pellet (e.g activated carbon, magnesium-aluminium silicate) substrate, soft/thin (membrane or film, cellulose fibre), rigid/thick (glass), however most immobilization of TiO_2 is done on glass substrate due to the advantage of transparency even after the immobilization and this improve the photocatalysis of the system by allowing the passage of light through the glass substrate [34]. The immobilization of TiO_2 on Fe_3O_4 magnetic NPs to produce TiO_2/Fe_3O_4 magnetic NPs has been successfully conducted and shows a 70-80% of phosphate removal activity from wastewater [35]. Research on the immobilization of TiO_2 on glass has shown a 75.8% reduction in the adsorption and photo degradation of methylene blue (MB) from waste water treatment [36]. The use of silica-doped TiO_2-coated glass plate in wastewater treatment has been show to result to 70 and 80% removal efficiencies for MB and indigo carmine respectively [37]. Polystyrene matrix has been reportedly used in polymer supported TiO_2 photocatalyst for environmental remediation, the use of polystyrene supported TiO_2 has proved effective in the removal of MB by adsorption and phtocatalytic reduction process for a period of 6.5 h resulting in 76 and 96 % in the removal and discoloration of MB from wastewater respectively [38]. Similarly, the use of polyacrylamides as a polymer support for TiO_2 nanogel composite has been prepared by using dispersion crosslinking radical polymerization technique. The prepared polyacrylamide immobilized TiO_2 nanogel composite has been posited to have removal capacity range from 445 to 485 mg/g for both organic and inorganic pollutants from wastewater [39]. Research on the improvement in the solar disinfection of water with photo reactive TiO_2/single wall carbon nanotubes (SWCNT) composite coated on plastic PET bottles has been successfully experimented. It was reported that at an irradiation time of 180 min, the blank control sample hold 63% of the initial bacteria concentration, while both the TiO_2 and TiO_2/ SWCNT decreased the initial concentration of bacteria to half its initial value. It was also reported that at an irradiation time of 360 min, the blank control sample hold 30% of the initial bacteria concentration, while both the TiO_2 and TiO_2/ SWCNT were able to decrease the initial concentration of the bacteria to 6 % of its initial value. However, it was posited that only the TiO_2/SWCNT was able to reduce the bacteria concentration below the Environmental Protection Agency (EPA) standard of 500 cf/mL of Coliform of bacteria in water [40]. The application of TiO_2 coated activated carbon to form a composite as a regenerative technology for water treatment has been successfully conducted. The photocatalytic decolorization of MB and reactive red from wastewater has been reported to have reduction efficiencies of 30 and 80 % for reactive red and MB respectively [41]. Similarly, TiO_2-activated carbon (AC) composite has been used in wastewater treatment by the removal of endocrine distrupting compounds such as Tartrazine. TiO_2-AC composite was reported to exhibit a high photocatalytic activity for the degradation of Tartrazine with the rate constant four-fold faster than that of TiO_2 powder in the suspension mixture with AC, but the best performances with TiO_2-AC composite can be explained by the vicinity of photocatalyst and AC adsorption sites. A comparative study on the reutilization of TiO_2 mixed with AC and TiO_2-AC composite

for the degradation of tartrazine was about 50 and 80 % respectively, however after the 4th cycle on the reutilization of TiO_2-AC composite, only about 15 % of its adsorption capacity was reportedly lost [42]. The immobilization of TiO_2 on aluminium foam has been successfully used in water treatment, it was observed that the initial rate of formic acid and phenol degradation were 0.007 and 0.001 mmol/L/min respectively. However, the use of immobilized and reference TiO_2 powder for water treatment revealed apparent quantum yields for formic acid was 2.2 and 2.7 %, correspondingly. While that of phenol revealed quantum yields of 0.4 and 0.7 % for immobilized and reference TiO_2 powder respectively [43].

Doping of TiO_2 NPs

The photocatalytic activity of TiO_2 NPs takes place under ambient operating conditions and is largely dependent on the band gaps (3.0-3.2 eV), which constrain its photoactivity due to the narrow wavelength spectrum for the photonic activation of the semiconductor, which absorb from the UV region of the solar spectrum [34, 44]. However, only about 3-5 % of solar flux comprises UV radiation incident at the earth surface is able to excite the TiO_2 NPs, therefore in order to extend its absorption ability to the visible spectral regime and improve its photocatalytic activity, researchers have been working on the modification of the optical band gap energy of TiO_2 by employing certain techniques such as doping, which deals with the incorporation of dopants such as metal, non metal or organic sensitizer into TiO_2 NPs in order to reduce the band gap of the semiconductor [34, 44-46].

Modification of TiO_2 NPs by doping at different temperature heat treatment with metal and non metal such as nitrogen, carbon and sulphur have been reportedly used to red-shift the absorption spectrum of TiO_2 thereby reducing the band gap and enhancing the photocatalytic activity of the TiO_2 NPs, it must be emphasized that not every doping activity of TiO_2 NPs result in a decrease in the band gap, exhibit a positive effect or enhances the photoactivity of TiO_2 NPs [34, 44-45]. However, It has been reported that doping of TiO_2 NPs with rhodium, carbon and iron dopant will exhibit a positive effect on the band gap and photo degradation activity of TiO_2 NPs under visible light, while the use of platinum, aluminium, and cobalt dopant will exhibit a negative effect on the band gap and photo degradation activity of TiO_2 NPs under visible light [34, 44, 47].

The doping of TiO_2 NPs with silver (Ag) has been reported to minimize the photogenerated recombination of electron-hole, while doping with nitrogen (N) and phosphorus (P) has been reported to extend the photo-absorption edge to visible region, however tri-doping of TiO_2 NPs with Ag, N and P has been reported to exhibit synenergetic effect toward enhancing its photocatalytic degradation and removal of 4-Nitrophenol from water with removal efficiencies of 73.8 and 98.1% under UV and visible radiations respectively [48].

Research on the sol-gel synthesis of TiO_2/SiO_2 thin films doped with gold bipyramid NPs (AuBP) has been successfully investigated for the UV photocatalytic degradation of formic acid, it was reported that an increase in Au loading into the TiO_2/SiO_2 thin films resulted in a successive decrease in its optical band gap values of 3.11, 3.02, 2.92 and 2.90 eV corresponding to TiO_2/SiO_2, TiO_2/SiO_2/AuBP (0.1%), TiO_2/SiO_2/AuBP (0.5%) and TiO_2/SiO_2/AuBP (1%) respectively [49].

It was also reported that TiO_2/SiO_2/AuBP (1wt %) have the highest photocatalytic degradation activity and was twice more efficient than TiO_2/SiO_2 thin film, thereby indicating that an increase of Au loading leads to an improvement in the initial rates of formic acid degradation. However, investigation on a three cycles reutilization of TiO_2/SiO_2/AuBP (1wt %) as UV photocatalyst was observed to have no change in the initial rates of formic acid degradation, while visible irradiation was posited to have no significant effect on the photo catalytic properties of the composites, thereby indicating there is no formation of electronic contact between TiO_2 and AuBP [49].

Coupling of TiO_2 NPs with other Technologies

The coupling of TiO_2 with other treatment technologies such as sonocatalysis/Fenton process, biodegradation, wetland technology, electro coagulation, electro catalysis, ion-exclusion and cation-exchange chromatography (IEC/CEC) have been experimentally shown to improve the degradation efficiency of organic pollutants as well as the treatment of large quantities of wastewater [34, 50]. Research on the application of combined electro coagulation and TiO_2 photo assisted for the treatment of pharmaceutical and cosmetic wastewater has been successfully showed to reduce the initial effluent chemical oxygen demand (COD) from a value of 1753 mg/L to 160 and 50 mg/L after treatment with electro coagulation and electro

coagulation/TiO_2 photo catalysis respectively [34, 51].

Experimental study on the use of advance oxidation process for the mineralization of bisphenol A from wastewater by the use of TiO_2, ultrasound and photo-fenton and has shown that the removal of dissolve organic carbon (DOC) by the individual processes were 5, 6, and 22% respectively. However, it was reported that the synergic effect of the combined approach was able to remove 93 % of DOC from wastewater [34, 52]. The coupling of biological oxidation with TiO_2 photo catalysis has been experimentally used for the mineralization of a mixture of 2-chlorophenol, 2,4-dichlorophenol, 2,4,5-trichlorophenol, and pentachlorophenol with a total concentration of 100 mg/L in tap water. It was reported that the biological oxidation and combined biological-photo catalytic treatment removed chlorophenols from the tap water at a rate of 10.5 and 25.8 mg/h respectively [34, 53]. The coupling of IEC/CEC with TiO_2 photo catalysis for the photo oxidation of ionic nitrogen compounds such as triethanolamine, trim ethylamine, and urea has been successfully monitored. It was observed that the process of photo catalytic decomposition of the organic nitrogen was found to depend on the chemical structure of the organic nitrogen [50].

Application of TiO_2 Nanoparticles

Application in Water and Wastewater Treatment

The use of modified and unmodified TiO_2 NPs has been successfully experimented as adsorbent and photo catalyst in the removal of organic and inorganic pollutants from water and wastewater [35, 38, 39, 54-55]. Research on the use of TiO_2 for photo degradation of phenol has been reported to show 99 % removal efficiency under UV irradiation for a period of 6 h, furthermore it was also observed that the degradation of phenol was more effective under acidic than alkaline medium [59]. Similarly, the degradation of chlorophenol (CP) by the use of bio-reactor and TiO_2 NPs at an initial concentration of 10 mg/L for 40 minutes was enough to eliminate 100 mg/L of CP from the wastewater, this result correspond to more than 82% reduction of total organic carbon (TOC) and BOD_5/COD increase from to 0.2 (BOD21/COD = 0.44) [60].

The immobilization of TiO_2 on calcium alginate support has been used in the degradation of different organic dyes, it was reported that the rate of degradation depends on the chemical structure of the different dyes as well as the adsorption of the dyes by the TiO_2 which is directly proportional to the surface area and dispersion of the catalyst as well as the adsorption of light by the dye. However, the kinetics of COD removal was reported to be slower than the discoloration of the solution, while the reutilization of the immobilized TiO_2 was observed to be effective without loss in efficiency [61].

TiO_2 NPs has been reported to have 96 % efficiency for the removal of heavy metals such as chromium and lead form electroplating wastewater, while the introduction of TiO_2 NPs into constructed wetland was reported to show 90-96 % efficiency for the removal of chromium, cadmium and lead from electroplating wastewater [62].

Application in Biomedical Operation and Devices

The medical applications of modified and unmodified titanium can be classified according to their biomedical functionalities which vary from antimicrobial, hard tissue replacement, cardiac and cardiovascular, as well as other applications [3, 63-65]. The use of unmodified TiO_2 NPs has been reported to have a high antimicrobial activity for the removal of microorganisms from water, similarly the use of Polyethylene Imine (PEI), Polyacrylic acid (PAA) and nylon fabric for the preparation of polyelectrolyte multilayer modified TiO_2 NPs has been experimentally used for antibacterial activity. It was reported for the antimicrobial activity against *S. Aureus* and *E. coli*, an increase in the concentration of TiO_2 from 0.05 to 0.1 and finally to 0.2 g/L, the percentage reduction in number of colonies increases from 61 to 71 and finally to 95 % respectively [25-28, 66-67]

Recently, the self-cleaning ability of TiO_2 has been reportedly applied by the health sector in the photo catalytic coatings for the decontamination and sterilization of re-useable surgical devices, similarly, mesoporous TiO_2 electrodes which can be prepared by electrophoresis coatings has been reportedly used for the amperometric detection of glucose via electro reduction of released hydrogen peroxide [65, 68]. TiO_2 has also been reported to be effective in the area of cancer treatment, the adsorption of TiO_2 NPs onto the surface of Hela cell (cervical carcinoma) have been observed to kill it. It was also observed that, the rate of cell

killing increases with increase in the levels of TiO_2 loading in the range of 0-120 µg/mL [69].

Application in Photovoltaic Devices

During the last decade, there has been a wide interest in the research area involving the use of TiO_2 nanocrystalline as photo anode in the manufacturing of Dye- and Quantum Dots-Sensitized Solar Cells (DSSCs and QDSSCs, respectively) [32]. A DSSC is a device for the conversion of visible light power into electricity based on the sensitization of wide band gap semiconductors, the preference of TiO_2 as a semiconductor in the production of DSSC is as a result of the easy availability, non toxicity, low cost and the ability of TiO_2 NPs to conduct electrons as a wide band gap semiconductor [33, 70]. The use of TiO_2 as photo anode in QDSSC has been reportedly prepared by subjecting the semiconductor to sintering process at 450^0C for 30 min and sensitizing it by direct adsorption of of CdTe-GSH quantum dots on the cells active area of 0.16 cm^2 [33]. By the use of spin-coating at 2000 rpm for a period of 10 sec, the photo anode was reportedly fabricated by depositing the anode on a 10 × 10 × 2 mm size fluorine doped tin oxide coated glass (FTO glass) with a surface resistivity of 13 [Ω/sq] and 85% transmittance [33].

it has been reported that the availability of accessible large surface area as well as an increase in the electron density of the of mesoporous TiO_2 nanocrystalline films, the solar conversion efficiency of DSSC is increased by 50 % when compared to anatase form of TiO_2 nanocrystal in a similar thin film, while the use of hybrid TiO_2 nanocrystalline Electrode exhibit a higher efficiency to convert solar to electric energy than when a single nanocrystal TiO_2 was used in DSSC [10].

Application in Environmental Remediation

It has been reported that TiO_2 in its bulk form is the most widely used white pigment because of its brightness and high reflectivity, however, series of research has been successfully conducted on the solar activation of TiO_2 NPs for the purification of automobile exhaust, waste incinerators and atmospheric air by the conversion of air pollutants such as nitrogen oxides (NOx), sulpher oxides (SOx), volatile organic compounds (VOCs), carbon monoxide (CO), and ozone to more environmentally acceptable products such as calcium nitrate and carbon dioxide [64, 71]. It has been experimentally revealed that in the presence of sunlight within the vicinity of a pollution source, the coating of surfaces with the use of TiO_2 NPs is capable of removing nitrogen oxides and VOCs from approximately 200 m^3 and 60 m^3 of air per day respectively [65, 73]. The use of modified and unmodified TiO_2 NPs for the removal of organic contaminants from soil surfaces by photo degradation has been successfully reported, however it was posited that an increase in the soil pH and photon flux enhances the rate of photo degradation [65].

The photo catalytic self cleaning ability of TiO_2 due to its high hydrophilic surface has enhanced its application in the production of TiO_2-coated building materials. Super hydrophilic materials were developed by using semiconducting TiO_2 photo catalyst to coat glass, ceramic tiles or plastics. It was however observed that the light illumination of the TiO_2 results in the removal of grease, dirt and organic contaminants, thereby making them easily swept away by water (rain) [65, 74-75]. TiO_2 Photocatalytic oxidation has also been reportedly applied for anti fogging agent and in door decomposition of organic compounds by converting them primary to CO_2 and water, while TiO_2-coated ceramic tiles have been shown to kill bacteria at an extremely high rate thereby enhancing their application in hospital and health care facilities [65, 74-75].

Challenges of TiO2 Nanoparticles

One of the major challenges affecting the utilization of TiO_2 in water and wastewater treatment is the difficulty associated with its separation from the treated water suspension, which makes it costly and jeopardize the use of this water treatment technology [54]. Contrary to the report that the bulk form of TiO_2 is generally considered safe, several studies have suggested that the chronic inhalation of TiO_2 NPs is harmful has reported in the case of a series of experiment conducted on aquatic and terrestrial organisms [69, 71, 76]. However the ecological toxicity of TiO_2 is reportedly depended on the exposure concentration, condition, and the crystal structure of the NPs as well as the exposure routes such as oral, dental and inhalation [76-77].

The advantageous physical properties of TiO_2 NPs such as small size, large surface and strong electrostatic attraction has contributed to its capability for absorbing toxic metallic particles which has the ability to bioaccumulate in organisms and the ecosystems, thereby acting as a magnifier for toxic metal pollution [71, 78].

Although there has been a safe report to on the use of TiO_2 NPs in manufacturing of sunscreen and cosmetic products, however, an in vitro experiments has revealed that sunlight illuminated TiO_2 NPs is capable of damaging DNA, disrupting the function of cells and interfering with the defense activities of immune cells [69, 71, 79-81].

CONCLUSION

In this paper, the various methods for the syntheses of TiO_2 NPs was briefly reviewed, the modification of TiO_2 NPs by the use of immobilization technique was also reviewed and reported to be a solution on how the problem of separation difficulty associated with the use of TiO_2 NPs in the treatment of water and wastewater can be solved. It was also reported in this review that doping is a suitable technique that can be effectively used to decrease the band gap of the TiO_2 NPs, in order to enhance the absorption of light in the visible region for photo catalytic reactions. The coupling of TiO_2 NPs with other treatment technologies in wastewater treatment has been reported to be more effective than when a single treatment technology is applied. Furthermore, it was reviewed that TiO_2 NPs has been successfully applied in various field such as water and wastewater treatment, photovoltaic devices, environmental remediation as well as in the area of biomedical operation and devices. Finally, it was reported in this review that chronic inhalation of TiO_2 NPs can result to health related problems, thereby constituting a great challenge to the ecosystem.

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