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The applications of titanium dioxide (TiO_2) in aqueous system: A short review

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ABSTRACT

This article provides the readers an overview of the titanium dioxide (TiO_2) application in liquid state. TiO_2 is an excellent photocatalyst that is utilized in photodegradation, antibacterial and antiviral activity self-cleaning system, acted as pigment and additive to improve tribological properties with the presence of ^{-}OH. The article reviews the applications of TiO_2 in aqueous system. TiO_2 is widely used in an aqueous system due to its chemical and thermal stability. Nevertheless, TiO_2 which is appeared in powder form has limited its usage in terms of reusability and recyclability. The article assesses the immobilization of TiO_2 on different types of host materials towards sustainability in aqueous systems.

1.0 INTRODUCTION OF TITANIUM DIOXIDE (TiO_2)

Titanium dioxide (TiO_2) is catagorised as transition metal oxide which also known as titania or titanium (IV) oxide. TiO_2 occurs as odorless white coloured powder like starch with average particle size of 21 to 30 nm and molar mass of 79.866 g/mol. It appears naturally in polymorphs: anatase, rutile and brookite which are commonly phases in TiO_2 powder. In addition, some polymorphs can be form by high-pressure effect such as TiO_2 (II) and TiO_2 (H). The basic structure unit for TiO_2 crystals are TiO_6 octahedrons structure as shown in Figure 1 (Rohini, 2018). The structure of anatase and rutile contain six atoms per unit cell in tetragonal structure while the structure of brookite consists of eight atoms per unit cell. Anatase and brookite are metastable and readily to transform into rutile phase at high temperature ($\geq 450^{o}$C) as reported by Joanna (2016). Most of the studies reported that the precipitates of titania precursor that obtained are in amorphous structure, in which calcination is required to attain crystalline products. Rutile phase

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of TiO_2 can be obtained from phase transformation of anatase phase through calcination at high temperature at 450ºC or higher. Among the polymorphs, anatase is the most active photocatalyst based on the dynamics of charge carriers and thermodynamically stable (Arsou et al., 2019).

The most fascinating application of TiO_2 is as photocatalyst due to its light sensitivity. The mechanism of photocatalytic reaction for TiO_2 will be activated by the absorbed photons which energy is exceeded its band gap energy. Band gap energy is the width of a forbidden band between the valance band and conduction band that electron energy does not exist. TiO_2 is type of semiconductor with wide band gap, the band gap energies are mainly dependent on the phases of TiO_2 (Evyan et al., 2017). Valance band is the band filled with electrons while conduction band is the band which electrons excited from valance band after gaining enough energy to be freely moved around in it. Band gap determines the optical absorption wavelength for particular photocatalyst, i.e., peak at around 380 nm for TiO_2. When TiO_2 is under radiation of electromagnetic wave of 380 nm or within the UV range (100 - 400 nm), electrons (e^-) in valance band of TiO_2 will be excited to conduction, leaving positive holes (h^+) in valance band as displayed in Figure 2 (Evyan et al., 2014). The electrons that released will combine with O_2 to form superoxide while the holes will take electrons from H_2O to form hydroxyl radicals. Both superoxide anions and hydroxyl radicals play important roles in decomposition of organic compound (pollutants) through oxidation and reduction to produce H_2O and simpler form of substances (e.g., CO_2). The related chemical reactions of photocatalysis mechanism are as the following equations (Evyan et al., 2017):

Photoexcitation : $TiO_2 + h\nu \rightarrow h^+ + e^-$ ...(1)
Photoexcited e^- scavenging : $(O_2)_{ads} + e^- \rightarrow O_2^{\bullet -}$ ...(2)
Protonation of superoxide : $O_2^{\bullet -} + OH^\bullet \rightarrow HO_2^\bullet$ ...(3)
Co-scavenging of e^- : $HO_2^\bullet + e^- \rightarrow HO_2^-$ ...(4)
Oxidation of hydroxyls : $OH^- + h^+ \rightarrow OH^\bullet$ ...(5)
Photodegradation by $OH^\bullet$: $R - H + OH^\bullet \rightarrow R^\bullet + H_2O$ ...(6)
Direct photoholes : $R + h^+ \rightarrow R^{+\bullet} \rightarrow$ Intermediate(s) ...(7)

There is an important condition for the photocatalytic mechanism as discussed above: the reactions need to be conducted in aqueous media, at least with the presence of dissolved oxygen and water molecules. The reactive $OH^\bullet$ will not be produced and thus TiO_2 not able to decompose or degrade the organic compounds that appear in liquid state. In this article, the application of TiO_2 will be focused on those in aqueous system. With the physical appearance as nanosized powder, it is not practical to insert directly the powder in the aqueous system. The nano-sized TiO_2 powders are difficult to be separated from the solution and might cause lost or stripping of TiO_2 during the cyclic of usage. It is important to prepare a host in order to hold the nano-sized TiO_2 and prepare as an easy-removal material from the treated aqueous system. The review will be deliberated various types of host materials for TiO_2 in different application accordingly.

2.0 THE APPLICATIONS OF TiO_2 IN LIQUID AND AQUOEUS SYSTEM

TiO_2 as semiconductor that first discovered since 1970s with its outstanding properties in electrochemical photolysis of water (Fujishima and Honda, 1972). Fujishima's research team had proven that TiO_2 exhibits the highest performance effective in liquid state with the occurrence of dissolved oxygen and water molecules as well as aqueous media, thus, unless there are simple organic compound, for instant, formic acid and oxalate can be mineralized using electrochemical oxidation method. In this section, some application of TiO_2 in aqueous system are reviewed based on different fields.

2.1 Pigment

Based on TiO_2 physical appearance as white and bright powder, it is a great white pigment. The mixing of pigment into a substance must be conducted in aqueous solution. TiO_2 is added in the production of all kinds of paints, ink, plastics, paper, synthetic fibres, rubber, condensers, ceramics, food, cosmetics, and electronic components (Lum et al., 2020). On top of that, it is also creating opaque appearance in aqueous system due to its multi-dimension structure. With the addition of TiO_2, nano-paint can be produced. Nano-paint is not only acted as white pigment but also as self-cleaning agent to enhance the quality of life on the painted product due to their fascinating antimicrobial and antibacterial properties. Tian et al. (2013) produced anatase TiO_2 white pigment from unenriched industrial titanyl sulfate solution. TiO_2 white pigment was formed through short sulfate process in order to save time, cost and energy.

2.2 Self-cleaning, Antimicrobial and Antiviral

Based on photocatalytic property of TiO_2, it will eliminate environmental contamination, virus sterilisation and restraining and keeping away rust (Macwan et al., 2011). As exposed to UV sunlight, TiO_2 can break down almost any organic compound. There are various of businesses are trying to capitalise the reactivity of titanium dioxide by creating a wide variety of environmental-friendly goods, including self-cleaning mirrors and glass that are critical in building construction. The self-cleaning products are working well with the presence of ^-OH which can even be found in the air with humidity. In a thin TiO_2 film with graphene oxide (GO), proved that the photocatalytic behaviour of TiO_2 embedded GO film has its own self-cleaning properties by photo-degradation of 64% of methylene blue as the pollutant model (Azani et al., 2020). TiO_2 also has been applied in medicinal where it is capable of destroying the cell membrane; solidifying the proteins of the virus, limiting and capturing the activation of the virus. Based on the research gap, Akhtar's research group (2019) has conveyed the potential of nano-colloidal of TiO_2 on antiviral activities in aqueous system. The research group managed to treat the Newcastle virus (NDV) with a minimum dose of 6.25ug/ml (Akhtar et al., 2019). TiO_2 destroys up to 99.97 % of bacteria. Titanium dioxide is non-toxic that it is beneficial in special pharmaceuticals such as sunscreens, liquid face foundation and skin concealer which are safe on human skin. All these applications will be effective with the present of -OH as in aqueous system.

2.3 Water Treatment

TiO_2 is famous as catalyst in water treatment by mortifying hazardous organic compounds into safe inorganic molecules deprived of subordinate treatment or through the biodegradation by microbes (Laxma Reddy et al., 2017). The rapid industry growth is resulting the process and accumulation of by-product waste into the environmental emissions. One of the biggest issues is water contamination, as it is linked closely to the mankind. An advanced oxidation procedure

(AOP) has recently become the most efficient and desirable method of water treatment. AOP is innovative and environmentally friendly, driven by nanoparticles under the irradiation of suitable light source. It is the most attractive and energy saving method for the high-performance removal of organic pollutants in wastewater. In the catalysis process, hydroxyl radicals are formed with the appearance of photons. In purification and degradation of aqueous system, toxic organic matter such as organic chlorine compounds, tetrachlorethylene and trihalomethane can be broken down into simpler form by TiO_2. The application of TiO_2 in aqueous system is unlimited and continued expanding up to date.

2.4 Photocatalysis of TiO_2 in Aqueous System

The fabrication of TiO_2 with modified morphologies and properties has captured attention of researchers based on their specific application. From zero-dimension, the original TiO_2 nanopowder which is assumed to be sphere-shaped to three-dimension, the TiO_2 designed in 3-D structure, it is still perform well in aqueous system. Dimensionality obviously is the main factor which can affect photocatalytic activity and has a significant influence on the properties of TiO_2 materials (Nakata and Fujishima, 2012). Table 1 compared the benefits and applications of TiO_2 in aqueous system based on the dimensionality of the TiO_2 structure.

3.0 APPLICATION OF TiO_2 IN NANOFLUID

The tribological properties of the materials capture the interest of researchers, especially in the application of liquid state and aqueous system. An earlier article of research indicates that TiO_2 nanoparticles that modified with tetrafluoric benzoic acid demonstrate strong performance of wear while reduce friction in bearing steel (Li et al., 2018). In contrast, the ductility of TiO_2 nanocomposites was increased by additive of Mg has been documented using powder metallurgy combined with hot extrusion, while the strength of the nanocomposite remained unchanged (Sathish et al., 2019).

Table 1: The application of TiO_2 in aqueous system according to its dimensionality.

Dimensionality	Properties	Benefit and Application	References
Zero **(0-D)**			
TiO_2 pure powder P-25	Sphere-shaped. High specific area, high pore volume and high pore size. High crystallinity.	High performance in degradation of organic dye and antibacterial activities. P-25 is the most excellent commercial photocatalyst. Production of paint and printing	Marziyeh Salehi et al. 2012
One **(1-D)**			
Nanotubes	Higher in length	Decomposition of organic molecules.	Peng and Ni, 2019;
Nanowires	High in antase crystallinity after annealing.	Decomposition of organic dye. Enhancement of photovoltaic performance of back-illuminated dye-sensitized solar cell demonstrate practical route for architecting photoactive 1-D porous functional materials in	Ahmed et al., 2020; Evyan et al. 2021 & Lee et al. 2016.

		photocatalysis system or solar energy conversion.	
***Two* (2-D)**			
Nanosheet	Nanosized flake-shaped with flat surface. High aspect ratio. Very thin (1–10nm) Different sizes from sub-micrometer to ten of micrometers.	Decomposition of organic molecules. Self-cleaning surface (self-cleaning glass).	Wang et al., 2019
***Three* (3-D)** coating on structured ceramic/ polymer Immobilization of TiO_2 on 3-D structured materials	Large surface-volume ratios. High potential in carrier mobility. Various shapes and structures can be designed.	Efficient diffusion pathway for organic pollutant into framework. Support on purification, separation and storage. Decomposition of organic dye. Self-cleaning structure. Photocatalyst for use against drug residues	Nakata and Fujishima, 2012; Sangiorgi et al., 2019; Sevastaki et al., 2020

According to Hui's research group (2017), TiO_2 nanoparticles on ferritic stainless steel (FFS) 445 in innovative water-based nanolubricant is investigated for its tribological behaviour. From the study, it was shown that 0.4 - 0.8 wt% concentrations of TiO_2 water-based nanolubricants can greatly reduce the coefficient of friction of the disks, the anti-wear ability under all lubrication conditions is depending on the concentration of TiO_2. In a separate study by Filip and Cristina (2016), the lubricant is prepared by adding TiO_2 nanoparticles with new technology in order to improve the oil-solubility of nanoparticles. The tribological tests shown that TiO_2 nanoparticles evenly spread in the base oil and lowered wear property and friction (Filip & Cristina, 2016). In another study, TiO_2 nanoparticles dual-coated with silane coupling agents as lubricant additives in water. Tribological properties in water based lubricating fluid were improved during the rubbing process. This was proven from the worn surface analysis (Gu et al., 2014).

The Additive of TiO_2 into liquid to produce nanofluids has become one of the famous research areas. By adding this engineered suspension into fluid, it is aimed to improve the properties of density, specific heat, thermal conductivity, thermal diffusivity, viscosity and other relevant properties. Addition of TiO_2 in nanofluids results in higher thermal transfer performance in engineering such as oil recovery and heat exchanger meanwhile this enhancement also brings advantages in medical in drug delivery (Ali et al., 2018). The main factors that affected the nanofluid are concentration of nanoparticles, size and dispersion method or shear rate. Table 2 displays different studies on TiO_2 as additive in nanofluids.

On the other hand, Kong's research team (2016) found that the dispersing mechanism with different concentrations of TiO_2 nanoparticles in aqueous rolling liquids. The contact angle gradually decreases with the increased addition of the nanoparticles, and the viscosity of which rises, which contributes to the ameliorating frictional behaviour of aqueous suspensions. There is a great reduction of friction and wear in aqueous suspension with 0.7 wt% TiO_2. On top of that, the research from Malaysia and Japan on palm oil biolubricant demonstrated strong friction and attributes of wear reduction with the addition of TiO_2 nanoparticles to TMP ester (Rao et al., 2018).

From the review, the addition of TiO_2 nanoparticles has enhanced the tribological and mechanical properties of metal-based system as well as innovation of nanolubricant. Similar to the performance of photocatalysis, TiO_2 work well in liquid state or in aqueous system.

Table 2: Advantages of TiO_2 as additive in nanofluids.

Dimensionality	**Concentration of TiO_2**	**Size of TiO_2 (nm)**	**Advantages**	**Reference**
Zero-dimension (0-D) Pure TiO_2 powder Original spherical powder	0.5 - 2.5	(Contributed 69.23% in enhancement of thermal conductivity)	Increase concentration to increase thermal conductivity	Maheshwary et al., 2017
	0.25 – 0.8 wt.%	10 – 15	TiO_2 at all concentration shown higher heat transfer rate and pressure drop and result in higher thermal conductivity.	Tabari et al., 2016
	0.5 – 4.5 vol.%	~ 40	Higher cooling rate of water integrated water-based lubricant (as Minimum quantity lubricant)	Najiha et al.,
	3.85	100	Viscosity reduced by 25% when temperature increase	Zhang, S and Han, X, 2018;
	0.27 – 1.39 Vol%	100	Viscosity of the nanofluid obviously increased for nanoparticles mass fraction of 1% and the fluid shown Newtonian behaviour Dispersion possesses thermal conductivity	Rajan and Silambarasan, 2012
One-dimension (1-D) TiO_2 nanotubes		10	Added with TiO_2 nanosheets according to ratio for higher stabilities of binary nanofluids	Shao et al., 2015
Two – dimension (2-D) TiO_2 nanosheets	0.2 – 1.0 wt.%	40 - 80	Perform greater velocity of fluid compared with the same concentration of particles of TiO_2 nanotubes	Shao et al., 2015

4.0 IMMOBILIZATION OF TiO_2 NANOPARTICLES FOR AQUEOUS SYSTEM APPLICATION

The immobilization is targeted to be a route that promoted a stable surface, cost effective and efficient photocatalytic. There are several semiconductors that have been proven their benefits as photocatalysts in water treatment or other aqueous system. The materials that can be used to support TiO_2 should be sustainable in the aqueous system. The immobilization of TiO_2 on the host also towards recyclability and reusability. There are different types of materials can be used as reinforcement for TiO_2 in aqueous system such as metal substrates and glass, polymer is the most famous used as host to hold the nano-sized TiO_2 or to form TiO_2 composites in the aqueous system application which are discussed in the following sub-sections.

4.1 Polymer

Polymer becomes a virtuous choice as host material for immobilization of nanoparticles due to its biocompatibility, non-toxic, carriers for safe and stable. Besides that, polymer can be designed as long lasting or biodegradable system. For instant, organic polymer is widely used because of their chemical and thermal stability, it also offers flexibility in shaping of the required parts or systems. Organic polymers can function as ion exchanger in sorbents, electrodes, photocatalyst-conducting materials and biomedical materials. The properties of electrical, magnetic and optical of the nanoparticles can be sustained by the polymer matrix and an inorganic hybrid nanoparticle/polymer can be produced as a catalyst. Some of the composite materials of inorganic TiO_2/organic polymers are reusable and recyclable as samples prepared from the previous study with reusable and recyclable bifunctional (Evyan et al., 2017) as displays in Figure 3.

From Wong's research team, ferric ion on TiO_2 nano-particles has demonstrated an ability to facilitate aggregation with the development of Fe(III)-hydroxy-colloids that can be quickly separated from the aqueous medium (Wang, 2017). Nevertheless, humic acid (HA) as an aggregated power barrier may prevent TiO_2 nanoparticles from being aggregated and thus TiO_2 nanoparticles are stable in aqueous media. Predicting the fate and mobility of TiO_2 nanoparticles in aqueous media is useful.

In addition, the demand for microfiltration or ultrafiltration on the aqueous system has increased tremendously especially in drinking water, production of milk and any drinks in the food industry. With this rapid growth in the industry, microfiltration and ultrafiltration membrane has attracted the interest of the researchers around the world to improve the system as drinking water and beverages are essential to human being. Various nanoparticles are introduced to improve polymeric membranes, such as zirconia, silica, silver, TiO_2, alumina, etc. TiO_2 is a famous photocatalyst since they are solution- and chemical-stable, human- and eco-environmental and non-hazardous photocatalyst. TiO_2 membrane is one of the famous filtration membranes that provide several advantages. TiO_2 membrane can solve the problem of separation and recovery in photocatalytic activity during filtration (Moushoul et al., 2016). A large number of nanoparticles have been presented to form the matrix polymer, for example, Fe_3O_4, Al_2O_3, SiO_2, and TiO_2. TiO_2 has been widely exploited due to its photocatalytic, super hydrophilicity effects and chemical stability (Sotto et al., 2011). Physical blending and sol-gel method are the recent two main routes to prepare TiO_2 nanoparticle matrix polymer. In order to ensure secure and eco-friendly mixed matrix polymers, stable interactions between nano-material and polymer matrices are important.

Nowadays, most of the textile are made from synthetic fibres which mainly formed by polyester, nylon and acrylic. TiO_2 also immobilize on textiles as templates in aqueous system application (Carneiro, 2016). The samples were tested under visible light irradiation for photocatalytic properties.

In order to evaluate the possible dangers of appertaining to TiO_2 nanoparticles in photocatalysis aqueous system, previous research was conducted where heat treatment was used to build a macroporous reinforcement that operates with high-performance TiO_2 (Valério et al., 2020). Tetracycline and carbamazepine have been used as model contaminants, and nanoparticle discharges have been measured between degradation cycles. Polyurethane (PU) Foam is used as macroporous support with TiO_2 which synthesized by heat treatment, the release of catalyst and possible environmental hazards are evaluated by means of zebrafish embryonic development (Valério et al., 2020). It has been concluded that TiO_2 nanoparticles cannot be absolutely healthy to release in the aquatic environment. According to Venkata's research team, the effect of TiO_2 on few types of harmful microbial pathogens in aquatic media was reported through disinfection, the conventional water purification processes proven to be improved by both processes of disinfection and decontamination simultaneously (Venkata et al., 2017). These may be served as the drawbacks of using polymer as host material for the immobilization of TiO_2.

4.2 Other Materials as Host

Metal acts as a good support for application of TiO_2 system. For metal, TiO_2/gold are synthesized with poly (ethylene)106-poly (propylene oxide) 70- poly (ethylene) 106 triblock copolymers as structure through a sol-gel process (Jenny et al., 2014). TiO_2/Ti film that immobilized with exposed facets were prepared by Murtaza's research team (2016) using simple hydrothermal pathway. The prepared films abled to degrade norfloxacin from aqueous media. TiO_2/Ti has demonstrated an excellent photocatalytics efficacy against degradation of the norfloxacin in different water matrices. Figure 4 demonstrates the production of various reactive species and their inclusion in the photocatalytic degradation of norfloxacin by TiO_2/Ti film (Murtaza et al., 2016). Metal is high in strength and a good conductor. It will be a good support in the system that required conduction. However, the choices of metal could be limited in liquid state system to avoid corrosion.

There is research studied on the immobilization of TiO_2 on glass. For glass, immobilization is mostly conducted by using coating technique, e.g., hydrolysis of titanium oxysulfide ($TiOSO_4$) on borosilicate glass (Adamek et al., 2019). Glass is high in refractive index, transparent and low cost, they are beneficial in certain application in the aqueous system as they are chemically stable and high melting point. The research indicated that commercial P-25 immobilized onto glass fibre mat has displayed positive result on decolourization in anionic dye and antibiotics under UVA irradiation in distilled water and artificial wastewater (Adamek et al., 2019). Borosilicate glass spheres (5 mm in diameter) have been coated with TiO_2 film, the immobilized photocatalyst performed degradation of higher than 96% in methylene blue (MB) within 90 min of reaction (Deivisson et al., 2018). Glass can be an ideal host to TiO_2 since it is chemical stable, smooth surface and transparent. With the appearance of transparent, it is very useful in photocatalytic activity which UV irradiation can pass through glass without reduce of intensity. In contrast, slightly absorption of UV light will occur when UV light pass through polymers.

TiO_2 successfully immobilized on cotton fabrics to form self-cleaning fabrics. The covalent bonding between TiO_2 and poly(2-hydroxyethyl acrylate-PHEA) was grafted the chains that can sustained 30 cycles of continuous washing or 150 commercial/ domestic laundry (Yu et al., 2013). The antibacterial and self-cleaning fabrics are expanding their application in medical environments as laboratory coats or conditions that full of bacteria and dust to protect the skin and body of the workers and to avoid any diseases caused by bacteria. On the other hands, researchers are looking for a better method to form the materials with textile structure that can hold the nano-sized TiO_2 stronger. The in-situ method is hardly withstood by the textile at high temperature which crystallization of TiO_2 occur at 400^oC and above.

From the discussion above, the main purpose for immobilization of TiO_2 is to hold TiO_2 on the template in order for this powerful photocatalyst to be reused and recycled for a longer period of time.

5.0 SUMMARY

The properties of TiO_2 have make it widely applied in various fields including paint, cosmetic, water filtration, medical and etc. The TiO_2photocatalyst is working well with the presence of ^-OH in order to complete the chemical reaction during photocatalysis. The review high-lighted aqueous systems that consisted of TiO_2. However, the nano-sized of TiO_2 is limiting the application in certain aqueous system which separation is required. One of the solutions towards recyclable and reusable nano-sized TiO_2 in aqueous system is by mobilizing it on a suitable host depending on the usage. The common host materials are polymer, fabrics, metals and glass. The review prepared a podium for the researchers to choose the host materials for incorporating with TiO_2 nanoparticles according to the application in aqueous system.

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