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The application 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 application of titanium dioxide (TiO_2) in the aqueous system. TiO_2 is an excellent photocatalyst that beneficial in photocatalytic activities, photovoltaic cell, sensor, sunscreen, antimicrobial activities and medical application. TiO_2 nanoparticle which is in powder form has limits its usage to be reusable and recyclable practically. In order to overcome the problem, various of material have been used as hosts and incorporated with TiO_2. TiO_2 is widely used in an aqueous system due to its chemically stable and thermally stable in liquid solution. The article assesses the development of TiO_2 immobilized on the organic and inorganic materials, especially in aqueous system.

1. INTRODUCTION

Titanium dioxide (is also known as titania or titainum (IV) oxide, TiO_2) is an oxide under the family of transition metal oxides. It appears naturally in polymorphs: anatase, rutile and brookite which are commonly used, plus TiO_2 monoclinic which has received attention from the researchers.

The most fascinating application of TiO_2 is as photocatalyst material. The hydroxyl radicals will be activated when TiO_2 under irradiation of UV light and ready to oxidize organic pollutants [1] in purification, filtration, anti-bacterial and photodegradation system. Based on its high dielectric constant [2], it is also a popular dielectric material for photovoltaic cells. In additional, TiO_2 can be applied in other applications, namely electrochromic device, hydrogen storage, sensor and medical application due to its high constancy, cost efficiency and also safe to human and the environment.

2. PHOTOCATALYTIC MECHANISM

Photocatalysis is a chemical reaction that occurs when light hits chemical compound that is light sensitive, such as TiO_2, Fe_2O_3, WO_3 and etc. The chemical reaction will be taken place continuously in the intermediate region when light strikes on these semiconductors with photocatalytic activity, results in the breakdown and removal of variety of organic toxins and inorganic contaminants [3]. This reaction enables TiO_2 to be used in numerous valuable applications.

The mechanism of photocatalytic reaction for TiO_2 begins from the absorption of photons with energy larger than the band gap energy of TiO_2. Band gap is the energy width of a forbidden band between the valance band and the conduction band where electron energy does not exist. 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 [4]. Band gap determines the optical absorption wavelength for particular photocatalyst, i.e. peak at around 380nm for TiO_2.

Electrons (e^-) in valance band of TiO_2 move to conduction band when they are irradiated to light of 380nm or lower within the UV range, leaving positive holes (h^+) in valance band as displayed in Figure 1. The energy level at the top of the valance band determines the oxidizing ability of photogenerated holes. The band gap of TiO_2 dependent on phases, generally anatase with band gap energy (E_g) of 3.20 eV, E_g of rutile is 3.02 eV and E_g of brookite is 2.96 eV [5] and they are considered as large band gap semiconductor. Among the polymorphs, anatase is the most active photocatalyst based on its charge carrier dynamics, chemical properties and photocatalytic activity organic compound as reported by most of the researcher groups.

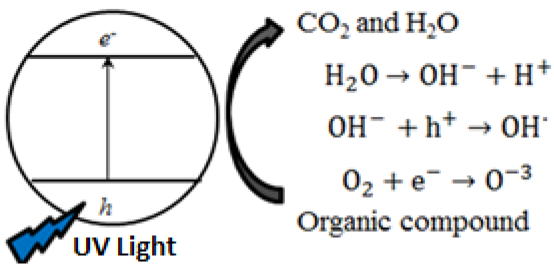

Figure 1 The band structure of a semiconductor.

3. APPLICATION OF TITANIUM DIOXIDE

Apart from having suitable band gap energy, TiO_2 also possesses advantages, such as highly stable in aqueous media and non-toxic photocatalytic materials, etc. Anatase is preferable for solar cell application due to its slightly higher Fermi level, lower absorbance of oxygen and its capacity of hydroxylation is higher than those for rutile. However, rutile which is considered as less active photocatalytic, able to enhance high photocatalytic activity compared to a single-phase anatase TiO_2 system. TiO_2 is the most famous nano-materials that is high in availability, biocompatibility, low cost, non-toxicity and high chemical stability. Titanium oxide nanoparticles are significant from its many applications including elimination of environmental pollution, sterilization, rust prevention, and biodegradation.

In the past, there are many researches on antibacterial or antimicrobial activities of TiO_2 have been reported. applications wherein it has the ability to destroy the membrane of cells; solid the proteins of viruses, restrain the virus activation, and catching them. It kills bacteria up to 99.97%. TiO_2 can also kill coliform, green suppuration bacillus, golden grape coccus, mildew, suppuration fungus, etc. Based on the research gap, Akhtar's research group has conveyed the potential of nano-colloidal of TiO_2 on antiviral activities. The research group managed to treat the Newcastle virus (NDV) with minimum dose of 6.25ug/ml [6].

In terms of environmental applications, TiO_2 breakdown the the origin of the odor (ammonia, aldehyde gas [smoke], etc) instead of covering it up like conventional air fresheners. TiO_2 foams have been prepared to photo- assist oxidation of gas nitrogen oxide according to ISO 22197-1. On the other hand, TiO_2 is widely used in aqueous system, including water purifying, wastewater degradation and filtration wherein it breaks down harmful organic matter such as organic chlorine compounds, tetrachlorethylene and trihalomethane.

4. IMMOBILAZATION OF TIO_2 ON DIFFERENT TYPES OF TEMPLATE IN AQUEOUS SYSTEM

Materials that are prepared in the form of nanoparticles or powders are not ideal to apply practically in the real system especially in aqueous solution. 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 immobilization is targeted to be a route that promoted a stable surface, cost effective and efficient photocatalytic. The ordinary hosts of the nanoparticles that have been widely used are metal substrates, ceramic, glass, and polymer. TiO_2 is modified with Pt-polypyrrole through simultaneous in situ reduction of Pt(IV) and the oxidative polymerization of pyrrole monomers at ambient temperature show positive results on photocatalytic activity [7].

Most of the studies on TiO_2 composites are based on organic polymer mainly because of their chemical and thermal stability. In addition, organic polymers can be retained in the function as ion exchanger in sorbents, electrodes, photocatalyst-conducting materials, and biomedical materials. The electrical, magnetic, and optical properties of the inorganic nanoparticles can be polymer matrix [8], creating an inorganic nanoparticle/polymer composite as an effective catalyst. Some of the TiO_2/organic polymers composite are reusable and recyclable as samples prepared from the previous study with reusable and recyclable bifunctional [9].

Rapid industry development has accelerated the production and accumulation of by-product wastes which have resulted in severe environmental pollutions. Water pollution is one of the major concerns since it is much related to humankind survival. Recently, the most effective and attractive water treatment method is an advanced oxidation process (AOP). AOP is innovative and environmentally friendly especially for water treatment which is driven by a suitable light source depending on the type of photocatalyst. Hydroxyl radicals are generated in the presence of photons during the catalysis process and they are the strongest oxidant after fluorine in aqueous solution. They play an important role in the degradation of toxic organic compounds into simple and safe inorganic molecules without the appearance of secondary byproducts.

Various semiconductor materials have been investigated as photocatalysts in AOP or known as heterogeneous photocatalytic oxidation, e.g. ZnO, Fe_2O_3, WO_3, etc. TiO_2 is one of the famous photocatalysts because they are photo-stable and chemical-stable in solution, non-hazardous for humans and eco-environment. The aggregation behavior of TiO_2 nanoparticles in aqueous medium, with the presence of metal ions and/ or humic acid (HA, one of the most significant fractions of natural organic matter) under different pH, in terms of aggregate size and zeta potential has been investigated. Ferric ion coated on HA as an aggregation energy barrier could inhibit the aggregation of TiO_2 nanoparticles, and thus TiO_2 nanoparticles are stable in aqueous media followed by risk on human and environment. The authors highlighted that it is useful to predict the fate and transport of TiO_2 nanoparticles, along with their risks in aqueous media [10].

On the other hand, 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. According to a research by Olabarrieta's research group, the removal of TiO_2 nanoparticles from water by low pressure pilot plant filtration wherein it was found out that nano-TiO_2 retention depends strongly on the aqueous media whereas the combination of humic acid and bicarbonate highly increased the nano-TiO_2 release [11]. 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. By adding of inorganic nanoparticles to form matrix polymer, it is proven specific functionalities can be provided while remaining the intrinsic separation performance of bare polymer. A variety of nanoparticles have been introduced to modify the matrix polymer, such as Al_2O_3, SiO_2, TiO_2, and Fe_3O_4. TiO_2 has been widely utilized in recent years due to its photocatalytic, super hydrophilicity effects and chemical stability. It is shown that reusability of the photocatalysts decreased at higher TiO_2 loading even after 5 cycles. Meanwhile, the antibiotics degradation is successfully achieved in water and wastewater matrix [12].

Other than polymer matrix, TiO_2 also immobilize on fabrics or textiles as templates in aqueous system application. For functionalization, the chemical method is focused on an aqueous solution with a wetting compound which resulted in a higher deposited mass than the padding method. In the mechanical method, potassium hydroxide (KOH) solution used to activate OH^- groups on the surface of textile substrates [13]. PU Foam is used as macroporous support and is functionalized with high-performance TiO_2 which synthesized by heat treatment. Tetracycline and carbamazepine were used as model pollutants, and the discharge of nanoparticles was measured between degradation cycles [14]. The relationships between photocatalysis, catalyst release and associated potential environmental hazards were assessed using zebrafish embryonic development as a proxy. Immobilized nanoparticles have been demonstrated a safe approach to the environment, as the process eliminates remnant additives while preventing the release of nanoparticles. However, it was concluded that a completely safe release of TiO_2 nanoparticles into the aquatic environment cannot be advocated.

5. SUMMARY

The photocatalytic activity or namely advanced oxidation process of TiO_2 plays an important role in various fields especially in aqueous system. The immobilization of TiO_2 on variety templates according to the specific application in aqueous system is needed to be encountered towards sustainability in development and technology by production of recyclable and reusable materials. The review prepared a podium for the researchers to choose the materials/ templates for immobilization of TiO_2 nanoparticles dependent on the specific application.

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