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APPLICATION OF TITANIUM DIOXIDE (TiO2) AS PHOTOCATALYST FOR WASTEWATER TREATMENT

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ABSTRACT:

In the current anthropocene, environmental pollution is a global problem that is inextricably linked with rapid industrialization and urbanization. Pollution hampers the environment sustainability and ecosystem services. Realizing the importance of keeping our planet clean, researchers are actively working for eco- friendly alternative technologies for all areas of daily life. With the environmental safety becoming the research focus, water environmental security, as an updating research direction has also been the concern. Nano- titania photo catalysis can prevent environmental pollution from the sources and ensure the fundamental productions in the industry. The main aim of this review paper is to give an overview of the enhanced photo catalytic activities of titanium dioxide (TiO_2) nanoparticles. This review includes the basic properties of photo catalyst and mechanism of photo catalysis process followed by unique photo catalytic properties and research of TiO_2 nano particles as photo catalysts. An effort has also been made to give an overview of expedient photo catalytic activity of these doped nano particles. The applications of nano particle photo catalytic technology in environmental safety are reviewed. Emphasis is put on the applications of nano- titania photo catalytic technology in wastewater treatment, and the latest achievements in scientific research of nano particle photo catalytic technology in wastewater treatment are given.

KEYWORDS:

PHOTOCATALYSIS, TITANIUM DIOXIDE, POLLUTION, WASTE WATER TREATMENT.

INTRODUCTION

Environmental pollution is not a new phenomenon, yet it remains the world's greatest problem facing humanity, and the leading environmental causes of morbidity and mortality. Man's activities through urbanization, industrialization, mining, and exploration are at the forefront of global environmental pollution. Both developed and developing nations share this burden together, though awareness and stricter laws in developed countries have contributed to a larger extent in protecting their environment. Despite the global attention towards pollution, the impact is still being felt due to its severe long-term consequences. Pollution is viewed from different angles by different people but is commonly agreed to be the outcome of urban- industrial and technological revolution and rapacious and speedy exploitation of natural resources, increased rate of exchange of matter and energy, and ever-increasing industrial wastes, urban effluents, and consumer goods. Holgate (1979) defined environmental pollution as the introduction by man, into the environment, of substances or energy liable to cause interference with legitimate uses of environment. Singh (1991) has defined pollution in a very simple manner, i.e., "Disequilibrium condition from equilibrium condition in any system." This definition may be applied to all types of pollution ranging from physical to economic, political, social, and religious. [1]

Over the past couple of decades, various sources of pollution were identified that altered the composition of water, air, and soil of the environment. The substances that cause pollution are known as pollutants. A pollutant can be any chemical (toxic metal, radio nuclides, and organic-phosphorus compounds gases) or geochemical substance (dust, sediment), biological organism or product, or physical substance (heat, radiation, sound wave) that is released intentionally or inadvertently by man into the environment with actual or potential adverse, harmful, unpleasant, or inconvenient effects. Such undesirable effects may be direct (affecting man) or indirect, being mediated via resource organisms or climate change. Realizing the importance of keeping our planet clean, researchers are actively working for eco-friendly alternative technologies for all areas of daily life. Sustainable energy production and pollutant destruction are two of the areas in which intense research is being carried out.

As a part of advanced technologies semiconductor -mediated photo catalysis is a well-established technique for pollutant degradation and hydrogen (clean fuel) production by water splitting. Photo catalysis can be defined as a "catalytic reaction involving the production of a catalyst by absorption of light". The appropriate positioning of valence (VB) and conduction (CB) bands in semiconductors makes them suitable materials for the absorption of light and photo catalytic action. Nano-crystalline titanium dioxide (NTO) is a multifunctional semiconductor photo catalyst that can be an energy catalyst (in water splitting to produce hydrogen fuel), an environmental catalyst (in water and air purification), or an electron transport medium in dye-sensitized solar cells. Compared to other available semiconductor photo catalysts, NTO is unique in its chemical and biological inertness, photo stability (i.e., not prone to photo anodic corrosion), and low cost of production. Photo catalytic water and air purification using NTO is a predominant advanced oxidation process (AOP) because of its efficiency and eco-friendliness.

TiO_2 plays the most important role owing to its excellent chemical and physical properties. However, the TiO_2 band edge lies in the UV region that makes them inactive under visible irradiation. In this regard, considerable efforts have been made to increase the visible light activity of TiO_2 via the modifications of its electronic and optical properties. Doping TiO_2 using either anions or cations is one of the typical approaches that has been largely applied TiO_2 is very well known and well researched material due to the stability of its chemical structure, biocompatibility, physical, optical, and electrical properties.[2]

TiO_2

Titanium dioxide, also known as titanium oxide or titania is the naturally occurring oxide of titanium-chemical formula TiO_2. When used as a pigment, it is called titanium white, Pigment white 6.

A naturally occurring oxide sourced from ilmenite, rutile and anatase, it has a wide range of applications. It is widely used as a white pigment, catalyst support, and photo catalyst. At room temperature, bulk TiO_2 exists in three phases: rutile, anatase, and brookite. TiO_2 as a photo catalyst has been used for solar energy conversion and for the removal of organic pollutants from wastewater. It is well established that anatase TiO_2 has a higher photo catalytic activity than the rutile or brookite phases. For example, one of the most active commercial TiO_2 photo catalysts, Degussa P25, is 60-80% anatase phase. The pure anatase phase is thermodynamically less stable than rutile at room temperature, and it can undergo thermal conversion into the rutile phase in the temperature range of 700-800°C.The most important commercial route for the production of TiO_2 nano particles and larger particles is based on the chloride process where purified $TiCl_4$ is oxidized at high temperature (1200-1700°C) and modest pressure (~300kPa), in an oxygen plasma or flame.

Many people are familiar with titanium dioxide as an active ingredient in sunscreen. Titanium dioxide nanoparticles, also called ultrafine titanium dioxide or nano crystalline titanium dioxide. Nano sized particles of titanium dioxide tend to form in the meta stable anatase phase, due to the lower surface energy of this phase, relative to the equilibrium rutile phase.[3]

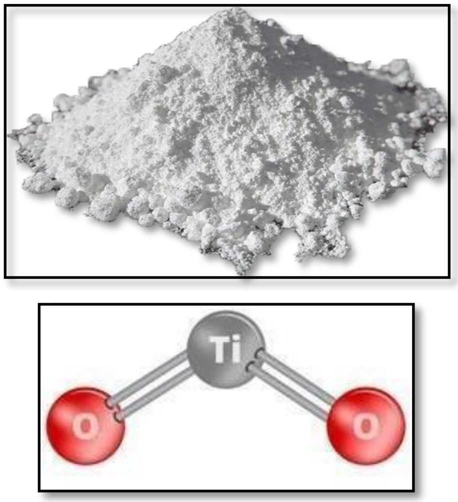

FIG. 1. TITANIUM DIOXIDE ALONG WITH STRUCTURE

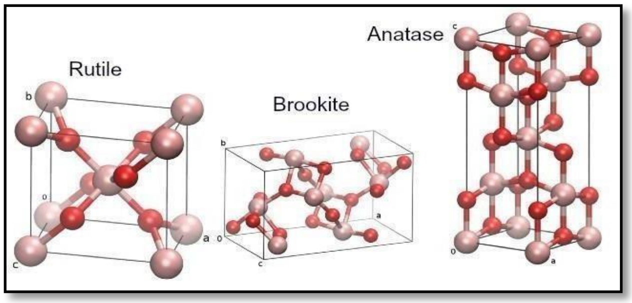

FIG.2. THREE PHASES IN WHICH TITANIUM DIOXIDE OCCUR

HISTORICAL OVERVIEW

TiO_2 powders have been commonly used as white pigments from ancient times. They are inexpensive, chemically stable and harmless, and have no absorption in the visible region. Therefore, they have a white colour. However, the chemical stability of TiO_2 holds only in the dark. Instead, it is active under UV light radiation, including some chemical reactions. The activity under sunlight was known from the flaking of paints and the degradation of fabrics. Inco-operating TiO_2, TiO_2 has the most efficient photo activity, the highest stability and the lowest cost. More significantly, it has been used as a white pigment from ancient times, and thus, its safety to humans and the environment is guaranteed by history. There are two types of photochemical reaction proceeding on a TiO_2 surface when irradiated with ultraviolet light. One includes the photo-induced redox reactions of adsorbed substances, and the other is the photo-induced hydrophilic conversion of TiO_2 itself. The former type has been known since the early part of the 20th century, but the latter was found only at the end of the century. The combination of these two functions has opened up various novel applications of TiO_2, particularly in the field of building materials, which was also known that TiO_2 itself does not change through the photoreaction, although the ‘‘photo catalyst’’ terminology was known but called a photo sensitizer.[4]

Initially TiO_2 powders was dispersed into various organic solvents such as alcohols and hydrocarbons followed by the UV irradiation with an Hg lamp. They observed the auto oxidation of solvents and the simultaneous formation of H_2O_2 under ambient conditions.

It is interesting to note that they had already compared the photo catalytic activities of variousTiO_2 powders using twelve types of commercial anatase and three types of rutile and concluded that the anatase activity of the auto oxidation is much higher than that of rutile, suggesting a fairly high degree of progress of the research. In those days, however, the photo catalytic power of TiO_2 might have attracted only partially limited scientists’ attention in the field of either catalysis or photochemistry, and the study of TiO_2 photo catalysis had not developed widely in eitheracademic or industrial society.[4]

CONSIDERATIONS FOR TiO_2

PROPERTIES

Titanium dioxide has a number of unique characteristics that make it ideally suited to many different applications. It has an extremely high melting point of 1,843ºC and boiling point of 2,972ºC, so occurs naturally as a solid, and, even in its particle form, it is insoluble in water. TiO_2 is also an insulator. Unlike other white materials that may appear slightly yellow in light, because of the way TiO_2 absorbs UV light, it doesn’t have this appearance and appears as pure white.

Importantly, titanium dioxide also has a very high refractive index (its ability to scatter light), even higher than diamond. This makes it an incredibly bright substance and an ideal material for aesthetic design use. Another crucial property of titanium dioxide is that it can show photo catalytic activity under UV light. This makes it effective for environmental purification, for different kinds ofprotective coatings, sterilization and anti-fogging.

TABLE NO. 1 PROPERTIES OF TITANIUM DIOXIDE

TITANIUM DIOXIDE PROPERTIES	
Chemical formula	TiO_2
Molar mass	79.866 g/mol
Odor	Odorless
Solubility in water	Insoluble
Appearance	White solid
Density	4.23 g/cm^3 (rutile) 3.78 g/cm^3 (anatase)
Band gap	3.05 eV (rutile)
Refractive index	2.488 (anatase) 2.583 (brookite) 2.609 (rutile)
Melting point	1843^{o}c
Boiling point	2972^{o}c

OCCURRENCE

Titanium dioxide occurs in nature as the mineral rutile and anatase. Additional two high-pressure forms are known minerals: a monoclinic baddeleyite-like form known as aragonite, and the other is an orthorhombic α-PbO_2-like form known as brookite, both of which can be found at the Riis crater in Bavaria. It is mainly sourced from ilmenite ore. This is the most widespread form of titanium dioxide-bearing ore around the world. Rutile is the next most abundant and contains around 98% titanium dioxide in the ore.

The metal is also mined from other ores such as ilmenite or leucoxene, or one of the purest forms, rutile beach sand. Star sapphires and rubies get their asterism from rutile impurities present. Titanium dioxide (TiO_2) is found as a mineral in magmatic rocks and hydrothermal veins, as well as weathering rims on perovskite.

FIG. 3. TIO_2 AS A MINERAL IN MAGNETIC ROCKS

PRODUCTION

How pure titanium dioxide is extracted from titanium-containing molecules depends on the composition of the original mineral ores or feedstock. Two methods are used to manufacture pure TiO_2: a sulfate process and a chloride process. The principal natural source of titanium dioxide is mined ilmenite ore, which contains 45-60 percent TiO_2. From this, or an enriched derivative (known as titanium slag), pure TiO_2 can be produced using the sulfate or chloride process. Of the two methods of extraction, the sulfate process is currently the most popular method of producing TiO_2 in the European Union, accounting for 70 percent of European sources. The remaining 30 percent is the result of the chloride process.

On a global level, it is estimated about 40-45 percent of the world's production is based on the chloride process. As widely used substance with multiple applications, research is being carried out to improve the production process to reduce the levels of chemicals used and waste produced, and to recycle any by-products. In the sulfate route, there are three main stages. The ore, usually an ilmenite, is dissolved in sulfuric acid to form a mixture of sulfates. Any iron is removed from the solution so the color of the final product is not spoiled. The titanyl sulfate is then hydrolyzed in solution to give insoluble, hydrated titanium dioxide.[5] The final stage involves heating the solid in a calciner to evaporate the water and decompose the sulfuric acid in the solid. It also turns the solid into seed crystals which can be milled to the size needed. These crystals can be coated with another substance, such as aluminium oxide, to make the titanium dioxide mix more easily with liquids or extend the life the paint manufactured from them. There are two main stages to the chloride process. First, the dry ore is fed into a chlorinator together with coke and chlorine to make titanium chloride. Once the fluid bed has been preheated, the heat of reaction with the chlorine is sufficient to maintain the temperature and recycled liquid titanium chloride may be used to control the temperature.

The next step involves the oxidation of titanium chloride by burning it in oxygen together with another combustible gas (often carbon monoxide). By adding seed crystals, the titanium dioxide is formed as a fine solid in a gas stream and is filtered out of the waste gases. Crystal growth is controlled by adding nucleating agents to the gas stream and the products are cooled by mixing with chlorine gas. The product is then washed and dried before milling and surface treatment.

The surface treatment of the base pigment is very important and the surface finishing unit can account for up to one- third the cost of a titanium dioxide plant. The treatment is needed to maximize optical properties, improve durability and reduce yellowing, and improve dispersibility.

The sulphate process employs simpler technology than the chloride route and can use lower grade, cheaper ores. However, it generally has higher production costs and with acid treatment is more expensive to build than a chloride plant. But the latter may require the construction of a chlor-alkali unit.[5] The chloride route produces a purer product with a tighter range of particle size, but anatase pigments can only be produced by the sulphate route. The sulphate route is perceived to be less environmentally friendly but acid recycling or neutralization, combined with other by product developments, can make it as clean as the chloride route.

COMMON APPLICATION

Titanium dioxide (TiO_2) is a bright white substance used primarily as a vivid color in a wide array of common products. It also has a number of lesser- known qualities that make it an extremely useful and important ingredient in our battle to fight climate change and prevent skin cancer. Prized for its ultra-white color, ability to scatter light and UV- resistance, TiO_2 is a popular ingredient, appearing in hundreds of products we see and use every day, bringing significant benefits to our economy and overall quality of life.

Across the EU, applications for TiO_2 include paints, plastics, paper, pharmaceuticals, sunscreen and food. As a photocatalyst titanium dioxide can be added to paints, cements, windows and tiles in order to decompose environmental pollutants. As a white pigment, TiO_2 is one of the most important raw materials for paints and coatings.[6]

Titanium dioxide (TiO_2) is a multifaceted compound. It's the stuff that makes toothpaste white and paint opaque. TiO_2 is also a potent photocatalyst that can break down almost any organic compound when exposed to sunlight, and a number of companies are seeking to capitalize on titanium dioxide's reactivity by developing a wide range of environmentally beneficial products, including self-cleaning fabrics, auto body finishes and ceramic tiles. Also one development is a paving stone that uses the catalytic properties of TiO2 to remove nitrogen oxide from the air, breaking it down into more environmentally benign substances that can then be washed away by rainfall. Other experiments with TiO_2 involve removing the ripening hormone ethylene from areas where perishable fruits, vegetables, and cut flowers are stored; stripping organic pollutants such as trichloroethylene and methyl-tert-butyl ether from water; and degrading toxins produced by blue green algae. It remains to be seen, however, whether the formation of undesirable intermediate products during these processes outweighs the benefits offered by TiO_2's photo catalytic properties.

Titanium dioxide is a well-known photocatalyst for water and air treatment as well as for catalytic production of gases. The general scheme for the photo catalytic destruction of organics begins with its excitation by supra-band gap photons, and continues through redox reactions where OH radicals, formed on the photocatalyst surface, play a major role. Titanium dioxide is non-toxic and therefore is used in cosmetic products (sunscreens, lipsticks, body powder, soap, pearl essence pigments, tooth pastes) and also in special pharmaceutics. Titanium dioxide is even used in food stuffs, for instance in the wrapping of salami. Titanium dioxide's photo catalytic characteristics are greatly enhanced due to the advent of nanotechnology. At nano-scale, not only the surface area of titanium dioxide particle increases dramatically but also it exhibits other effects on optical properties and size quantization. An increased rate in photo catalytic reaction is observed as the redox potential increases and the size decreases.[7] Sterilization, restraining virus; TiO_2 photocatalyst can 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 kill coli form, green suppuration bacillus, golden grape coccus, mildew, suppuration fungus, etc. The ability of sterilization can be tested through coli form and golden grape coccus.[8]

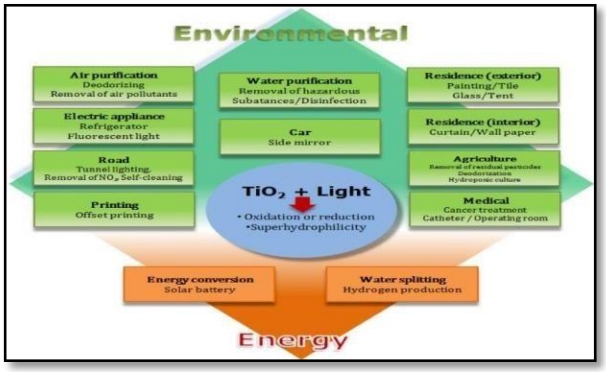

FIG.4. VARIOUS APPLICATIONS OF TIO2 PHOTOCATALYSIS IN ENVIRONMENT AND ENERGY FIELDS. ADAPTED FROM S.-Y. LEE, S.-J. PARK / JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY 19 (2013) 1761–1769 1763

WHAT IS PHOTOCATALYSIS?

In chemistry, photo catalysis is the acceleration of a photoreaction in the presence of a catalyst. In photolysis, light is absorbed by an adsorbed substrate. In photo generated catalysis, the photo catalytic activity (PCA) depends on the ability of the catalyst to create electron–hole pairs, which generate free radicals able to undergo secondary reactions. Photo catalysis is the activity occurring when a light source interacts with the surface of semiconductor materials, the so called photo catalysts. During this process, there must be at least two simultaneous reactions occurring, oxidation from photo generated holes, and reduction from photo generated electrons. The photocatalyst itself should not undergo change and therefore a precise synchronization of the two processes needs to take place.

Photo catalysis can be successfully used in a real environment to decompose pollutants and enhance the quality of the atmospheric air. Photo catalysis can therefore be used in the building sector to improve indoor air quality.[9]

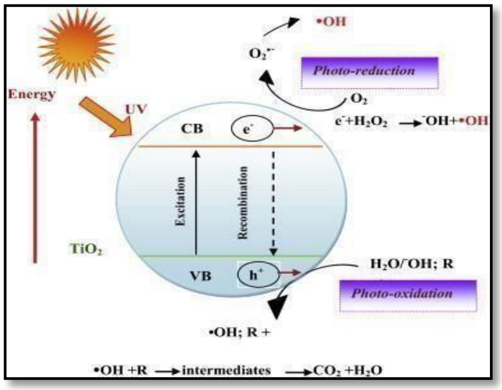

FIG.5. SCHEMATIC ILLUSTRATION ON REMOVAL OF POLLUTANTS BY THE FORMATION OF PHOTO INDUCED CHARGE CARRIERS (E_/H+) IN A SEMICONDUCTOR TIO2 PARTICLE SURFACES. ADAPTED FROM S.-Y LEE, S.-J. PARK / JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY 19 (2013) 1761–1769 1763

TYPES OF PHOTOCATALYSIS

HOMOGENEOUS PHOTOCATALYSIS

In homogeneous photo catalysis, the reactants and the photo catalysts exist in the same phase. The most commonly used homogeneous photo catalysts include ozone and photo-Fenton systems (Fe^+ and Fe^+/H_2O_2). The reactive species is the •OH which is used for different purposes. The mechanism of hydroxyl radical production by ozone can follow two paths.

$$O_3 + h\nu \rightarrow O_2 + O(1D) \quad (1)$$

$$O\ (1D) + H_2O \rightarrow \bullet OH + \bullet OH \quad (2)$$

$$O\ (1D) + H_2O \rightarrow H_2O_2 \quad (3)$$

$$H_2O_2 + h\nu \rightarrow \bullet OH + \bullet OH \quad (4)$$

Similarly, the Fenton system produces hydroxyl radicals by the following mechanism.

$$Fe^{2+} + H_2O_2 \rightarrow HO\bullet + Fe^{3+} + OH- \quad (5)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO\bullet 2 + H^+ \quad (6)$$

$$Fe^{2+} + HO \rightarrow Fe^{3+} + OH^- \quad (7)$$

In photo-Fenton type processes, additional sources of OH radicals should be considered: through photolysis of H_2O_2, and through reduction of Fe^{3+} ions under UV light:

$$H_2O_2 + h\nu \rightarrow HO\bullet + HO\bullet \quad (8)$$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + HO\bullet + H^+ \quad (9)$$

The efficiency of Fenton type processes is influenced by several operating parameters like concentration of hydrogen peroxide, pH and intensity of UV. The main advantage of this process is the ability of using sunlight with light sensitivity up to 450 nm, thus avoiding the high costs of UV lamps and electrical energy. These reactions have been proven more efficient than the other photo catalysis but the disadvantages of the process are the low pH values which are required, since iron precipitates at higher pH values and the fact that iron has to be removed after treatment.[10]

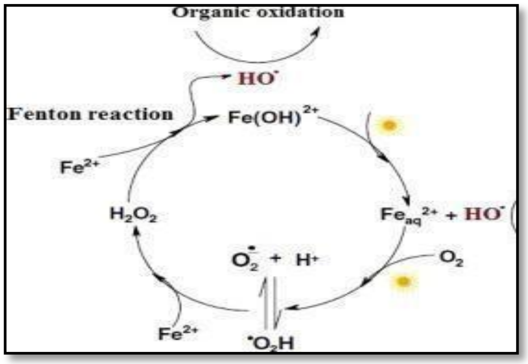

FIG. 6. HOMOGENEOUS REACTION IN WHICH

PHOTO CATALYTIC GENERATION OF HYDROXYL RADICALS.

HETEROGENEOUS PHOTO CATALYSIS

Heterogeneous catalysis has the catalyst in a different phase from the reactants. Heterogeneous photo catalysis is a discipline which includes a large variety of reactions: mild or total oxidations, dehydrogenation, hydrogen transfer, $^{18}O_2$–$^{16}O_2$ and deuterium-alkane isotopic exchange, metal deposition, water detoxification, gaseous pollutant removal, etc.

Most common heterogeneous photo catalysts are transition metal oxides and semiconductors, which have unique characteristics. Unlike the metals which have a continuum of electronic states, semiconductors possess a void energy region where no energy levels are available to promote recombination of an electron and hole produced by photo activation in the solid. The void region, which extends from the top of the filled valence band to the bottom of the vacant conduction band, is called the band gap.

When a photon with energy equal to or greater than the materials band gap is absorbed by the semiconductor, an electron is excited from the valence band to the conduction band, generating a positive hole in the valence band. Such a photo generated electron-hole pair is termed an exciton. The excited electron and hole can recombine and release the energy gained from the excitation of the electron as heat. Exciton recombination is undesirable and higher levels lead to an inefficient photo catalyst. For this reason efforts to develop functional photo catalysts often emphasize extending exciton lifetime, improving electron-hole separation using diverse approaches that often rely on structural features such as phase hetero-junctions (e.g. anatase-rutile interfaces), noble-metal nanoparticles, silicon nanowires and substitution cation doping. The ultimate goal of photo catalyst design is to facilitate reactions between the excited electrons with oxidants to produce reduced products, and/or reactions between the generated holes with reductants to produce oxidized products. Due to the generation of positive holes and electrons, oxidation-reduction reactions take place at the surface of semiconductors.

In one mechanism of the oxidative reaction, the positive holes react with the moisture present on the surface and produce a hydroxyl radical. The reaction starts by photo-induced exciton generation in the metal oxide surface (MO stands for metal oxide):

$MO+h\nu \rightarrow MO\ (h^{+}+e^{-})$ (10)

Oxidative reactions due to photo catalytic effect:

$h^{+} + H2O \rightarrow H^{+} + \bullet OH$ (11)

$2h^{+}+2H_2O \rightarrow 2H^{+}+H_2O_2$ (12)

$H_2O_2 \rightarrow 2\ \bullet OH$ (13)

Reductive reactions due to photo catalytic effect:

$e^{-}+O_2 \rightarrow \bullet O_2^{-}$ (14)

$\bullet O_2^{-} + H_2O + H^{+} \rightarrow H_2O_2 + O_2$ (15)

$H_2O_2 \rightarrow 2\ \bullet OH$ (16)

Ultimately, the hydroxyl radicals are generated in both the reactions. These hydroxyl radicals are very oxidative in nature and non-selective with redox potential of (E_0 = +3.06V)[10]

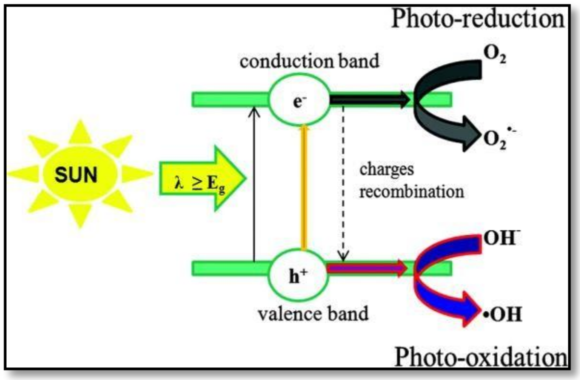

FIG.7. HETEROGENEOUS REACTION SHOWING PHOTO-REDUCTION AND PHOTO-OXIDATION

TIO₂ AS PHOTOCATALYST

Various semiconductors have been used as a photo catalyst TiO_2, ZnO etc. The electronic structure of a semiconductor plays a key role in photo catalysis. A semiconductor consists of Valance Band (VB) and Conduction band (CB) and the energy difference between these two levels is called the band gap having energy less than 3.5 V. Both the electrons and holes are in valence band without excitation. When semiconductor surface is exposed to light, then by absorbing particular wavelength electrons are transferred from the VB to the CB, leaving behind a hole (h^+) in the valence band and thus form electron–hole pairs.

Electrons and holes migrate to the surface of the semiconductor and can reduce and oxidize the reactants which are absorbed by the semiconductor, respectively. The reduction and oxidation potential of these photo-induced electrons and holes is much higher than that of hydrogen and ozone, respectively. Therefore, these electron– hole pairs act as a strong redox system. The photo-produced holes generate hydroxyl radicals by the oxidation of OH^- and H_2O molecules which are absorbed on TiO_2 surfaces. Simultaneously, the electrons in the conduction band could facilitate reduction of O_2 molecules which exist in absorbed air on TiO_2 surfaces and finally form peroxyl radicals. The photo- produced hydroxyl and peroxyl radicals in turn oxidize and degrade organic/inorganic materials. The reduction and oxidation reactions are the fundamental mechanisms of photo catalytic hydrogen production and photo catalytic water/air purification, respectively.[11]

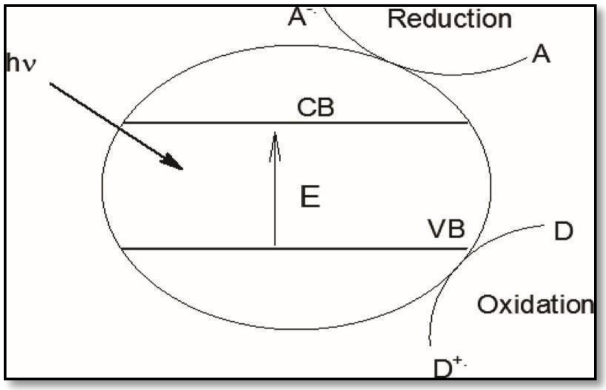

FIG. 8. THE REDOX REACTION WHICH INVOLVES OXIDATION AND REDUCTION.

Investigations reveal that among various photo catalyst TiO_2 is the most efficient photo catalyst. Titanium dioxide (TiO_2) was discovered in 1791 from ilmenite. In 1929, the photo activity of TiO_2 was first noticed when it was used as white pigments in buildings. Many polymorphs of TiO_2 exist. The well- known phases of titanium dioxide are anatase, rutile and brookite which were discovered in 1801, 1803 and 1825 respectively. The metastable anatase and brookite forms can irreversibly convert to stable rutile which is the naturally occurring phase of TiO_2 by heating. Titanium dioxide (TiO_2) has been widely used as a photo catalyst in many environmental and energy applications due to its efficient photo activity, high stability, low cost, and safety to the environment and humans.[9]

The photo catalytic activity of titania depends on its phase. It exists in three crystalline phases; the anatase, rutile and brookite. The anatase phase is metastable and has a higher photo catalytic activity, while the rutile phase is more chemically stable but less active. Some Titania with a mixture of both anatase and rutile phases exhibit higher activities compared to pure anatase and rutile phases. When Titania is irradiated with light of sufficient energy, electrons from the valence band are promoted to the conduction band, leaving an electron deficiency or hole, h+, in the valence band and an excess of negative charge in the conduction band. The free electrons in the conduction band are good reducing agents while the resultant holes in the valence band are strong oxidizing agents and can both participate in redox reactions.

The most promising area of TiO_2 photo catalysis is the photo degradation of a large variety of environmental contaminations such as complex organic compounds and inorganic material turn into CO_2 and harmless inorganic anions respectively. TiO_2 as a photo catalyst has shown a great potential for detoxification or remediation of wastewater. TiO_2 nanoparticles can be freely suspended in wastewater or deposited on substrates during the decontaminations process.[2]

PROPERTIES	**OF**	**TiO_2**
NANOMATERIALS		**AS**
PHOTOCATALYST		

Nano size material size ranges between 1 and 100 nm. They exhibit properties which lie into the region of transition between the molecular and the bulk phase. In the bulk material, the electron excited by light absorption could possess with different kinetic energies in conduction band. As the particle size of nano-particles is same or smaller than the size of the first excited state then, the electron and hole generated upon irradiations cannot fit into such a particle until or unless they assume a state of higher kinetic energy. Hence, as the size of the semiconductor particle is reduced below a critical diameter, the spatial confinement of the charge carriers within a potential well, like a ‘particle in a box’, causes them to behave quantum mechanically.

According to solid state terminology it means that the bands split into discrete electronic states (quantized levels) in the VB and CB and the nanoparticles behaves more and more like a giant atom. Nano sized semiconductor particles which exhibit size- dependent optical and electronic properties are known as quantized particles (Q- particles) or quantum dots. Such type of researches explains their quantum- mechanical aspect to understand the activity of nanoparticles.[12]

Various investigations have shown that various properties of nanocrystalline semiconductor particles are different from those of bulk materials. Both surface adsorption as well as photo catalytic reactions can be increased by nano sized semiconductors because of having more available reactive surface area. [32]

In recent scenario nano science has more advantages than ongoing technologies because nano materials completely mineralize most of organic compounds and completely removed from polluted water. Nano photo catalyst are non-toxic, chemically and thermally stable. In addition, these photo catalyst are easily available, inexpensive and resist for corrosion in the presence of water and other chemicals.[3]

Nano- TiO_2 have been synthesized in various sizes and shapes such as nanoparticles, nano tubes, nanowires, inverse opals, nano ribbons and nano sheet arrays. There are different methods such as hydrothermal, sol-gel, precipitation, etc. are available to synthesize different shape of *NPs*. Generally, nano-TiO_2 is synthesized by using various titania precursors such as titanium tetra-iso-prop oxide (TTIP), tetra butyl titanate (TBOT) and titanium tetrachloride ($TiCl_4$).[13]

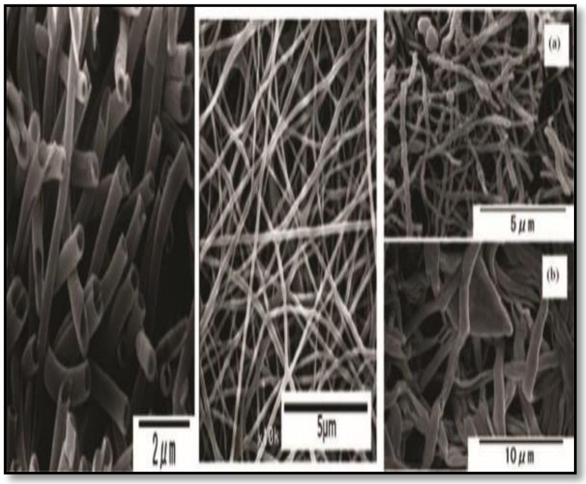

FIG.9. (I) SEM IMAGE OF TIO_2 NANOTUBES FORMED BY CALCINATION OF PVA-TTIP HYBRID NANO FIBRES. (II) SEM IMAGE OF TIO_2 NANO FIBRES OBTAINED BY CALCINATION AT 400°C FOR 5 HOURS IN AIR. (III) SEM IMAGES OF (A) NON-HOLLOW TIO_2 NANO FIBRES AND (B) WALL-BROKEN TIO_2 NANOTUBES.

TiO_2 nanostructures due to high surface-volume ratio offer increase light absorption rate, increasing surface photo-induced carrier density which lead to higher surface photo activity and enhanced photo catalytic activity of TiO2 nano catalysts. Some researchers reported that smaller crystallite size of nano doped TiO_2 induced a larger band gap due to the increased redox ability. Moreover, the quantum size effect of nano- doped- TiO_2 increases its photo catalytic activity.[14]

The anatase and rutile forms are the common crystallographic phases found in the formation of nano- TiO_2, where anatase phase is favored for its high photo catalytic activity and exceptional thermodynamic stability in nano scale dimensions. The crystalline structure of nano- TiO_2 is shown as octahedral TiO_6. In order to achieve high photo catalytic degradation efficiency, nano- TiO_2 should be mesoporous and should exhibit high crystalline and specific area. Nano- TiO_2 having large specific surface area, high percentage of anatase phase and small crystallite size although give favorable contribution towards high photo catalytic activity.

Photo catalytic properties of nano- TiO_2 can be effectively utilized in the removal of the environmental pollutants under UV-visible irradiation. Catalytic TiO_2 nanoparticles could also oxidize hydrocarbons, alcohols, carbon monoxide, ammonia, SO_2 and bacteria in air under UV irradiations/solar light. TiO_2 nanoparticles can destroy various organic species directly under light irradiation and have been employed in photo catalytic cancer therapy [15]

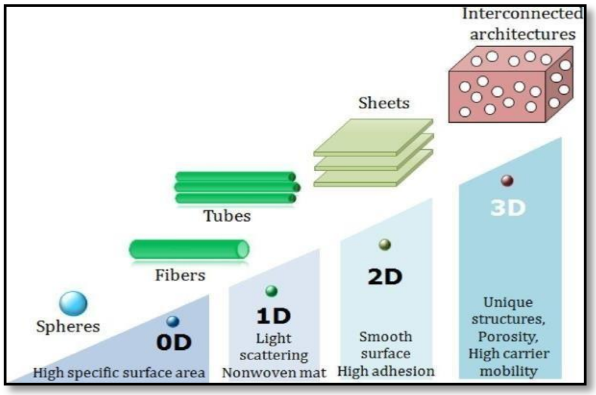

FIG.10. TIO_2 STRUCTURES ACCORDING TO THE STRUCTURAL DIMENSIONALITY AND EXPECTED PROPERTY.

MODIFICATION OF TIO_2 AS PHOTOCATALYST

A large number of research works have been published on TiO_2 modification to enhance its photo catalytic properties. These modifications have been done in many different ways which include metal and non-metal doping, dye sensitization, surface modification, and fabrication of composites with other materials and immobilization and stabilization on support structures. The properties of modified TiO_2 are always intrinsically different from the pure TiO_2 with regards to light absorption, charge separation, adsorption of organic pollutants, stabilization of the TiO_2 particles and ease of separation of TiO_2 particles.[16]

PHOTOCATALYTIC ACTIVITY OF DOPED - TIO_2

The performance of photo catalyst can be improved by depositing or incorporating metal ion or non-metal do pants into the TiO_2. Doping techniques have been applied in photo catalysis to overcome limitations of nano TiO_2 such as wideband gap, ineffectiveness of photo catalysis under the sunlight and thermal instability. Most of the do pants have the potential to increase the photo catalytic efficiency of nano-doped- TiO_2. To broaden the effective range of light sensitivity of photo catalyst from the ultra-violet (UV) region to the visible light region, do pants can modify the electronic structure of nano- TiO_2. [31]

Do pants having their worth for the ability to confer excellent physicochemical properties such as high crystalline (high percentage of anatase phase), high specific surface area and small crystallite size. Do pants could create a charge space carrier region on the surface of TiO_2 and prohibits the recombination of the photo generated electron- hole pairs, which in turn accelerate the formation of hydroxyl radical and thus enhance the rate of photo catalytic process. In addition to this, do pants can act as active site for the adsorption of pollutants and increase the rate of photo degradation.[13]

PHOTOCATALYTIC ACTIVITY OF METAL DOPED

TIO_2 NMS

Metal doped TiO_2 is promising photo catalyst especially metals having variable valency. That is, Iron acts as a trap for the electron–hole pairs and consequently inhibits their recombination. On the other hand, the radius of Fe^{3+} (0.79 Å) is similar to that of Ti^{4+} (0.75 Å). This trait increases the easy incorporation of Fe^{3+} ions into the crystal lattice of TiO_2. It was found that Fe^{3+} doped TiO_2 prevents the agglomeration of the particles, forming well nanocrystalline particles with high surface area and thus ensuring high photo catalytic efficiency with band gap of 2.6 eV.

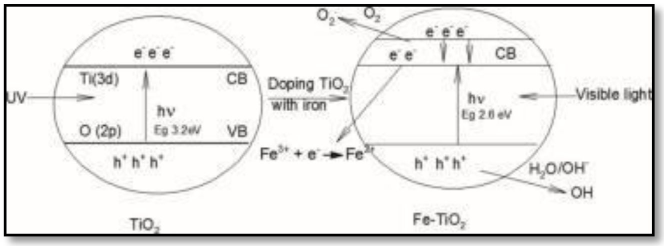

FIG.11. ENERGY LEVEL OF IRON DOPING WITH TIO_2.

The effects of the co-addition of Zn^{2+} and Sodium dodecyl benzene sulfonate on the photo catalysis performance and wetting properties of the resulting TiO_2 nano particle films were investigated. It was reported that both the photo catalytic activity and the hydrophilicity was improved with the addition of Zn^{2+}, which can be attributed to surface oxygen vacancies.

Amphiphilic TiO2 nano tube arrays (TiO2 NTs) were fabricated through electrochemical oxidation of Titania in solution containing H_3PO_4 and NaF. It was found that the TiO2 NTs have the capability of self-cleaning due to Amphiphilic and the photo catalytic activity.[13]

PHOTOCATALYTIC ACTIVITY OF NON-METAL DOPED TIO_2 NMS

The photo catalytic activity of nitrogen-doped TiO_2 nano materials was investigated by degradation of MB aqueous solution under visible light irradiation. It was observed that the wavelength range of nitrogen-doped TiO_2 was shifted to visible light.

It is difficult to make the substitution of O by N because the ionic radius of N (1.71 Å) is so much greater compared to O (1.4 Å). Thus, to maintain the electro neutrality and to form an oxygen vacancy, three oxygen atoms should be replaced by two nitrogen atoms. In the presence of nitrogen in Titania, the energy of oxygen vacancies is reduced from 4.2 to 0.6 eV, showed that nitrogen favors the formation of oxygen vacancies. These oxygen vacancies promote the absorption in the visible region (from 400 to 600 nm) and ensure the activation of N-doped TiO_2.

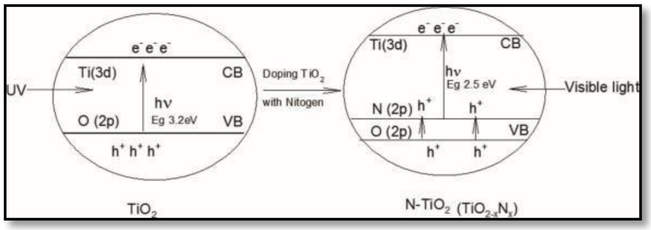

FIG. 12. ENERGY LEVEL OF NITROGEN DOPING WITH TIO_2.

By two-step process of hydrothermal and post-impregnation method Cr and N-co doped TiO_2 nano tubes were prepared. The enhanced photo catalytic activity for the degradation of methyl orange up to 97.16%, has been reported. The photo catalytic activity of nanocrystalline S, N-co doped TiO_2 thin films and powders under visible and sun light irradiation was evaluated by the degradation of MO. [30]

It was found that MO solution was discolored completely under sun light in 75 min in the presence of the modified TiO_2 powder. It was reported that Sulfur doping can generate the small particle size with great surface area which accelerate the photo degradation process.

The methylene blue dye degradation ability of sulfur doped hollow TiO_2 nano catalyst is shown to be 98.6% compared to that of standard Degussa P25 (30%). This catalyst is able to degrade 71% methylene blue dye during fifth times recycling without any further treatment.[13]

TiO_2 AND ENVIRONMENTAL EFFECTS

Titanium, the ninth most common element in the Earth's crust, is a metal commonly found in plants and animals. Titanium naturally interacts with oxygen to form titanium oxides, commonly found in ores, indigenous dusts, sands and soils. In the environment, titanium dioxide nanoparticles have low to negligible solubility and have been shown to be stable once particle aggregates are formed in soil and water surroundings. These TiO_2 promote photosynthesis and nitrogen metabolism, resulting in the enhanced growth of plants. It increases the absorption of light and accelerates the transfer and transformation of the light energy. It was also found that treatment with nano-sized TiO_2 significantly increased the level of antioxidant enzymes, and decreased the ROS accumulation and malonyl dialdehyde content in chloroplasts under visible and UV irradiation. TiO_2 also increased the superoxide dismutase activity of germinating soybean, enhanced its antioxidant ability, and promoted seed germination and seedling growth. [28]

Titanium dioxide (TiO_2) is one of the most attractive transition-metal oxides because of its superior physical and chemical properties, which has been widely applied in environmental clean- up (photo catalytic pollution removal), energy conversion (hydrogen production and solar cells), energy storage (lithium batteries and super capacitors), security (sensors), panel display (transparent conducting films), biomedical devices, and so forth.[17]

The research on photo catalyst shows that it is a promising technique for the decomposition of organic contaminant using clean solar energy without yielding any harmful by-products. This technique can be envisaged as one of the most promising Advanced Oxidation Process (AOPs) due to its specific advantages, such as bland reaction conditions, the possibility of using molecular oxygen as oxidant species, the total mineralization of pollutants into substances innocuous to the environment. Photo catalysis is based on the interaction between semiconductor materials and light by considering that 'free' light from the sun, the idea of using solar light energy as resource to clean up the environment is an ideal and promising approach. The efficiency of photo catalytic materials, such as titanium dioxide (TiO_2), to degrade organic contaminants in the air and water has been studied for more than 30 years. Titanium dioxide (TiO_2) has been widely used as a photo catalyst for solar energy conversion and environmental applications and building materials such as tiles, concrete, paints and glasses due to its interesting properties that include chemical stability, good optical transparency, high refractive index, low cost, and non- toxicity. [29]

The photo catalytic disinfection efficiency is attributed to the oxidative damage mainly induced by reactive oxygen species (ROS), like $O_2{\bullet}-$, H_2O_2 and HO•. These reactive oxygen species are produced on the surface of TiO_2 when illuminated by photons with energy greater than its band gap, so electron will exit from valance band to the conduction band thus creating an electron-hole pair. With holes (h+) and hydroxyl radicals (OH•) generated in the valence band, and electrons and superoxide anions ($O2{\bullet}-$) generated in the conduction band, irradiated TiO2 photo catalyst can decompose and mineralize organic compounds by a series of oxidation reactions leading to carbon dioxide. The mechanism of radical's generation (•OH and $\bullet O_2^-$) is presented as follows.

$$TiO_2+h\nu \rightarrow TiO_2(e^-+h+) \quad (17)$$

$$H_2O+TiO_2(h+) \rightarrow TiO_2+\bullet OH+H+ \quad (18)$$

$$O_2+TiO_2(e^-) \rightarrow TiO_2+\bullet O_2^- \quad (19)$$

Antimicrobial coatings have been developed for a variety of different applications to reduce the proliferation of bacteria, fungi, and viruses on surfaces. Two significant effects related to photoactive TiO_2 coatings nature had been by this time discovered:

i. The effect of self-cleaning due to redox reactions on the photocatalyst surface when excited by sunlight (or in general, weak U.V. light);

ii. The photo-induced hydrophilicity of the surface of the catalyst, which enhances the self- cleaning effect, dirt and stains on surfaces that caused by in organics, can be easily removed due to soaking the rainwater between the adsorbed substance and the surface of TiO_2.

Photo catalytic glasses give an example of self-cleaning and anti-fogging (wetting) properties.[9]

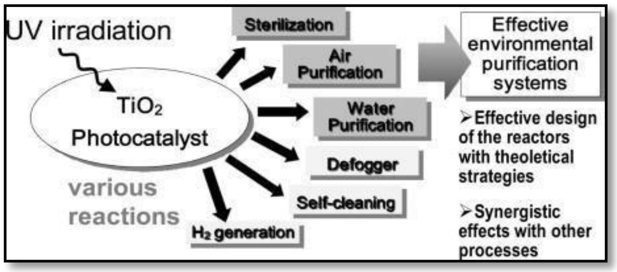

FIG.13. SCHEMATIC REPRESENTATION OF THE USES OF TIO_2 AS PHOTOCATALYTIC

ENVIRONMENTAL BENEFITS

Due to its various properties, titanium dioxide has been found to be useful for many different environmentally friendly applications. When used in a paint coating on the outside of buildings in warm and tropical climates, the white, light-reflecting qualities of TiO_2 can lead to considerable energy savings, as it reduces the need for air-conditioning. Also, its opaqueness means it doesn't need to be applied in thick or double coats, improving resource efficiency and avoiding wastes. As a photo catalyst, titanium dioxide can be added to paints, cements, windows and tiles in order to decompose environmental pollutants. As a nano material, it can also be used as a crucial DeNOx catalyst in exhaust gas systems for cars, trucks and power plants, thus minimizing their environmental impact.[8] Researchers are discovering new potential uses for titanium dioxide in this form. This includes clean energy production.

Pure titanium dioxide is a fine, white powder that provides a bright, white pigment. Titanium dioxide has been used for a century in a range of industrial and consumer products, including paints, coatings, adhesives, paper, plastics and rubber, printing inks, coated fabrics and textiles, as well as ceramics, floor coverings, roofing materials, cosmetics, toothpaste, soap, water treatment agents, pharmaceuticals, food colorants, automotive products, sunscreen and catalysts.[9] Titanium dioxide is produced in two main forms. The primary form, comprising over 98 percent of total production, is pigment grade titanium dioxide. The pigment form makes use of titanium dioxide's excellent light-scattering properties in applications that require white opacity and brightness. The other form in which titanium dioxide is produced is as an ultrafine (nano material) product. This form is selected when different properties, such as transparency and maximum ultraviolet light absorption, are required, such as in cosmetic sunscreens. [27]

Pigment-grade titanium dioxide is used in a range of applications that require high opacity and brightness. In fact, most surfaces and items that are white and pastel, and even dark shades of color, contain titanium dioxide.

Pigment-grate titanium dioxide is used in a range of applications, including:

- **Paints and Coatings:** Titanium dioxide provides opacity and durability, while helping to ensure the longevity of the paint and protection of the painted surface. [3]
- **Plastics, Adhesives and Rubber:** Titanium dioxide can help minimize the brittleness, fading and cracking that can occur in plastics and other materials as a result of light exposure.
- **Cosmetics:** Pigment-grade titanium dioxide is use in some cosmetics to aid in hiding blemishes and brightening the skin. Titanium dioxide allows for the use of thinner coatings of make-up material for the same desired effect.
- **Paper:** Titanium dioxide is used to coat paper, making it whiter, brighter and opaque.
- **Food Contact Materials and Ingredients:** The opacity to visible and ultraviolet light offered by titanium dioxide protects food, beverages, supplements and pharmaceuticals from premature degradation, enhancing the longevity of the product. Specific classes of high purity pigment-grade titanium dioxide are also used in drug tablets, capsule coatings and as a decorative aid in some foods.

  Ultrafine-grades of titanium dioxide are most commonly used in the following specialty applications:

- **Sunscreen:** Nano scale titanium dioxide becomes transparent to visible light while serving as an efficient UV light absorber. Because the particle size is so small, nano- titanium dioxide does not reflect visible light, but does absorb UV light, enabling a transparent barrier that protects the skin from the sun's harmful rays. According to the Skin Cancer Foundation, using sunscreens containing titanium dioxide can help prevent the occurrence of skin cancer.
- **Catalysts:** Nano scale titanium dioxide is used as a support material for catalyst applications. Major uses include in the automotive industry to remove harmful exhaust gas emissions and in power stations to remove nitrous oxides.[3]

TiO_2 PHOTOCATALYST FOR WATER TREATMENT APPLICATIONS

Photocatalyst system is selected as an attractive choice in organic effluent treatment due to its properties. This process has been widely investigated as a promising technology for the efficient wastewater treatment since the photocatalyst is an environmentally friendly process and has considerable advantages such as the ability to destroy pollutants without the exertion of potentially hazardous oxidants (e.g., ozone, chlorine). This process can be conducted under room conditions and organic pollutants can be completely decomposed into CO_2 and H_2O[9]

WATER TREATMENT METHODS

Recently, many water treatment technologies, such as biological treatment, coagulation/precipitation techniques, Fenton oxidation treatments, and advanced oxidation techniques, have been assessed to address the worsening clean water shortage. In line with national development, growth and policy, industrial was tewater is becoming more contaminated and difficult to process. In particular, there are few effective and economic treatment methods for livestock manure and litter leachate. Organic compounds and toxic pesticides, and manure emission from each industry are polluting drinking water and rivers, which is becoming a worldwide contamination with increased severity. The wide area of water pollution, diversification and non biodegradable problems has become a problem that cannot be solved by the natural cleansing cycle.[14]

Moreover, in the case of water treatment technology, which includes non- biodegradable organic compounds, it is very difficult to remove pollutants completely with existing biological treatment technology, which includes coagulation/precipitation techniques, and Fenton oxidation treatment technology. Biological treatment technologies use the microbial metabolism. [25]

The methods are reliable, economical and safe, but the process efficacy for removing suspended solids is low highlighting the need for better operation management. The coagulation and precipitation technique method that precipitates suspended solids by forming flocs after the addition of a polymer coagulator or inorganic coagulants (Fe, Al, etc.), which can coagulate with pollutants to be moved by adding a water-soluble metal salt and adjusting the pH or adding polymer coagulant to form sludge flocs to precipitate or separate suspended or dissolved solids from waste water. This has high treatment efficiency but the use of chemicals, environmental problems and biological sludge causes pipe blockages and water deterioration. Fenton oxidation treatment technology breaks down organic matter by the strong oxidation power of the Fenton's reagent because it generates OH radicals (OH^-) via a reaction of hydrogen peroxide and iron salts, which are the Fenton's reagents. [26]

This process involves a coagulation process to remove the iron salts, neutralization, and oxidative reactions due to Fenton's reagent. Therefore, additive devices are not used excessively compared to other high-level oxidation methods or photo oxidation method, and the process is easy to apply. On the other hand, its disadvantages include the amount of sludge produced, and the excessive operating expense for secondary processing.[11]

APPLICATION OF PHOTOCATALYSIS IN WASTEWATER TREATMENT

The problem of wastewater from pollution and contamination by various types of discharges is now the focus of attention all over the world. As a potential technology to solve the energy crisis and control environmental pollution, photo catalysis has been studied widely in recent years. The main application areas in catalysis are photo catalytic electrolysis of water, environmental protection, solar cells, storage equipment and soon, especially the application in wastewater treatment. The pollutants in waste water can be divided roughly into organic pollutants and inorganic pollutants. [33]

PHOTOCATALYTIC DEGRADATION OF ORGANIC POLLUTANTS

Organic pollutants such as dye, pesticide, pharmaceutical waste, exist widely in wastewater, which are very harmful to the biological safety and ecological system. Especially toxic and difficultly degradable organic pollutants (such as heavy metal pollutants, dye, pesticide) have a long half-life, and only trace can lead to biological variation. TiO_2 photo catalysis, as a green catalytic technology, can almost degrade all organic pollutants without selection. Studies show that more than 3000 kinds of difficultly degradable organic compounds can be degraded by TiO_2 photo catalytic technology.[18]

PHOTOCATALYTIC REMOVAL OF INORGANIC POLLUTANTS

The inorganic wastewater pollutants mainly include heavy metal pollutants, cyanide- containing waste, NO2— containing waste, and so on. Photo catalytic removal of inorganic pollutants usually has two kinds of mechanism: photo catalytic reduction and photo catalytic oxidation. Heavy metal ions mainly come from waste water discharge of manufacture leather, metallurgical industry and electroplate factory, which have characteristics such as toxic, long half-life, vivo enrichment, difficult to degrade, etc. [34]

Currently more research on photo catalytic treatment of heavy metal pollutants in effluent is focused on the removal of Hg (II), Pb (II), Cr (VI). The photo catalytic mechanism is as equation (M*n*+ represents metal oxide, and M represents the photo catalysis product). $Mn^+ + e^- \rightarrow M$ Cyanide (especially free cyanogen root) is also severely poisonous, mainly coming from metallurgy industry, especially gold mines, electroplating industry and other corresponding chemical industry. The cyanide emission has increased in those fields recently. TiO2 photo catalysis can effectively reduce poisonous substances CN- to CO_2 or $CO_3^{2-}$and nontoxic N2.NO2$^-$is a dangerous environment pollutant which can cause cancer; especially low concentration NO2$^-$is more stable, and not easily decomposed. The research on photo catalytic treatment of NO_2^- in water has been a large field of relevant reports. It is the photo catalytic reactions premise step that NO2$^-$is adsorbed in the surface of the catalyst. [24]

ADVANCED OXIDATION TECHNOLOGY(AOT)

Advanced Oxidation Technology (AOT) is a method that uses a range of technologies to the increase oxidation power. For effective water treatments, a range of pollutants need to be removed economically at room temperature and under atmospheric pressure. AOT produces OH^-, which has stronger oxidation power than ordinary oxidants normally used in the oxidation process, in water (oxidation potential: 2.80 eV) and decomposes the organic compounds into relatively harmless compounds, such as CO_2, H_2O, or HCl

AOT with ozone is used worldwide. This technology inserts ozone gas directly into contaminated water. One method is to make the organic contaminants react directly with ozone, and another is to effectively cause oxidative decomposition through an indirect reaction with OH, which is generated by decomposed ozone. [23] On the other hand, the mechanism of ozone decomposition depends on the properties of the organic pollutants in polluted water. Hence, the organic pollutants in contaminated water can either promote or inhibit ozone decomposition. Therefore, the advanced technology using ozone can treat a range of organic pollutants that are difficult to decompose by a direct reaction with ozone, but the treatment efficiency for those pollutants that are highly reactive with ozone can deteriorate.

Fenton oxidation technology that uses the Fenton reaction is a method to generate OH in a Fe^{2+} and H2O2 mixture. This can decompose H_2O_2 by Fe^{2+} in the liquid phase without light irradiation, and generate OH. In the case where light is irradiated, the faster decomposition of H_2O_2 is possible due to ferrous or ferric ions and rapid OH generation is possible. These reactions can be performed under UV radiation and visible light, and the range can be expanded. On the other hand, the rate of OH generation decreases sharply when the initially injected Fe^{2+} is consumed completely. This is because a reduction reaction is much slower than the Fenton reaction, in which Fe^{2+} is oxidized by H_2O_2. In addition, the Fenton oxidation reaction is only applicable under the acidic conditions, i.e., pH < 4. Therefore, the process has disadvantages of high cost of operation due to the additional cost of the acid/base for pH adjustments. [19]

Hydroxy can be generated by directly decomposing water using an external energy source, such as an electromagnetic beam, ultrasound and microwave. When water is irradiated with an electromagnetic beam (gamma rays), water molecules are decomposed to OH, H^+, and aqueous electrons. Water molecules can also be decomposed by a high- voltage discharge in water. When high voltage pulses of approximately 10 kV, which has a fast voltage rise time in nanoseconds, are added between two electrodes installed with a narrow gap (a few centimetres) between them, a flame is generated as water discharge is caused. This generates localized high concentrations of OH. OH^- can also be generated by ultrasound or microwaves. When these energy sources pass through water, localized pressure differences with time generate micro bubbles, which acquire vibration energy and become unstable. These bubbles generate strong energy at high temperatures and high pressures, and the water molecule is broken down to OH and H^+.[19]

TIO_2 FOR ADVANCED OXIDATION TECHNOLOGY

A photocatalyst refers to a ‘‘catalyst that accelerates the solar photo reaction’’, and to become photocatalyst, the following conditions need to be fulfilled:

(i) the photo catalyst should not participate directly in the reaction or be consumed; and

(ii) Needs to provide other mechanism routes from existing photo reactions and accelerated reaction rate. Semiconductor molecules contain a valence band (VB) occupied with stable energy electrons and empty higher energy conduction bands (CB). The band gap of the semiconductor energy with higher energy is used to emit light inside the semiconductor to induce a reaction with the absorbent material on its surface via a redox reaction. This is called the photo catalytic reaction. Photo catalytic reactions are based on solar energy absorption in the bad gap of the semiconductor and the following photo-generated electron transfer. Therefore, all semiconductor materials can be used in photo catalysis. On the other hand, there are few effective semiconductors as photocatalyst, and TiO_2 is the most widely used among them.[18]

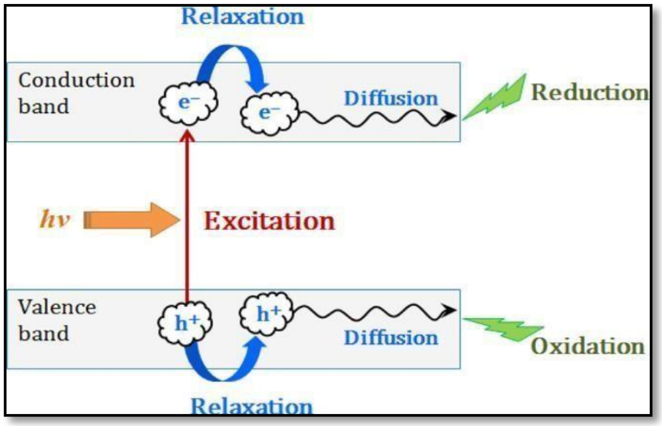

FIG.14. PHOTOCATALYTIC PROCESS SHOWING OXIDATION AND REDUCTION

To apply semiconductor photocatalyst for water treatment, the following needs to be fulfilled; the operation needs to be performed at room temperature or pressure, complete mineralization without secondary pollution, repetitive cycles and low costs for operations. TiO_2 photo catalysis is a photo-induced charge separation phenomenon that occurs on the TiO_2 surface, and very high reactive oxygen species can cause microbial inactivation and organic mineralization without secondary pollution. In addition, other characteristics of TiO_2 have attracted attention as environment purifying catalysts, and the contents are as follows. First, the decomposition reaction of polluted materials is mostly an oxidative reaction, and is dependent on the VB of the photocatalyst. Therefore, the oxidation reaction improves when the VB holes have higher oxidative power and there is a more positive electrochemical potential with respect to the normal hydrogen electrode (NHE) potential. The band gap of TiO_2 is generally a range of 3.0–3.2 eV, wavelength is about 400 nm. This means that UV light irradiation with a wavelength lower than 400 nm begins a photo-reaction. The characteristics of TiO_2 are the more powerful oxidative power of the VB holes than the reducibility of photo-induced electrons TiO_2 has very strong oxidation power, i.e., 3.2 eV for anatase TiO_2 and 3.0 eV for rutile TiO_2, considering the approximately 3.0 eV from the hydrogen reference potential and approximately 1.2 eV from oxidation potential of water. The photon energy of 400 nm corresponds to more than 30,000 8C of thermal energy. Therefore, when TiO_2 is irradiated with UV light below 400 nm, its surface is likely to achieve heat higher than 30,000 8C, and this extremely high temperature oxidizes all materials. Therefore, organic compounds are decomposed completely into water and carbon dioxide.[22]

This schematic illustration on removal of pollutants by the formation of photo induced charge carriers (e^-/h+) in a semiconductor TiO_2 particle surfaces is presented. In other words, when surface of the TiO_2 catalysts suspended in water are irradiated with UV light, the photo- induced electrons in the CB participate in the reduction processes, which typically react with dissolved oxygen in air to produce superoxide radical anions ($O_2^{\bar{}}$). The photo-induced holes in the VB diffuse to the TiO2 surface and react with adsorbed water molecules, forming OH^-. Actually, the OH^- is very important as a major active species during the photo catalytic oxidation reaction. [1]

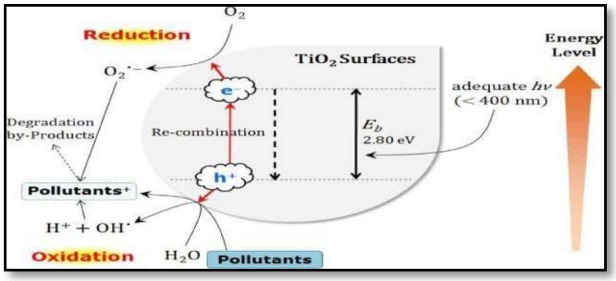

FIG.15. ILLUSTRATION ON REMOVAL OF POLLUTANTS BY THE FORMATION OF PHOTO INDUCED CHARGE CARRIERS (E^-/H+) IN A SEMICONDUCTOR TIO_2 PARTICLE SURFACES

In applying the TiO_2 photo catalytic system for the AOT for water treatment, TiO_2 has a very fast response and has a great advantage in good photo-efficiency even in weak light. Nevertheless, it is inactive in visible light and is unsuitable for a mass processing system. In addition, the TiO_2 photo catalytic system needs to solve these problems because it requires an additional recovery/ separation process from the slurry after the water treatment and an artificial light source suitable for TiO_2 photo catalysis. [19]

Advancements in TiO_2 photo catalysis for advanced oxidation technology

The photo catalytic activity of TiO_2 is observed under UV irradiation, but it can only use 5% of the solar energy that actually reaches the Earth. Therefore, increasing the activity of TiO_2 under the visible irradiation through the introduction of metals or heteroatom's onto the TiO_2 surfaces is a major research focus. Metallic nanoparticles including Pt, Pd, Au, Ag, Ru and Fe have been used to enhance the photo catalytic activity on the TiO2 surfaces by suppressing the $e^-/h+$ (electron–hole) recombination behavior. The photo- induced electrons migrate to the metal due to the relatively low Fermi level of metals, which make the photo- induced holes stable on the TiO2 surfaces by increasing the lifetime of the charge carrier.[20]

Therefore, more OH^- and superoxide radicals (O_2^-) are generated as an enhanced redox reaction. In addition to the characteristics discussed above, Fe^{3+}-doped TiO_2 show greatly improved photo catalytic activity compared to crude TiO_2. Fe^{3+} can be suitably inserted into the TiO_2 lattice structures, because the ionic radius of Fe^{3+} and Ti^{4+} is similar. Moreover, the photo catalytic activities of TiO_2 may be facilitated by creating the relatively high activity of the crystallographic facets. Of these processes, the reactive crystallographic facets of TiO_2 have increased quantitatively, the photo catalytic activities of TiO_2 promote the production of OH^-, and the degradation of organic pollutants can be achieved.[9]

Many studies have focused on modifying the morphology of TiO_2 to improve the photo catalytic activity. It involves the various dimensions of the structure of TiO_2. TiO_2 can exist in a range of morphologies; zero- dimensional TiO_2 spheres, one- dimensional with TiO_2 fibers rods, and tubes, two-dimensional with TiO_2 nano sheets, and three-dimensional with interconnected architectures. TiO_2 nano scales by optimizing the size and shape of TiO_2 particles can maximize the photo catalytic activities. This can enhance the photo catalytic activities during the water treatment process by maximizing the active surface area of TiO_2 with nano scales. In addition, the modification of TiO_2 surface according to the morphologies or scales enables an improvement in the adsorption capacity of the contaminants, which is useful in AOT for water treatment. TiO_2 nano tubes were reported to be more efficient in the adsorption and decomposition of non- biodegradable organic compounds compared to TiO_2 particles, which was attributed to the tube walls of the TiO_2 nano tubes exhibiting a shorter carrier- diffusion pathway and faster mass transfer of organic compounds on the nano tube surfaces and between the nano tube. [3]

Nano-dimensional TiO_2 has a highly specific surface area (large surface area-to- volume ratio), which promotes efficient charge separation and charge trapping of ions on the TiO_2 surfaces. The nano-sized TiO_2 shows increased oxidative power with opacity of the aqueous phase (suspended phenomenon) compared to the bulk- sized TiO_2. On the other hand, the nano- dimensional TiO_2 photocatalyst cannot be applied directly to water treatment because they tend to aggregate during the advanced oxidation processes due to the size and morphology, and physical and chemical properties. [21]

Recently, to solve these problems, many attempts have been made to enhance the photo catalytic activity of TiO_2 and anchor the TiO_2 onto carbon materials. The hybrid composites between TiO_2 and a range of carbon materials including activated carbon or activated carbon nano fibers, carbon nano tubes, and graphene, are considered a promising technology in many areas. Carbon materials are considered to be suitable as a support for TiO_2 owing to their excellent thermal, optical, mechanical, electrical characteristics, chemical resistance, and the design of an optimized pore structure and surface properties, resulting in rapid charge transfer on hybrid TiO_2 /carbon composites.[12]

Recently, hybrid composites of TiO_2 with graphene have attracted increasing attention. Graphene is used as a two-dimensional photocatalyst mat owing to its excellent redox properties. High quality graphene makes the electrons travel without scattering at a mobility higher than 15,000 m2/V/s at room temperature, meaning that it acts as an ideal electron sinks and electron transfer bridge. Band gap behavior of TiO_2 /graphene composites has a wide range (2.66–3.18 eV), according to the graphene content from 0.25 to 10 wt.%. This suggests that the newly formed Ti– O–C bands of TiO_2 /nano carbon composites can extend to the absorption edge, which can absorb the long- wavelength light of the visible region mobility higher than 15,000 m2/V/s at room temperature, meaning that it acts as an ideal electron sinks and electron transfer bridge.

TiO_2 /nano carbon composites have good effects on self-purification compared to ozonation and UV irradiation when applied to advanced oxidation technologies for water treatments. These composites are expected to be industrially effective in AOT for water treatment because these nano carbon materials can be used as a support for tight immobilization by preventing the loss of TiO_2 particles in a flowing fluid stream.[35] Nano- dimensional TiO_2 has a highly specific surface area (large surface area-to- volume ratio), which promotes efficient charge separation and charge trapping of ions on the TiO2 surfaces. The nano- sized TiO_2 shows increased oxidative power with opacity of the aqueous phase (suspended phenomenon) compared to the bulk-sized TiO_2. On the other hand, the nano-dimensional TiO_2 photocatalyst cannot be applied directly to water treatment because they tend to aggregate during the advanced oxidation processes due to the size and morphology, and physical and chemical properties. In order to solve these problems many attempts have been taking place for the advancement of this technology. Hybrid composites between TiO_2 and a range of carbon materials including activated carbon or activated carbon nano fibres, carbon nano tubes, and graphene, are considered a promising technology in many areas. Hybrid composites of TiO_2 with CNT and graphene have attracted increasing attention. CNT and graphene have the potential to contribute to the routes of enhancing photo catalytic activities, due to the large specific surface area, high quality active sites, retardation of e^-/h^+ recombination, and visible light catalysis by tuning the band gap.[36]

CONCLUSION

Recently, many studies have been focused on the broad applications of Titania in technology and medicine, from dye-sensitized solar cells, photodynamic therapy, to water remediation. It is possible because these nanoparticles reveal excellent photochemical properties and high biocompatibility. Moreover, TiO_2 particles are quite cheap and accessible components. Photosensitizing properties and manufacturing costs of these materials are usually related to the number of active sites on their surface. TiO_2 photocatalyst become widely used to treat effluent in the field of water environmental safety, for that it possesses many merits such as high photo catalytic activity, excellent stability, harmless to human beings, low cost and so on.

TiO_2 photocatalyst under either UV light or solar irradiation has become more prominent owing to its low cost, safety, high photo catalytic activity, etc., and as an advanced oxidation technology for the water treatment industry. In addition to the degradation of organic contaminants, the photo catalytic activity of TiO_2 has potential use as an additive in foods or medicines, electrodes of solar cells, etc. On the other hand, the utilization of solar energy is currently limited by the photo-inefficiency of the TiO_2 catalyst (only 5% of the solar spectrum can be used). Therefore, the development of an innovative TiO_2 photocatalyst and its optimization are needed this photocatalyst can be used commercially in photo catalytic water treatment technology.

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[1]

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