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Photocatalytic Nano-Titanium Dioxide for Environmental Application: An Overview

Suchilipsa Das

Assistant Professor, Department of Chemistry, Modern Institute of Technology and Management,
Bhubaneswar, Orissa, India

ABSTRACT: TiO₂ nanosize particles have been studied and used by many material scientists for environmental application. Nanosized TiO₂ is applied as photocatalyst with special semiconducting properties which is helpful in prevention and control of air, water and soil pollution. Functional TiO₂ nanoparticles act as photocatalysts in water treatment. The organic contaminants such as phenol, organochlorine, dyes are removed from water by photodegradation due to the semiconducting property of TiO₂. Nanosized TiO₂ photocatalyst is too much effective in removal of major air pollutants such as SO_x and NO_x from the atmosphere. Nano titanium dioxide plays a vital role for the remediation of organically contaminated soil and sludge. This semiconducting oxide is applied as a nano enhanced coating for antibacterial, antiviral, self-cleaning, self-sterilising, deodorizing, desoiling purpose.

KEYWORDS: TiO₂ nanoparticles, photocatalysis, semiconducting property, water treatment, air pollutants, soil pollution, nano enhanced coating.

I. INTRODUCTION

Photocatalysis is a process in which the catalyst, generally a semiconductor oxide is activated by ultraviolet (UV) or visible radiation causing the acceleration of the rate of chemical reactions. TiO₂ semiconductor is widely used as a photocatalyst due to its excellent and electronic properties and optical properties, non toxicity, low cost, chemical and thermal stability [1]. TiO₂ nanoparticles have outstanding optical and electronic properties incomparision to the compounds made through traditional chemical processes. Nano TiO₂ is used as a suitable photocatalyst due to its special semiconducting property in various photocatalytic reactions [2]. Nano TiO₂ is widely employed as a photocatalyst for purification of water, purification of air, remediation of soil, anti-bacterial and self-sterilizing, self-cleaning surfaces, paintings, and building materials. The objective of this review paper is to (i) study and evaluate the use of nano TiO₂ photocatalyst for remediation of the environment (ii) study various modifications on nano TiO₂ to enhance the photocatalytic ability for environmental application.

II. BACKGROUND OF NANOSIZED TITANIUM DIOXIDE

STRUCTURE: TiO₂ is found in three polymorphic phases such as rutile, anatase and brookite. The rutile and anatase have tetragonal crystal structures whereas the brookite has orthorhombic crystal structure. The rutile and anatase phase belong to different space group. The densities of the rutile, anatase and brookite phases are 4.25, 3.894 and 4.12 g/cm³ respectively. Nanostructured particles (20-30 nm) are effective for photocatalysis.

PREPARATION: Various methods are followed for synthesis of TiO₂ nanoparticles such as sulfate process, chloride process, hydrothermal method, direct oxidation of TiCl₄, impregnation, coprecipitation, metal organic chemical vapor deposition method, etc. Sol-gel method is widely used to synthesize various metal oxides due to low processing temperatures, low cost, ease of fabrication. It is the most convenient way to prepare the films, particles or monoliths.

PHOTOCATALYTIC PROPERTY: Anatase TiO₂ has band gap 3.2 e V which is equivalent to the energy of a photon of UV radiation of wavelength of 387 nm and more promising photocatalytic property whereas the

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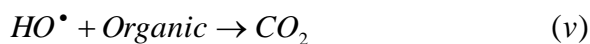
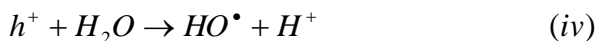
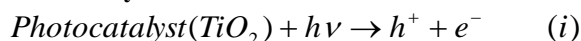
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rutile TiO₂ has band gap 3.0 e V equivalent to the energy of a photon of UV radiation with a wavelength of 387 nm. However the rutile TiO₂ functions efficiently under certain specific condition [3].

III. ENVIRONMENTAL APPLICATION OF PHOTOCATALYTIC NANO TiO₂

WATER TREATMENT : When the sunlight of energy equivalent to the band gap energy ΔE_{bg} (3.2eV), falls on the photocatalytic nano TiO₂ surface, an electron is excited from the valence band to the conduction band. Consequently a positive hole (h^+) in the valence band is formed and e^- exists in the conduction band. The pollutants present in the water are oxidised to CO₂ directly by the positive holes or water is oxidised to HO \cdot radicals by the positive holes and then HO \cdot radicals react with the pollutants to produce CO₂. On the otherhand the oxygen adsorbed on the photocatalyst (TiO₂) is reduced by the electron present in the conduction band.

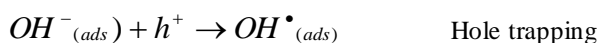
Photocatalytic Reaction



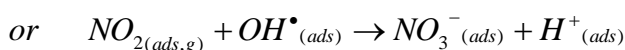
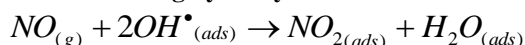
The photocatalytic performance of TiO₂ nanocomposites is more efficient than pure TiO₂. MWCNT/ TiO₂ nanocomposite, metal ion (Cr, V, Mn, Fe, Ni and Ar) implanted TiO₂ and Nano-ZnO/TiO₂ [4], have been synthesised by many researchers to enhance its photocatalytic acivity. Modification can be done in the bulk or on the surface of TiO₂. Bulk modification is mainly achieved by the doping metals or non-metals into bulk NTO. On the otherside surface modifications are done by anchoring colored inorganic semiconductors such as CdS and CdSe [5] or organic dyes on the TiO₂ surface [6], where they provide sensitization effect. These modified photocatalytic catalyst are used for water purification. Organic contaminants such as organochlorine, phenol, rhodamine 6G, rhodamine B, Bishphenol A, methyle orange and methylene blue are removed from polluted water in photocatalytic reactor by photodegradation.

AIR PURIFICATION : When TiO₂ nanoparticles are stimulated by sunlight, they convert air pollutants such as nitrogen oxides (NO_x), (SO_x), volatile organic compounds (VOCs), carbon monoxide (CO), and ozone to more environmentally acceptable products such as calcium nitrate and carbon dioxide.

Photocatalysis reaction for NO_x removal



Oxidation using hydroxyl radical: OH \cdot

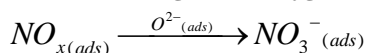


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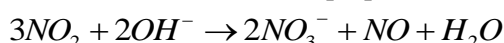
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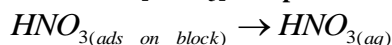
Oxidation using active oxygen: O_2^-



Reaction with Ti-OH via disproportion



Removal of $[HNO_3]$ complex from the surface of the block by water.



NO_x -removing catalytic clothing has been produced using the above reactions in united kingdom in which the TiO_2 nanoparticles and calcium carbonate are sprayed onto clothes, are added to fabrics or applied during washing [7]. TiO_2 nanoparticles coated surface is capable of removing significant quantity of NO_x , SO_x , and VOC pollutants from the atmosphere from the atmospheric air when placed as close as possible to the source of pollution [8]. It was reported by some researchers that nitrogen oxides and VOCs can be removed from approximately $200m^3$ and $60m^3$ of air per day, respectively by subjecting each square meter of titanium dioxide coating to sunlight [9]. TiO_2 paint coating is capable to adhere nitrous oxide (NO_x) and sulfur oxide (SO_x) whether the light is available or not. The harmful pollutants are converted into carbon dioxide and water vapor by a series of chemical reactions initiated by sunlight. Rainfall regenerates TiO_2 photocatalyst. A paint is promoted by Pacific Paints (Boysen) Philippines, Inc. in which TiO_2 nanoparticles present in the paint form hydroxyl and peroxy radicals, which then react with NO_x in the air to produce nitric acid.

REMEDIATION OF ORGANICALLY CONTAMINATED SOIL: TiO_2 photocatalysis is also applied for remediation of organically contaminated soil and sludge. Removal of organic pollutants from soil has been tried by using both pure and composite photocatalyst. TiO_2 was induced by UV-light to enhance photo degradation of organics on soil surfaces [10]. It was concluded that increase of the soil pH and photon flux enhances the photodegradation rate. Degradation of pesticide (diuron) under laboratory conditions was carried out using heterogeneous photocatalytic TiO_2 [11]. They evaluated the potential application of this technology in situ remediation. They investigated that the destruction of diuron carried out efficiently in the top 4 cm of contaminated soil by the photocatalytic treatment in presence of sunlight. Moreover the irradiation intensity has significant effect on degradation rate. TiO_2 modified by calcium also acts as an active photocatalyst [12]. An aqueous slurry has been prepared by mixing photocatalyst i.e TiO_2 in contaminated soils of 2-chlorophenol, atrazine and 2, 7-dichlorodibenzodioxin which was exposed to stimulated sunlight in the laboratory [13]. They observed that the organic contaminants were destroyed in comparatively short span of time and also reported that the contaminated soils could be chemically detoxified effectively by photocatalytic processes.

OTHER APPLICATION OF NANO ENHANCED SURFACE COATING OF TiO_2 : Nano TiO_2 is used as anti-bacterial and self-sterilizing, self-cleaning surfaces, paintings, and building materials. A protective film of photocatalytic titanium dioxide is a super oxidative, hydrophilic and antistatic material used for self-cleaning of buildings. Moreover the film oxidises the hydrocarbon from automotive exhaust and rain water washes away the dirt. Consequently the building exterior remains always clean. Nano TiO_2 Photocatalyst coating act as an invisible film which can be applied on ceiling, floor carpets, curtains, car interior, toilet seats etc. The micro-organic matters, such as bacteria, mold, viruses can be decomposed and tough odours can be removed by the application of this nano TiO_2 film.

IV. CONCLUSION

In this paper, the development of nano TiO_2 photocatalysis and its applications for environmental purification have been reviewed. Combining TiO_2 with other substances is a very effective method to achieve better visible light response. Nano TiO_2 coating or film perform excellently as self-cleaning and disinfectant agent.

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