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Chemistry Department

Photocatalysis by Titanium Dioxide for Drinking Water Purification

Research Project

Submitted to the Chemistry Department/College of Science/University of Salahaddin in Partial Fulfillment of the Requirements for the Degree of Bachelor of Science in Chemistry.

Prepared by:

Ali Hashim Razaaq

Supervised by:

Dr. Ropak Ahmad Sheakh Mohamad

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Abstract:

TiO2 based photocatalyst has potential material for disinfection of harmful

pathogens as well as removal of organic compounds. The formation of reactive

oxygen species is a key part for overall process but aggregation and band gap

constraint explore a new dimension to use of support for propounding its

physicochemical properties. Therefore, the modification of TiO2 using various

support alters photocatalytic action and promising ways of the mechanism based on

nature of substrates and environments. In addition, the immobilization of nano

dimension photocatalyst may reduce overall cost of operation and recovery of

photocatalytic materials. In this perspective, extensive range of support materials as

carbonaceous matters, clay, polymers, metal oxides have been studied by various

researchers; that have been compiled in this review article. The properties of support

were the key features for the assortment of appropriate supports for increase its

efficiency as photocatalyst. In brief, overall TiO2 based photocatalyst supported on

various substrates pave the ways toward new strategies for water disinfection.

Keywords: Photocatalyst, Water Disinfection, TiO2

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1.Introduction

Water is one of the most important resources for human being, as well as animal and plants in the world. With rapid development of science and technology, many industries such as chemical, petrochemical, textile and food etc. are set up worldwide and these industries discharge polluted water leading to contamination of natural water resources .The world is continuously shifting into a new arena due to fast economic growth, industrial development and increasing population, but necessity of clean and pure water is excessive demand. On an average 1.2 billion people still shortage of pure water and diseases are spread due to contaminated water, which led to infant and child deaths (Catley-Carlson, 2017). Worldwide, around 502,000 people are died because of waterborne pathogenic bacteria and viruses (WHO, 2017). The contamination of the water was increasing continuously due to industrial processes and urbanization in the natural water cycle. As soon as it was determined that semiconductors could be efficiently used for obtaining products such as H2 and O2, they were also recognized as efficient photocatalysts for degrading toxic materials. Titanium dioxide (TiO2) is the prominent photocatalyst, widely employed due its great photocatalytic activity, chemical and biological stability, insolubility in water, acid and base environment, resistivity towards corrosion, nontoxicity, low price. and availability in comparison to oxide. sulfide. and other materials. Heterogeneous photocatalytic oxidation of organic compounds in an aqueous solution in the presence of TiO2 as photocatalyst provides the opportunity for efficient treatment of waste, drinking, surface, and ground waters, as well as for obtaining the ultraclean water suitable for the pharmaceutical industry and microelectronics.

2. Photocatalysis

Photocatalyst is the process in which formation of reactive oxygen species and free radicals in the presence of light radiations; that could be useful for water disinfection. It has a capability to kill the microorganism without other chemicals and remove the pollutant in the water by photocatalytic process. Furthermore, cost of the process is lower and use of renewable energy sources as solar spectrum for photocatalysis process. Currently, various semiconducting materials as ZrO2, Fe2O3, WO3, ZnO, CdSe used for the same but among these TiO2 is the foremost advantages as cost effective, chemically stable, non-toxic with higher quantum efficiency (Patil et al., 2017; 2019). The term photocatalysis consists of combination of photochemistry and catalysis which implies that light and catalyst are necessary to promote a chemical reaction. The main difference of photocatalytic reaction with the conventional catalytic reaction is that catalyst is activated by light other than heat. In general, photocatalytic process can be classified as homogeneous or heterogeneous photocatalysis based on the difference in phases of catalyst and the reacting species. In homogeneous photocatalysis, a powerful UV lamp is used to illuminate the contaminated water in the presence of Fe3+, O3, or H2O2 which act as a catalyst and the reaction takes place in the bulk solution. On the other hand, heterogeneous photocatalysis can be defined as catalytic process during which one or more reaction steps occur by means of generation of electron-hole pairs by suitable light on the surface of the solid semiconductor materials.

2.1 TiO2 nanoparticle

Photocatalysis induced by light absorption of metal nanoparticles (NPs) has emerged as a promising strategy for exploiting efficient visible-light-responsive composites for solar-energy conversion.

Titanium dioxide (TiO2) is the most commonly used material due to its price and high oxidation efficiency; it is easy to modify using both physical and chemical methods, what wide allows for its use in industrial scale. Intensive research novel photocatalysts (e.g. ZnO and carbon based photocatalysis like graphene, carbon nanotube, carbon nitride and others) has been carried out. The future development of nano-disinfection containing metal/metal oxides and carbon based nanoparticles should focus on:

- Improving disinfection efficiency through different manufacturing strategies,
- □ proper clarification and understanding of the role and mechanism of interaction of the nano-material with the microorganisms,
- progress in scaling up the production of commercial nano-photocatalysts,
- □ determination of the extent of environmental release of nano-photocatalysts and their toxicity.

2.1.1 Properties of Nano-TiO2

Figure 1 describes the unit cell structures for rutile and anatase TiO2 respectively (Diebold 2003). Both rutile and anatase TiO2 have tetragonal crystal structure linked by a chain of TiO6 octahedral, i.e., each unit cell contains six oxygen atoms around one Ti atom. The crystal structures discussed above are different in assembly pattern of their octahedra chains and by distortion of their octahedron. In rutile TiO2, TiO6 octahedron exhibits an irregular orthorhombic distortion while it exhibits its symmetry lower than orthorhombic in anatase. They summarized that surface passivation has a crucial effect on phase stability and morphology of nanocrystals and concluded that surface hydrogenation triggers significant changes in rutile nanocrystals. The results also explained that size of rutile nanocrystal drastically increased when surface undercoordinated titanium atoms is H terminated. The crossover point for spherical NPs is 2.6 nm. They also reported that anatase is more stable than rutile phase below crossover point (Barnard and Zapol 2004). Their study about TiO2 NPs in water environments reported that transition size is larger in water than that under vacuum. They summarized transition enthalpy of rutile and anatase nanocrystals and concluded that thermochemical results for different facets could be different for size and shape of these nanocrystals The shape of the TiO2 NPs is also changed as described in Fig.2 (Barnard and Curtiss 2005). Direct interband transition of electron in pure semiconductors is the core mechanism for light absorption. In indirect semiconductors such as TiO2, this absorption phenomenon is very small because the crystal symmetry of such semiconductors could not allow the direct electron transitions among the band centers. Braginsky and Shklover described the light absorption enrichment in the crystallites of TiO2 by momentum non-conservation with indirect electron transitions at the interface. When the interfacial atoms have a larger share, this effect increases at the interface.

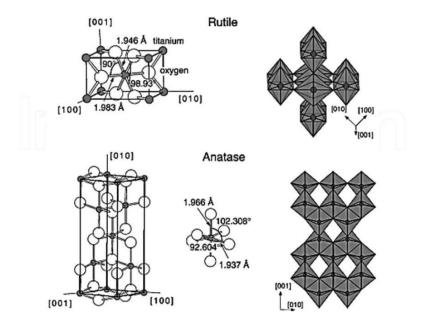
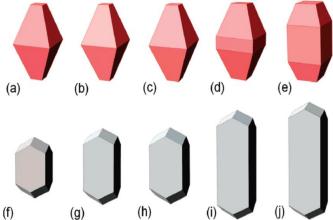
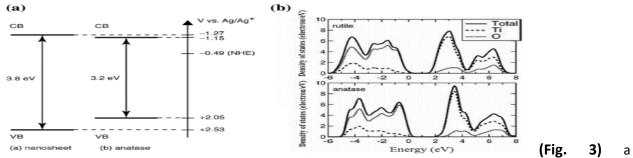


Fig.1) Rutile and anatase unit cell structures. Reprinted with permission from Diebold (2003)). Copyright 2003, with permission from Elsevier



(f) (g) (h) (i) Fig. 2) Morphology predicted for anatase and rutile respectively. a, f hydrogenated surfaces; b, g hydrogen-rich surface adsorbates; c, h hydrated surfaces; d, i hydrogen-poor adsorbates; and e, j oxygenated surfaces. Reprinted with permission from Barnard and Curtiss (2005). Copyright 2005, with permission from the American Chemical Society.

Electronic band structure and densities of states of TiO2 are illustrated in Fig 3. (Sakai et al. 2004; Sato et al. 2003). When the photons of equal or higher energy levels (> 3 eV) strike on the surface of TiO2 NMs, electrons are released from valence band to unoccupied conduction band leaving positive holes in the valance band. These excited electrons and holes are commonly known as charge carriers that try to recombine or may get trapped on the surface and react with absorbed species. The overall output of TiO2 NMs for different applications is determined by the competition of the following processes (Szczepankiewicz et al. 2000).



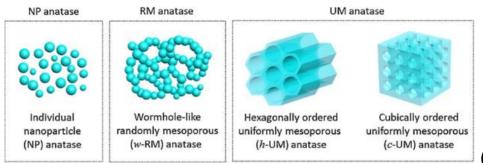
Electronic band description: (a) TiO2 nano sheets (b) anatase. Reprinted with permission from Sakai et al. (2004)). Copyright 2004, with permission from the American Chemical Society. b Total and partial densities of states for rutile and anatase respectively. Reprinted with permission from Sato et al. (2003)). Copyright 2003, with permission from the American Chemical Society.

2.1.2 Applications of nano-TiO2

The most promising applications of nano-TiO2 are photocatalytic and photovoltaic applications. The band gap of nanoTiO2 is usually larger than 3.0 eV. The optical properties of nano-TiO2 enables it a good choice for UV protecting applications.

2.1.3 Photocatalytic applications

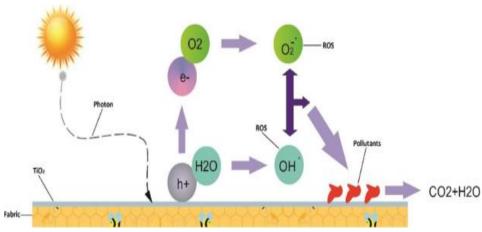
TiO2 is an environmentally benign and efficient material and extensively used in the photodegradation of numerous organic pollutants. Fujishima et al. described the mechanism of photocatalysis on surface of TiO2 and discussed its practical interest in water purification, self-cleaning, self-sterilizing surfaces, and light-assisted H2 production (Fujishima et al. 2008). Xiao et al. applied an inorganic TiO2/Al2O3 nanolayers onto dyed blend of polyamide/aramid fabric by atomic layer deposition process to develop multifunctional fabrics that exhibit resistance to UV light. The successful deposition of TiO2, Al2O3, and TiO2/Al2O3 nanolayers on the surface of fiber was confirmed by EDX. The nanolayer-coated fabric showed excellent UV-resistant properties under high-intensity UV light (Xiao et al. 2015). Gaminian and Montazer investigated the self-cleaning of Cu2O/TiO2 on polyester fabric for automotive and upholstery applications. The results confirmed that the developed fabric displayed significant photocatalytic efficiency during the photodegradation of MB for both washed and unwashed samples.



forms of anatase TiO2. Reprinted with permission from Hossain et al. (2015)). Copyright 2015, with permission from Elsevier

Ag and Fe3+ synergistically enhanced the photocatalytic performance of TiO2 for photodegradation of MB under both UV and visible light regions. The proposed photocatalytic mechanism of Fe3+:Ag/TiO2 is described in Fig. 19 (Harifi and Montazer 2014). Ghanem et al. described photocatalytic performance of hyperbranched PET/TiO2 nanocomposites. In a typical process, first TiO2 nanowires were synthesized in alkaline medium from TiO2 NPs by hydrothermal method which further hyperbranched with by polycondensation. The results summarized that the developed nanocomposites have extensively higher photocatalytic performance than the pure TiO2 nanowires and degradation time was also reduced to great extent (Ghanem et al. 2014). Arain et al. studied antimicrobial efficiency of cotton fabric treated with chitosan/AgCl-TiO2 colloid. In their study, they used diverse blend ratios of chitosan and AgCl–TiO2 colloid to obtain maximum antimicrobial efficiency against microorganisms. The results revealed that the AgCl-TiO2 colloid with chitosan provides much better antimicrobial properties to cotton fabric than the fabric treated without chitosan (Arain et al. 2013). Gupta et al. applied TiO2 and ZnO NPs on cotton fabric by using low amount of binder and studied the functional properties of the finished fabric. These results revealed that TiO2-coated cotton fabric exhibited significant self-cleaning efficiency on light exposure which could be improved by adding more amount of TiO2 NPs (Gupta et al. 2007). The mechanism of photocatalysis on surface of TiO2 deposited cotton fabric is presented in

Fig. 5 (Noman et al. 2018c). Zhou et al. investigated photocatalytic activity of iron-doped mesoporous TiO2 NPs prepared by sol-gel process against acetone. Their results explained that photocatalytic oxidation of acetone in air was significantly higher for iron-doped TiO2 NPs as compared to bare TiO2 and P25. Moreover, the doping of Fe in the mesoporous TiO2 powders reduces recombination rate of charge carriers during heterogeneous photocatalytic reaction (Zhou et al. 2005). El-Roz et al. prepared luffa/TiO2 nanocomposites from the hydrolysis of TiO2 precursor for photocatalytic applications. The photocatalytic performances of the developed nanocomposites were investigated against methanol. The results showed a good stability of luffa/TiO2 nanocomposites with enhanced photocatalytic performance under UV light irradiations, which provided a new class of green photocatalysts for photodegradation of organic pollutants (El-Roz et al. 2013). Doakhan et al. investigated the effect of TiO2/sericin nanocomposites on cotton fabric for enhanced antimicrobial properties. In a typical synthesis, sericin was extracted by boiling raw silk in hot water and then nano-TiO2 was dispersed in it which was further applied to cotton fabric with or without cross-linking agent by pad-dry-cure process. Antimicrobial property of modified cotton was estimated against gram-positive and gramnegative bacteria. The treated fabric showed more effective results against S. aureus than E. coli (Doakhan et al. 2013). Adnan and Moses developed UV-resistant fabrics by coating TiO2 on silk/lyocell union fabrics. The results showed that TiO2 as a UV finish significantly improve the UV absorbing activity of treated fabrics. Samples treated with TiO2 showed good fastness properties up to 25 washing cycles (Adnan and Moses 2013). Montazer et al. developed antimicrobial finish for wool fabric with silver-loaded nano-TiO2 under UV irradiations in an ultrasonic bath. The synthesized nanocomposite was stabilized on surface of wool by cross-linking with citric acid.



(Fig. 5) Photocatalytic process on the surface of CT nanocomposites. Reprinted with permission from Noman et al. (2018c)). Copyright 2018, with permission from Elsevier

2.1.4 Photovoltaic applications

The second most important use of TiO2 NMs is in photovoltaics applications. Gratzel discussed heterojunction variants involved in the fabrication of DSSC (dye-sensitized solar cell) and investigated the perspectives for future development in DSSC. He sum up that DSSC have become a credible alternative to conventional p-n junction semiconductor devices (Grätzel 2003). In another review, Gratzel investigated the phenomenon behind the harvesting of solar energy into electrical energy by using nanocrystalline TiO2 in DSSC. In a typical DSSC, a sensitizer is anchored on the surface of a semiconductor by which light is absorbed. At the interface, charge separation takes place from dye into the conduction band of semiconductor through photoinduced electron injection. Charge carriers are transported to the charge collector. Sensitizers with broader absorption band permits to harvest a large fraction of sunlight extended from UV to the near IR region. Perera et al. constructed a DSSC by depositing TiO2 nanofilms on conductive glass plates sensitized with different dyes. The results revealed that for all three dyes, heterojunction produces photovoltaic response to light absorption. This method extended the spectral response range and increased the efficiency of DSSC

(Perera et al. 2005). Wu et al. utilized hydrothermal method to fabricate hierarchical anatase nano-TiO2 comprised of ultra-thin nanosheets exposing high percentage (001) facets. The developed structures were utilized as a photoanode in QDSSC (quantum dot sensitized solar cells) with a power conversion efficiency of 3.47% (Wu et al. 2015). Xie et al. prepared an up-conversion luminescence electrode to fabricate DSSC by using TiO2 (Er3+, Yb3+) powder under hydrothermal conditions. The prepared powder converts infrared light into visible light which the dye can easily absorb with wavelengths of 510–700 nm, resulting in an increase in the photocurrent of the DSSC. Subramanian and Wang used TiO2 in a hierarchal multilayer-structured photoelectrode for DSSC and the comparison was made with Degussa P25. The results showed a superior performance for multilayer-structured photoelectrode as compared to other three electrodes. The improvement was attributed to higher dye adsorption, higher current conversion efficiency because of more fraction of light scattering, and good charge transportation (Subramanian and Wang 2014). Gomez et al. prepared highly efficient nanocrystalline DSSC by incorporating sensitizer into sputter deposited TiO2 films.

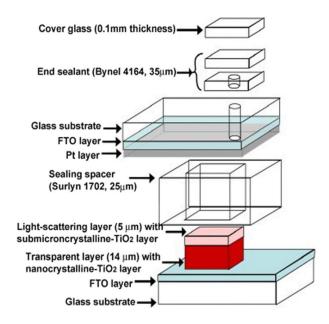


Fig. 6) Configuration of DSSC. Reprinted with permission from Ito et al. (2008)). Copyright 2008, with permission from Elsevier

3. Purification

Several strategies, such as coupling TiO2 tightly and incorporating other metallic components during synthesis, have increased the bandgap of TiO2 for visible light applications. Moreover, an overview of nanotechnology that could enhance the properties of TiO2-based catalysts in an environmentally friendly way to decompose pollutants is also presented. The various TiO2-based photocatalysts have wide applications in degrading recalcitrants.

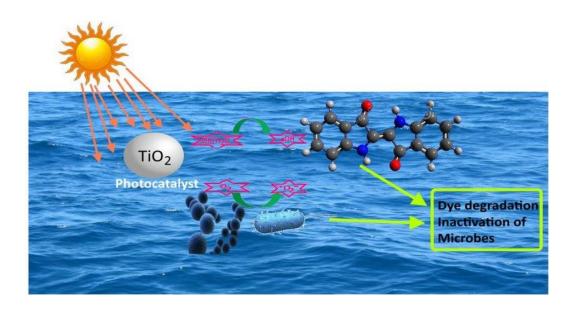


Fig. 7: The water disinfection process

4. Need of Supported Titanium Dioxide

To improve catalytic properties there is need to use supporting materials to overcome the limitations as reusability of the catalyst, increasing active hotspot of catalyst to increase their activity. The major limitation of TiO2, is unable use visible light spectrum for photocatalytic activity, therefore tuning or optimizing TiO2 into the visible light radiation is better route for increasing efficiency for the disinfection (Deshmukh et al., 2019). Some other routes have been performed such as doping, metallization, sensitization and supporting material. Moreover, supported metal nanoparticles have more efficiency for bacterial inactivation than other; therefore herein we reported TiO2 supported metal nanoparticles (Chen et al., 2010. Monite et al., 2015). To finalize, carbonaceous matters, clay and ceramics, polymers, and metal oxides can be used as supporting material for the TiO2

4.1 Polymers

Polymers are stable and inert in nature with the long life spans. The adsorption ability of TiO2, was improved due to polymer support with hydrophobic nature. Such nature of the polymer exhibits the effective support material for the photo catalysis process (Reddy et al., 2020). The polymer support is playing important role for recovery of catalyst and multiple use of photo catalyst. Among the various conducting polymers as polyaniline, poly-pyrrole, and polythiophene and their by-products were effective to shift of UV light to visible light spectrum to improve quantum efficiency of TiO2 photocatalyst. Polyaniline is photosensitizer and economical, stable and better electrical conducting ability (Tamboli et al., 2013). The polyaniline/titanium dioxide nanocomposites reduces bacterial growth of E. coli pathogenic organism and elective for the dye degradation also (Jeong et al., 2014).

4.2 Clays

Clays are phyllosilicates; compounds with a structure in which silicate tetrahedrons. They are earthy material that is sticky and easily molded when wet and hard when baked. Clay have astonishing properties as surface activity, better adsorption ability ,cation exchange, swelling and biocompatibility which provides them as alternative material for wide range of applications. Clay minerals are rich in environment and case to modify to increase efficiency for water disinfection (Mishra et al., 2018). The proper mixing of clay and photocatalytic materials as TiO2, may improve efficiency pave the way towards the better material for removal or toxic chemicals and pathogens from the water and act as active water disinfectant. TiO2_pillared clays with spongy structure were prepared through combining TiO2 nano-sol elements into the clays. It exhibits better photocatalytic activity against the methyl orange in the presence of UV radiation (Yang et al., 2015). Figure 8 shows the well-ordered TiO2 pillar clay.

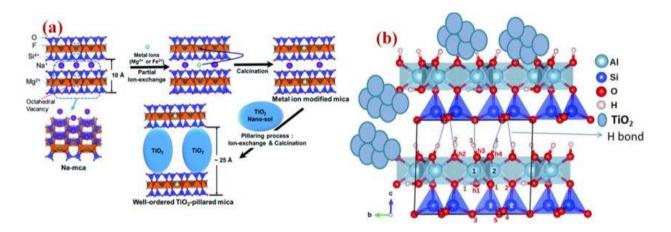


Fig. 8: Synthesis of well-ordered TiO2 pillared clay

4.3 Carbonaceous materials

Mentioning an additional class of the materials useful for their supporting actions due to their admirable properties is carbonaceous materials. Additionally, carbonaceous materials are consisting of carbon nanotubes, activated carbon, graphene and graphitic carbon nitride. Carbon based materials are efficient for adsorption of the pollutants or other contaminated chemicals in the water: it is also enhances the active surface of the catalyst and act as effective photocatalyst (Sakthivel and Kisch 2003). Several researchers are reported that quantum efficiency of TiO2 may be increased using carbonaceous materials in the visible spectrum as associated to pure TiO2, it is because of chemical linkage between them (Silva et al.. 2020). Carbon-supported TiO2 was prepared using hydrothermal route to study its adsorption ability and photocatalytic activity against phenol, naphthol blue black and reactive black in the presence of UV radiation (Nguyen et al., 2020).

4.4 Metal oxides

The crystalline nature, better optical properties and without mixed phases were the key properties for competent photocatalytic activity in the visible light radiation (Hunge er al. 2018a-b) Mahlambi et al. (2015) reported the recent development in TiO2 nano catalysts were playing major role for environmental remediation as removal of the

pollutant from the water bodies. Shi et al. (2018) reported recyclable light and heat assisted route for removal of the pollutant from the wastewater system. The TiO2, supported on Fe3O4 nanoparticles was revealed the enhanced proficiency for Rhodamine B dye degradation in the wastewater treatment.

5. Photocatalytic disinfection mechanism

Disinfection for water is a huge step to attain purification; as disinfection is the elimination of pollutants and contaminants in order to purify. Matsunaga et al. (1985) have been the first to demonstrate an inactivation process induced with a light and proposed that coenzyme A degradation by ROS generated during the reaction was the most probable mechanism of antibacterial action. The enzyme denaturation caused the stop of respiration activity, what led to final death of the cell (Matsunaga et al. 1985). Further research, however, has shown that a cell's death is caused by the damage of cellular wall or cellular membrane. The leakage of potassium ions followed by the flow of intercellular substances such as RNA and proteins leads to complete destruction of cells, what has been confirmed by transmission electron microscopy (TEM) images (Saito et al. 1992). The progress in investigations of photocatalytic disinfection mechanism leads to understanding and description of the most probable mechanism of cellular wall damage. ROS are crucial in the destruction microorganisms using semi-conductive materials and UV radiation, whereas the strongest effect is assigned to hydroxyl radicals (*OH) (Ganguly et al. 2018, Bogdan et al. 2014).

The inactivating properties of hydroxyl radicals lie in high oxidation potential and non-specific reactivity (Reddy et al. 2007). Photocatalytic mechanism, which leads to antimicrobial effect, starts with the destruction of cellular wall membrane, what results in leakage in intracellular substances such as RNA and proteins, followed by complete cell destruction and death (Doong et al. 2017). The leaked material is oxidized at photocatalytic sites of a semiconductor. It has been found, however, that the presence of extracellular polymeric substance (EPS) may lead to the decrease of antibacterial activity due to its competition toward ROS. Hence, it is important to remove EPS from the reaction environment in order to obtain desired disinfection effect (Davididou et al. 2017).

5.1 Photocatalytic purification with titanium dioxide

Antibacterial effect of nano catalysis depends on the activity and concentration of the photocatalyst, size of its particles, presence of other environmental contaminants, initial concentration of microorganisms, solution pH and temperature as well as light intensity (Friedmann et al. 2010). Maness et al. (1999) have shown that the highest photocatalytic activity, and hence the strongest antimicrobial effect, is revealed by two polymorphic nano-TiO2 forms – anatase and rutile, which are mixed at the ratio of 4:1 (trade name P25), and commonly used in research on disinfection properties of nano-TiO2.). Etacheri et al. (2010, 2013) have found that hetero-bonds between anatase and brookite TiO2 forms doped with carbon at the ratio of 80/20 assure sufficient inactivation of S. aureus under visible light radiation. The significant narrowing of bandgap is in this case caused by additional energy levels formed by carbonates, what results in excellent photocatalytic and antibacterial activity. Rincon and Pulgarin (2003) have stated that nano-TiO2 of diameter below 20 nm reveals better antibacterial properties than its less powdered form, because particles of diameter < 20 nm are able to penetrate cellular wall and permeate to cytosol (Desai and Kowshlik 2009), whereas TiO2 nanoparticles of size 20–80 nm are not able to pass through the wall (Wong et al. 2006). Other research studies indicate that photocatalytic effect of nano-TiO2 is also related with high microorganisms concentration (above 108 CFU/mL) (Maness et al. 1999). Upon using TiO2 in powdered form, there will be a major disadvantage, which is the separation of nanoparticles from treated stream. In order to minimize this effect, the efficient antibacterial activity is obtained by immobilization of nanoparticles on relevant supports (Liu et al. 2008). Second solution is the application of the TiO2 nanotubes (NTs). NTs structure is one of the most promising morphologies for antimicrobial applications due to a range of desired features, such as high aspect ratio, enlarged specific surface area and improved light harvesting and absorption (Byrne et al. 2018,

Podporska-Carroll et al. 2015, Garvey et al. 2016). The obtained, highly porous nanotubes can be directly involved in antimicrobial applications. Antibacterial properties investigations of TiO2 nanotubes using E. coli and S. Aureus have been found highly efficient to inactivate both examined species, at removal rates obtained during 24 hours UV radiation amounted to 97.53 and 99.94% for E. coli and S. aureus, respectively (Podporska-Carroll et al. 2015). Research on inactivation of E. coli, P. aeruginosa and S. aureus of TiO2 nanotubes has also been performed (Garvey et al. 2016). Wang, et al. (2021) have developed a UV-assisted electrochemical oxidation (UV-EO) process that employs blue TiO₂ nanotube arrays (BNTAs) as photoanodes. Studies have shown that the increase of calcination temperature and rutile content in TiO2 NTs results in poorer purification effect. The photocatalyst, which has contained the highest percentage share of rutile and has been calcined at 800°C has been the least toxic to microorganisms. In regard to temperature, it has been also shown that NTs calcined at 600 and 800°C are not able to reach the inactivation coefficient higher than 1 log10 (Garvey et al. 2016). On the other hand, non-calcined NTs or ones calcined at 200°C show high inactivation rate up to 2.7 log10 (Garvey et al. 2016).

6. Methods of improving the performance of TiO2 photocatalysis:

The researchres are continuously trying to improve the structural, electronic and photocatalytic characteristics of TiO2 for its efficient use in pollutant degradation. There are various methods mentioned in the literature which have been utilized to improve the performance of TiO2 photocatalysis. A brief review of those methods is summarized below.

6.1. Morphological aspects:

A large surface area can be determining factor in certain photodegradation reactions, as a large amount of adsorbed molecules promotes the reaction rate. However, powders with large surface area are usually associated with low crystallinity and large number of crystalline defects, which favour the recombination of electrons and holes leading to a poor photoactivity. A balance between surface area and crystallinity must be found in order to obtain the highest photoactivity. Particle size is an important parameter for photocatalytic efficiency, since the predominant way of electron/hole recombination may be different depending on the particle size (Zhang et al (1998)). It is well known that in the nanometer-size range, physical and chemical properties of titania are modified. Small variations in particle diameters lead to great modifications in the surface/bulk ratio, thus modifying the significance of electron-hole recombination. When the crystallite dimension of a semiconductor particle falls below a critical radius of approximately 10 nm, the photoactivity decreases because of enhancement in recombination rate of electrons and holes.

6.2 Doping:

When a small amount of a noble metal is doped into the TiO2, the electrons and holes produced by the light irradiation are retained on the noble metal and TiO2 semiconductor, respectively because the noble metal trap the electrons, which limit the recombination of the electrons and photo holes, and thus improve the reactivity of the photo catalyst. However, through this approach, the large band gap of TiO2 is not significantly reduced. Doping of TiO2 with precious metal (Pt), metal oxides such as ZnO, Fe2O3 and inorganic components such as N for extended visible light activities has been successfully conducted (Chen et a. (1999)). A recent preliminary investigation by a team of researchers revealed a significant enhancement of visible light activity (up to 60-70% absorbance) by doping a combination of N and C or silver into TiO2 in a nano sol-gel system. Many researchers had already reported that photo catalysts with visible light activity have only achieved light absorbance at < 30%. Doping of TiO2 with various metal ions may improve its photoactivity because of enhancement in light absorption capability, adsorption capacity, and interfacial charge transfer rate (Carp et al. (2004)).

6.3 Metal coating:

If the redox potential of the metal is higher than that of TiO2, electrons are removed from the TiO2 particles in the vicinity of each metal particle. This results in decrease in electron/hole recombination, as well as to an efficient charge separation (Hu et al. 2003)). As a consequence of the improved separation of electrons and holes, metal deposition on the TiO2 surface enhances photocatalytic reactions by accelerating the transfer of electrons to dissolved O2. Photo deposition is the most commonly used technique in obtaining metal deposits on TiO2 and involves the reduction of metal ions by CB electrons, while the anodic process is represented by the oxidation of water by VB holes. The deposition of metals can be either beneficial or detrimental for photocatalytic degradation in aqueous solution, depending on an amount of loaded metal, chemical nature of the pollutant, and chemical nature of the metal (Alfano et al. (2000)).

7. Conclusion

Photocatalysis by nanoparticles of titanium dioxide has been widely studied on lab scale by the researchers for decontamination of drinking water. One of the major advantages of this technology lies in its capability to completely mineralize the pollutants into harmless compounds (carbon dioxide, water and mineral acids) without producing any other waste streams in addition to the inactivation of pathogens including protozoa and viruses. A lot of work has been done to improve the performance of titanium dioxide photocatalysis. Despite the many advantages of titanium dioxide photocatalysis and extensive lab research done in this field, there has been very little work done for commercial or industrial use of this technology so far. The major reason for the same is lack of modeling & simulation tools, and scale-up strategies for the development of this technology for commercial use. Commercialization of photocatalysis technology for water purification is the focus of research these days. An overview has been presented in the present chapter on the conceptual as well as state-of-art aspects of titanium dioxide photocatalysis. The potential applications of this technology, for drinking water purification, strongly depend on the future development of the photocatalytic engineering.

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حکومهتی ههریمی کوردستان عیراق وهزارهتی خویندنی بالای تویژینه وهی زانستی زانکوی سه لاحه دین ههولیر کولیژی زانست کولیژی زانست بهشی کیمیا



رووناكچالاكى به تيتانيوم دايۆكسايد بۆ پاككردنهوهى ئاوى خواردنهوه

پرۆژەى دەرچوونە پۆشكەشە بە بەشى كىميايى كۆلنژى زانست زانكۆى سەلاحەدىن-ھەوللار وەك بەشلاك لە پنداويستىيەكانى بەدەستەينانى بروانامەى بەكالۆريۆس لە زانستى كىميادا

ئامادهکراوه لهلایهن:
علی هاشم رهزاق
به سهرپهرشتی:
د, رووپاك ئهحمهد شیخ موحهمهد