Chapter

Nano TiO_2-Based Smart Superhydrophilic Self-Cleaning Surfaces

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Abstract

In this chapter, we have focused on the use of self-cleaning coating or surfaces which have more concerning the field of research due to the rising demand for self-disinfected and hygienic surfaces. Self-cleaning coatings can be used in automobile windshields, textiles, antifouling membranes, paints, building construction material, optoelectronic devices like solar panels, and in the medical aids and food industry. This chapter gives an outlook on nano TiO2-based superhydrophilic self-cleaning surfaces. The mechanism of superhydrophilicity of nano TiO_2-based systems and photocatalytic properties are cautiously investigated. The photocatalytic behavior and superhydrophilicity of TiO_2 are based on the photogenerated electron–hole pair. This chapter gives a general idea of a variety of systems and methods that could improve the self-cleaning behavior of TiO_2 in the solar spectrum in view of the fact that TiO_2 is only ultraviolet responsive. Evidences have indicated that the superhydrophilic wetting and antifogging performance are affected by porosity and surface hydroxyl (-OH) contents. In this chapter, the effect of multilayer assembly and the role of cumulative concentration of –OH groups on photocatalytic behavior is also discussed.

Keywords: TiO_2, semiconductors, heterojunctions, self-cleaning, hydroxyl group, photocatalytic activity

1. Introduction

The discovery of photoinduced superhydrophilic behavior of Titanium dioxide (TiO_2) so that it is considered as most promising photo-responsive wetting material (Wang et al. in 1997) [1]. TiO_2 is a semiconductor, on excitation of titanium with suitable light energy, the photocatalysis process takes place on the surface so that organic dirt molecules adsorbed on the surface and decomposed with the process of photocatalysis. Photocatalysis is followed by the washing of surface with flow of water and finally surface will be clean and sterilized. TiO_2 an extensively acceptable applicant for superhydrophilic self-cleaning surfaces and coatings due to its superior optoelectronic properties, photostability, low-cost production, nontoxicity, and environmental friendliness. The structural and surface properties and also intrinsic electronic characteristics of titanium dioxide are responsible for its photocatalytic efficiency and photo-induced wettability and consequently its self-cleaning property. In recent times, the research has shown the most interest in field of the development and commercialization of self-cleaning coatings and surfaces with the properties of antireflective, antifouling, and antifogging. Self-cleaning coatings and surfaces have potential applications in major sectors such as the medical industry (especially medical aids with anti-microbial surfaces), food industry, optical industry (lenses, camera, and sensors), marine industry (corrosion protection), aircraft industry, construction industry (cement & paint), automobile industry, etc. In this review article, we give a significant evaluation of the superhydrophilic self-cleaning materials and surfaces, environmental applications, and sustainability. In this chapter, we introduce the concept of superhydrophilicity and self-cleaning action of TiO_2 as a photocatalyst and later water treatment mechanism of such systems. This review emphasizes the potential applications and practical challenges of self-cleaning surfaces and coatings in real-life situations.

2. Self-cleaning action of TiO_2 as photocatalyst

Once a metal oxide semiconductor is irradiated with an energy source that is higher than its band gap (3.2 eV) [2] leads to the absorption of photons and excitation of an electron (e−) in which way generate an electron–hole pair, with the hole (h+) left behind in the valence band. These electron–hole pair in turn undergoes recombination and non-radiatively emits the excess energy in the form of heat or light [3, 4]. This recombination process or charge obliteration reduces the efficiency of TiO_2 photocatalytic activity. Due to crystal defects and impurities present on the surface of TiO_2 this reaction would take place on the surface or within the bulk of TiO_2. Over the surface of TiO_2 excitons (electron–hole pair) were undergoes recombination, this electron–hole pair can combine with the adsorbed molecules and leads to the decomposition of organic volatile compounds. Evidently, electrons in the CB reacts with the oxygen molecules present on the surface and reduces it into superoxide radicals which can react with water to give hydroxyl radicals (% OH); on the other hand holes (h+) in the valence band reacts with water to form %OH radicals. These oxygen-generated species decompose the volatile organic compounds into CO_2 and H_2O on the catalytic surface by the process of free radical mechanism [5–8].

Thus the mechanism of superhydrophilicity on the catalytic surface can be explained by the combination of two processes. The first mechanism of superhydrophilicity includes the surface hydroxylation upon photoexcitation. This step consists of two steps (a) oxygen vacancy generation and (b) reconstruction of photoinduced Ti-OH bonds. The mechanism of superhydrophilicity propagates by the formation of photoinduced electrons in the system by the reduction of metal centers. For example, TiO2 (IV) gets reduced into TiO_2 (III) by the movement of conduction band electrons, however, the holes formed in the valence band oxidized into O_2^- anions, and thus vacancies are formed by the ejection of oxygen atoms. The hydroxyl anions are formed at these vacancies during the photocatalytic mechanism and water molecules get absorbed, leading to the hydrophilic nature of the surface [9]. Sakai et al. proposed that for the superhydrophilic characteristics of a surface photoinduced holes are more important than electrons, these holes can diffuse on the surface of catalyst and get trapped at the oxygen lattice because these photo-induced holes can diffuse on the surface and get trapped at the lattice oxygen sites, this leads to the formation of new hydroxyl bonds with the adsorbed water molecules [10].

2.1 Photoinduced hydrophilicity

Furthermore, it is evident that the hydrophilic conversion rate of TiO_2 can be increased by applying high positive electrode potential, and can be decreased by the usage of hole-scavengers in the photocatalytic reaction [11]. This interpretation suggests that for the hydrophilic conversion of the photocatalytic material, the diffusion of holes to the catalytic surface is very essential. The formation of Ti-OH bands on the TiO_2 surface is attributed to photoinduced hydrophilicity [12]. The diffusion of holes to the catalytic surface can weaken the Ti-O bonds, and water molecules adsorption to this surface can then break the weakened bond. This will lead to the charge separation and the formation of a new OH bond on the surface. Therefore one OH group which is doubly coordinated to Ti atoms converted into two OH groups. It is revealed that the highly amphiphilic catalytic surface of TiO_2 can leads to the reconversion of the surface wettability, which is due to the deposition of a hydroxyl group from the surface. The second mechanism of photocatalytic activity on the surface initiates the decomposition of the adsorbed pollutants on the surface which initiates by the absorption of UV light and thus reduced the organic pollutants on the surface. It has been recommended that in addition to the photocatalytic degradation of organic pollutants on a TiO_2 surface, desorption of water molecules on the surface is also initiated by UV irradiation. The subsequent breakdown in the H-bonded network is supposed to be essential for the hydrophilic conversion [13]. The results reveal that the photocatalytic activity on the surface is not an exclusive requirement for any surface to be hydrophilic or superhydrophjilic. It has been reported that many metal oxides such as vanadium oxide and tungsten oxide have superhydrophilic nature under UV light illumination without and photocatalytic activity mechanism on their surface. In consequence, it has been suggested that a combination of various mechanisms is required to explain the photoinduced hydrophilicity or photocatalytic activity on the surface. The combination of photoinduced hydrophilicity and photocatalytic activity are the major requirements to degrade the organic pollutants, and light-induced superhydrophilicity to sheet water for cleaning the surface by washing off the degraded pollutants, good optical transparency, photostability, and durability.

3. Water treatment

In recent times due to the ever-increasing urbanization and industrialization, the world is facing freshwater disaster. Heavy metal ions and organic pollutants cause foremost severe threats to aquatic life. Industrial and conventional treatment methods such as oxidation, biodegradation, absorption, coagulation, etc. have been used for water purification. Membrane technology is the most commonly used technique for water treatment due to its green and environment-friendly approach. However, membrane technology has faced a major problem of fouling of membranes due to prolonged use of technique. In this line of research, increasing the hydrophilicity of the membrane is considered an effective way to reduce the fouling behavior of the membrane which is caused by pore blocking and fouling material adhesion [14, 15]. By using this method of increasing hydrophilicity of membrane, the hydrophilic material also imparts water permeability stiffness and strength to the polymeric matric used for the preparation of these membranes. The introduction of TiO_2 in the membranes as hydrophilic photocatalytic materials can add self-cleaning behavior to the membrane, which upon photoexcitation degrades the natural organic volatile compounds adhered at the surface of the membrane or pores. It is also commonly seen that during the process of phase separation, TiO_2 particles have been settled down into the bottom of the polymeric bulk due to its high density. However, when TiO_2 nanoparticles hybridized with magnetic nanoparticles, the photocatalytic TiO_2 nanoparticles can be adhered to the surface of the polymer matrix with the help of an external magnetic field [16]. Oil–water separation is an effective technique to demonstrate the interplay of membranes between antifouling and wettability. The oil–water separation technique is very effective to clean offshores oil spills and discharging oil effluents which are very harmful for aquatic life and biotic environment. Another very helpful technique for oil–water separation of molecular sieving technique which allows only water molecules hence block the larger oil droplets, this technique has been worked under a specific applied pressure, hydrophilicity, and selective wettability. Porous materials such as metal meshes, fibers foams, and textiles can be used in addition to polymers and ceramics for oil–water separation. The major difficulty faced in the oil–water separation technique is rapid decline of water permeation due to the clogging of pores by oil droplets, therefore, lowering the filtration flux [17]. Also, significant fouling will occur over the surface of membrane due to the presence of hydroxide groups. A thin layer of TiO_2 has been used for the removal of fouling over the surface of the membrane [18, 19]. In recent times, cellulose acetate nanofiber membrane was fabricated by electro-spinning which is oleophobic in water, superhydrophjilic in oil, and superamphiphilic in air [13]. This membrane can be working for oil/water separation in wastewater treatment; also it has been used for oil/water emulsions and oil/corrosive medium. An interesting Janus membrane is fabricated by in situ growth of TiO_2 on poly (phenylene sulfide) membrane with F-TiO_2@poly (phenylene sulfide) followed by water–oil interfacial grafting in presence of perfluorodecyltriethoxysilane [20].

In addition to environmental remediation such as offshore spills, such multifunctional membranes find great applications in food industry, textile factories, and other chemical plants.

4. Antireflective coatings

High transmittance characteristics of antireflective coatings have great significance in high-performance devices along with the property of transmittance such as flat panel display, solar panels, lenses, telescope, etc. TiO_2 causes a high refractive index and refraction when it is applied to the transparent glass substrate. A very low concentration of TiO_2 in the self-cleaning coatings reduces the photocatalytic activity but at the same time minimized the surface refraction. Therefore for the practical application of self-cleaning coating there should be between balance antifogging and anti-reflective properties of the self-cleaning coating. Preparation of TiO_2 composite with SiO_2 adopted to have self-cleaning anti-reflective properties with a high refractive index. A hierarchical macro-mesoporous SiO_2 thin film with very high porosity showed a significant broadband anti-reflection with an average reflectance of 3.45%

in the wavelength range from 350 nm to 1200 nm [21] The macroporoporous template is superior to the conventional flat SiO_2/TiO_2 composite film.

The sandpaper abrasion test results show that the porous composite film was superhydrophilic with a water contact angle of 2.4° and this contact angle was retained even after 50 cycles of the abrasion test. Raspberry-like core-shell nanoparticles of SiO_2/TiO_2 were synthesized by a sol–gel single pot method. These synthesized SiO_2/TiO_2 core-shell nanoparticles were then fabricated onto glass by layer-by-layer self-assembly dip coating technique. The prepared coating exhibited superhydrophilicity both in the presence and absence of UV irradiation [22]. The SiO_2 particle with the size in the range of sub-micron provides a porous structure and anti-reflective property to the self-cleaning coating. However, the larger surface area of nanoparticles and higher surface roughness in the coating are the main factors in imparting its superhydrophilic property. An example of a high antireflective self-cleaning coating is $Ag/TiO_2/Si$ forest-like hierarchical nano/microstructures like a moth-eye. This type of coating shows solar-weighted reflectance values of 3.5% and 3.3%, respectively, over the wavelength range of 300 – 1000 nm [23]. The estimated contact angle over the surface was <5° which exhibits outstanding anti-fogging and self-cleaning properties by the use of plasmonic silver nanoparticles [24]. The self-cleaning coating also shows photocatalytic dye degradation and self-cleaning under UV–vis light irradiation. Along with these combinations, several researchers have developed double-layered and multilayered TiO_2-SiO_2 films with reduced reflectance [25, 26]. Three-dimensional TiO_2 nanostructures such as nanopores, nanorods, and hierarchical structures with larger surface area have been reported with reduced surface reflectance losses but with enhanced photocatalytic activity [27, 28]. TiO_2 can also be used as a protective layer for thermochromic self-cleaning coating in Vanadium (IV) oxide (VO_2). Vanadium oxide VO_2 is a unique material practically used for thermochromic applications due to its large optical and electronic behavior and because first-order phase transitions from monoclinic to tetragonal geometry [29, 30]. A multifunctional transparent $VO_2/SiO_2/TiO_2$ thin film showed considerable improvement in visible light transmittance which is accompanied by thermochromic and self-cleaning properties. Therefore, these coatings can be applied for energy-efficient, intelligent window applications [31]. TiO_2/VO_2 bilayer composite coating is also capable of supporting the TiO_2 for increasing air purification by absorbing Infrared rays.

4.1 Coatings for building materials

Self-cleaning coatings are the probable substitute for high energy consumption. TiO_2-coated self-cleaning surfaces has been used in construction material such as in cement, tiles, limestone, glass can behold their artistic appearance without contamination or getting dirt throughout their lifetime [32–38]. A number of esthetic images and buildings reported preserving with the help of TiO_2 as a photocatalytic material [39–42]. Sedimentation methods and spray coating methods are usually used for the building materials. According to the report by n-Tech Research in 2015 the self-cleaning market is expected to reach a market of US $3.3 billion by 2020. Pilkington has been marked as the first commercially available coating over the glass. Additionally, these self-cleaning coatings should withstanding varying climatic changes to the outdoor environments. During the development of self-cleaning coatings, a number of weather variables like light, temperature, humidity, etc. should be considered [39–42]. Humidity plays a very important role in stain removal, by influencing the hydration state of TiO_2 this will increase the cumulative hydroxyl ion concentration that will lead to sustainable self-cleaning materials for buildings [43–50].

5. Future outlook and conclusion

This chapter gives emphasis on the specific idea of TiO2-based self-cleaning surfaces. Self-cleaning surfaces cover a significant research area in this era of fast urbanization and industrialization. Also, self-cleaning surfaces are an answer for cleaning contaminated surfaces to compromise large energy consumption. The chapter gives a brief about the outstanding examples of TiO_2 composites for water purification techniques such as TiO_2 hybrid composite with grapheme, Heterojunction of TiO_2 with some other metals, dye-sensitized TiO_2, etc. Applications of TiO_2 and TiO_2 composite materials or hybrids as a superhydrophilic photocatalysts in water purifying membranes, antibacterial surfaces, fabrics, oil–water separation techniques, and in antireflective coatings are discussed in detail. Superhydrophilicity mechanism in semiconductor metal oxides is investigated from different models. Although in this field, there is great progress in the development and fabrication of self-cleaning coatings and surfaces, however, there are still some technical problems and challenges with self-cleaning coatings that will cause bridging the gap between industry and fundamental research.

Mechanical durability and chemical stability are the major concern for the fabrication of self-cleaning coatings. Exposure of these coatings to solvents and outdoor temperature differences can lead to the detachment of the material from the surface of the coating due to which there will be a gradual decline in the performance of coatings. However, the surfaces which are responsive to indoor light sources are more durable and persistent with superhydrophilicity because photoinduced wettability recovers the hydrophobic nature of coating in the dark within minutes to hours. As a result, self-cleaning coatings should be designed in such a way that they should have anti-bacterial, antifogging, and antireflective properties and have good adherence to different surfaces like mirror, ceramic, and furniture. A significant emerging class of self–cleaning coatings and surfaces responds to various external stimuli such as changes in temperature, pH, chemical environment, stress, and humidity. The most recent study also predicts that this field has a promising trend in developing self-cleaning surfaces which has a combination of self-cleaning and photocatalytic properties in this way a single surface find a wide variety of application. Coatings with a combination of anti-bacterial, anti-fogging, and anti-reflective properties can find application in endoscopic surgery examples. The self he antireflective and antifogging can make them more appealing to building materials, solar panels, automobile windshields, etc. under inconsiderate environmental conditions.

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