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Review on: Titanium Dioxide Applications

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Abstract

Titanium dioxides (TiO_2) have been widely studied, due to its interesting general properties in a wide range of fields including catalysis, photocatalysis, and antibacterial agents and in civil as nano-paint (self-cleaning) that affect the quality of life. Therefore, TiO_2 and doped with noble metal are good candidates in the performance these applications. The fascinating physical and chemical features of TiO_2 depend on the crystal phase, size and shape of particles. For example, varying phases of crystalline TiO_2 have different band gaps that rutile TiO_2 of 3.0 eV and anatase TiO_2 of 3.2 eV, determine the photocatalytic performance of TiO_2. This chapter explains some applications and theoretical concepts of nanostructure of TiO_2 nanoparticles. Also, it demonstrates electrical, optical and morphological properties which make TiO_2 preferable for environmental applications.

Keywords: TiO_2, Anatase, Rutile, TEM, paint, self-cleaing, photocatalysis

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1. Introduction

Titanium dioxide, also known as titanium(IV) oxide or titania also known as Titania belongs to the family of transition metal oxides, is the naturally occurring oxide of titanium, chemical formula TiO_2 [1].

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TiO_2 is a white color found in all kinds of paints, printing ink, plastics, paper, synthetic fibers, rubber, condensers, painting colors and crayons, ceramics, electronic components along with food and cosmetics [2]. When used as a pigment, it is called titanium white, Pigment White 6, or CI 77891. TiO_2 exists naturally in three crystalline forms; anatase, rutile and brookite [3]. The great efforts devoted to the research on TiO_2 material produced many promising uses in areas which range from photovoltaics and photocatalysis to photo-electrochromics and sensors[4]. These uses can be generally classified into "energy" and "environmental" types, many of types rely not only on the properties of the TiO_2 material itself but also on the changes in the TiO_2 material host (e.g., with inorganic and organic dyes) as shown in (Fig. 1) .

Fig. 1. Applications of TiO_2.

The exponential growth of research activities has been seen in nanoscience and nanotechnology in the past decades [5, 6]. New physical and chemical properties come out when the size of the material becomes smaller down to the nanometer scale. Properties also differ in terms of the shapes in the shrinking nano-materials change among the unique properties of nanomaterials, the motion of electrons and holes in semiconductor nano-materials is primarily controlled by the common quantum confinement and the transport properties connected with phonons and photons are largely influenced by the size and geometry of the crease by a considerable amount with drop in the a material size [7]. The surface area of small particle size is helpful to many devices which are based on TiO_2, making easy interaction between the devices and the interactive media, which chiefly \happen on the surface or at the interfaces and depends by a considerable amount on the material surface [8]. Therefore, TiO_2 is one of the most popular commercially available nano-size materials that has found application in a variety of fields due to its wide availability, biocompatibility,low cost and non-toxicity and high chemical stability[9].

1.1. Mechanism of TiO_2 as Photocatalysis

Photo-catalysis is the composing of photochemistry and catalysis with both light and a catalyst being desired to onset or precipitate a chemical conversion [10]. The photo-catalytic process starts with the absorption of electromagnetic radiation, which excites an electron from the valence band to the conduction band, leaving a hole in the valence band. (Fig. 2) is a schematic representation of this process. In this process UV light irradiation is used by photon energy equal to or greater than TiO_2 band gap energy ($h\nu \geq 3.20$ eV at $\lambda \leq 380$ nm); electron-hole pairs (The charge carrier) are generated [11]. The negatively charged electron moves from the valance band (VB) to the conduction band (CB) leaving behind the positively charged hole. Then, the electron and hole take part in reduction oxidation reactions with species that are adsorbed on the surface of TiO_2, such as water, hydroxide (OH^-) ions, organic compounds or oxygen. The valence band hole (h^+) is highly oxidizing while the conduction band electron (e^-) is highly reducing [12]. The charge carrier h+ oxidizes H_2O or OH^- ion to the hydroxyl radical ($OH^\bullet$) that is a highly potent, non-selective oxidant. It easily attacks pollutants adsorbed at the surface of titanium dioxide or in aqueous solution degrading them to H_2O and CO_2 [13]. On the conduction band (CB) the electron reduces adsorbed oxygen (O_2) species to superoxide ($O_2^\bullet$), then undergoes a series of reactions to give the $OH^\bullet$ radical. The reaction of these radicals with organic substance, environmental pollutants or harmful microorganisms results in the decomposition of the latter [14].

In a case where the above discussed processes do not occur, recombination of the charge carriers results and energy is released in the form of heat. This causes great reduction in TiO_2 photocatalysis efficiency [15, 16]. Electron-hole recombination is reaction competing with hole-donor and electron-acceptor electron-transfer reactions. Recombination can occur either in the semiconductor bulk or at the surface resulting in the release of heat (or light) and is detrimental for the photocatalytic activity as the redox properties of the semiconductor are quenched [17,18 , 19] .

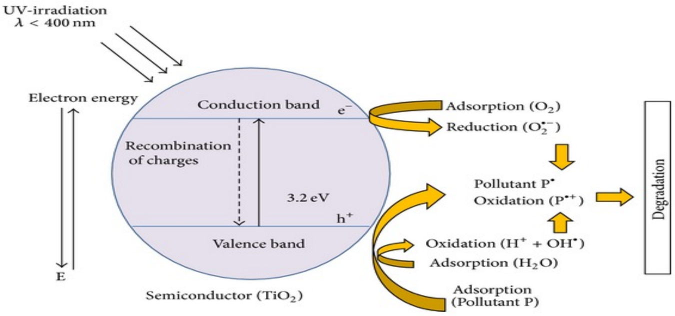


Fig. 2. Principal photo-catalytic process in the TiO_2 particles.

The photocatalysis performances are affected by several parameters such as mass/concentration, light intensity, wavelength, pH, and temperature, the nature of a photocatalyst, Particle Size, Surface area, the adsorption nature and concentration of the substrate [20, 21]. There are many fields of applications for TiO_2 nanoparticles due to perfect properties included air purification, water purification, decontamination, antibacterial, tooth paste, UV protection, photocatalysis, sensing and paint application, (Fig. 3) shows many TiO_2 applications in this chapter focuses on some of these applications due to its impotence in our daily live [22, 23]

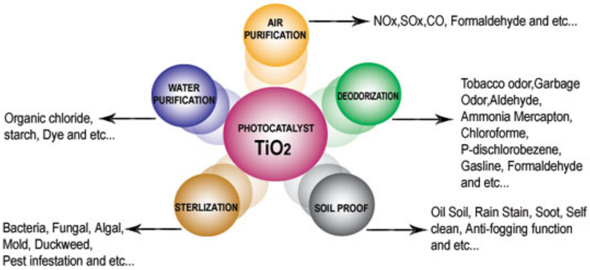


Fig. 3. Applications fields of TiO_2 NPs [2]

Some approaches have been carried out, including improving the TiO_2 surface by hydrophilic polymer dispersants such as polyethylene glycol with local paint [2]. Better surface appearance, perfect chemical resistance, reduce in permeability to corrosive environment and hence better corrosion properties, optical clarity, increase in modulus and thermally stable, simple to clean surface, anti-skid, anti-fogging, anti-fouling and anti-graffiti characteristics, perfect thermal and electrical conductivity, perfect retention of gloss and other mechanical characteristics such as scratch resistance, anti-reflective in nature, chromate and lead free, good adherence on various type of materials. Nano-coating can be related with self- cleaning painting, as shown in (Fig. 4).

Fig. 4. Self -cleaning TiO_2 coated high building [2]

Table 1. Overview of different photocatalysis applications

Self-cleaning	Material for residential and office buildings	Exterior tiles, kitchen and bathroom components, interior furnishings, plastic surfaces, building stones
	Indoor and outdoor lamps and related systems	Translucent paper for indoor lamp covers, coatings on fluorescent lamps and highway tunnel lamp cover glass
	Materials for roads	Tunnel wall, soundproofed wall, traffic signs and reflectors
	Others	Tent material, clothes for hospital garments and uniforms and spray coating for cars
Air-cleaning	Indoor air cleaners	Room air cleaner, photocatalyst-equipped air conditioners and interior air cleaner for factories
	Outdoor air purifiers	Concrete for highways, roadways and footpaths, tunnel walls, soundproofed walls and building
Water disinfection	Drinking water	purification river water, groundwater, lakes and water storage tanks
	Others	Fish feeding tanks, drainage water and industrial wastewater
Antitumor activity	Cancer therapy	Endoscopic-like instruments
Self-sterilizing	Hospital Tiles	to cover the floor and walls of operating rooms, silicone rubber for medical catheters and hospital garments and uniforms

1.2. Self- Cleaning Coating

A self-cleaning technology coating has improved vastly in last few years. As a commercial product, their potential is numerous and their market truly global. Due to the extensive range applications which possible, from glass window and textiles to cement, self-cleaning coatings may become an important labour- saving device. Already some of this potential is being realized: self-cleaning paint is currently available in Europe [24], in the past few years self-cleaning windows have made an effective, with several national glazing companies releasing products [25]. The capability of a surface to clean itself is charming in terms of cost, maintenance, and the environment; all three of which are correlating. There is a cost related with cleaning solvents, and a time cost in scrubbing roofs, along with a replace cost from solvent use. Elimination these costs not only advantages an unique, but also advantages society as an each by eliminating dissolvent vapour into the environment, while also elimination the harmful effects of bacteria from the surface. Main properties of solid surfaces are wettability and water repellence; both of them are depend straightly on the surface energy and surface roughness. Surface energy, however, is an intrinsic property of the material utilized, such that the wettability of the surface is uneasy to control when exposed to UV- light over an extended period of time [26].

The field of self-cleaning coatings can be classified into two categories: hydrophobic and hydrophilic as showed in (Fig. 5) These two types of coating both of them clean themselves through the work of water, the formulation by rolling droplets and the latter by sheeting water that carrying away dirt. Hydrophilic coatings, have an additional characteristic: they can break down chemically adsorbed dirt in sunlight or UV light [26].

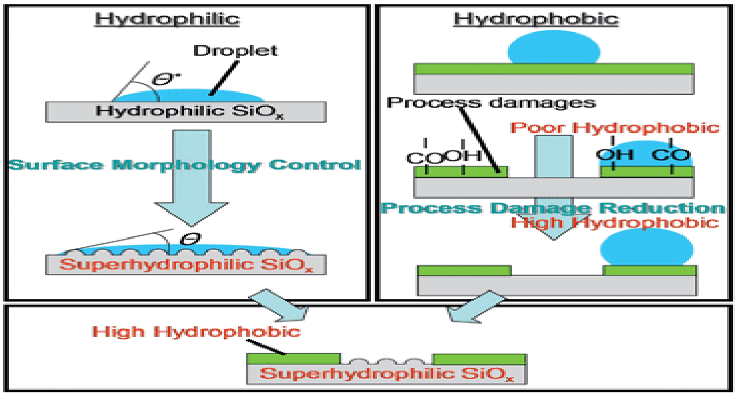


Fig. 5. Categories of self- cleaning surface [26].

Surface and interfacial tensions are existent whenever there are one or more condensed phases measured in energy per unit area. Surface tension is the occurrence of one condensed phase, while interfacial tension is the appearance of two brief phases in contact with one another. Contact angle is one of the few measurable quantities in surface science at the interchange of three phases, typically solid, liquid and vapor phases. The contact angle is a measure of the competing tendencies of a drop to spread, so as to cover a solid surface or to round up so as to decrease its own area. The contact angle computes the wetting gradient, generally of a liquid droplet on a solid and also appoint the boundary condition for the computation of meniscus shapes from the Young-Laplace equation. Wherefore, the contact angle can be used to compute the surface tension of a solid surface and a liquid drop [27]. For small drops, hydrostatic effects are deemed negligible to where the contact angle is calculated from the measured height, h, and contact radius, a [28].

$$\tan(\theta_c/2) = h/a \tag{1}$$

Contact angle of water droplets was firstly studied by Thomas Young, who modeled the static contact angle of a droplet on a smooth surface. Young concluded that the interaction between the solid with liquid, liquid with vapor, and solid with vapor surface free energy can be determined by the water contact angle. The phenomenon of wetting is described quantitatively using Young’s Equation, in which relation among contact angles to interfacial tensions (γ_{sg}, γ_{lg}, γ_{sl}); where s, l, g are the solid, liquid, and gas or vapor phases respectively. If a droplet of liquid is placed on a solid surface, liquid can either dispersal totally gives a zero value for contact angle measures, or pack up a contact angle which measurable, θ_c. For a θ_c value bigger than zero, a three-phase wetting line is made between the liquid, solid, and vapour as illustrates in (Fig. 6) Substrates with contact angles less than 30º are called super-hydrophilic, between 30-90º are hydrophilic, while more than 90º are called hydrophobic [29].

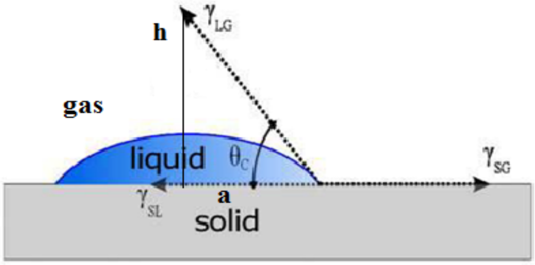


Fig. 6. Contact angle between solid-liquid-gas phase of a liquid drop on a flat substrate [29].

Young's equation in general is the total of the force vectors at equilibrium and can be employed to calculate the surface tension of a solid substrate given the three known liquid surface tensions, coupled with the three measured contact angles [30].

$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cos(\theta_c) \tag{2}$$

1.3. Influence of Surface Roughness Wenzel Equation

The wettability of a solid face is not only governs by the chemical composing, but also by the geometrical micro/nanostructure of the surface as observed in (Fig. 7) [31].

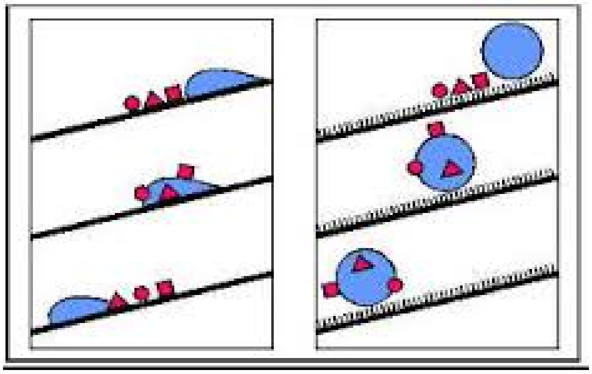


Fig. 7. Sliding Water Droplet on an Ordinary Hydrophobic surface versus a rolling water droplet on a roughened hydrophobic surface [31].

Surface roughness has a main role in contact angle science, as a water droplet put up on a micron strong hydrophilic surface due to the water to sink into the grooves, hence decrease the contact angle. This influence, however, has versus effect on a hydrophobic surface where Guo *et. al.* who explained a linkage between the contact angle and surface roughness, where excess the surface roughness of a hydrophobic paint rising the contact angle at all regularly. This can be caused by the excess in surface energy by roughening, causing a maximal polymorphism in energy between the water droplet and the surface, causing the droplet to recede, thus formation larger contact angles [32]·

For surfaces that are rough and heterogeneous on a scale over the molecular size, while under a scale where optical techniques could though be employed, the surface roughness can be explained by the Wenzel equation [33].

$$\cos\theta_{app} = R_{rough} \cos\theta \qquad (3)$$

where : θ_{app} is the obvious contact angle observed seen by eye or optical microscope, and R_{rough} is the ratio between the effective and expected surface area, and is constantly more than or equal to one ($R_{rough} \geq 1$). This equation thus explained that for $\theta < 90^{\circ}$, surface roughness reduction the obvious contact angle, while for $\theta > 90^{\circ}$, surface roughness growing the obvious contact angle.

Most of solidary surfaces are chemically non-uniform, to where the obvious contact angle is a function of two chemical types within or on the surface. Cassie [34] supposed a smooth two components surface, where two various areas with contact angles θ_1 and θ_2 take the surface rates f_1 and f_2, giving an obvious contact angle rate as [34]:

$$\cos\theta_{app} = f_1 \cos\theta_1 + f_2 \cos\theta_2 \qquad (4)$$

2. Experimental Methods:

2.1. Pint Application

There are many methods for improving the self-cleaning properties of nanocrystalline films. Some strategies for improved coatings might involve increasing the surface area of the film by additive of nanoparticles like TiO_2 NPs have an important effect on both quality and cost [35] . Furthermore, increasing the number of electron–hole pairs generated, increasing the lifetime of the pairs in the material by reducing the recombination rate or creating coatings that are activated by lower energy light, thus using a higher proportion of the solar spectrum [36].

2.2 Incorporating a Mixture of two Phases of NPs into Local Paint

TiO_2 NPs with two phases (anatase and rutile) and with different concentrations were mixed under magnetic stirring for two hours at 50˚C until a homogenous mixture with pH in the range of (6-7) was achieved. Then, polyethylene glycol (PEG) was added as a dispersant agent [37] with an average relative molecular mass of 6000, and a mass four times that of the mixture nano-TiO2 catalyst. Finally, the suspension was mixed using a magnetic stirrer for 15 min at 60˚C. The final mixture of nano–TiO_2 with two phases and PEG was added to local water-based paint and mixed for two hours using an electric mixer for modifying the local paint properties. TiO_2 amount was varied as 1%, 1.5% and 2% from the paint weight. Table 2 shows composition of nano-TiO2 and the ratio of anatase and rutile.

Table 2. The concentrations ratio of TiO2 nanoparticles and respective anatase/rutile phases ratio.

Sample Number	TiO_2 Percentage (wt %)	Anatase: Rutile
1	1	10:90
2	1	50:50
3	1	90:10
4	1.5	10:90
5	1.5	50:50
6	1.5	90:10
7	2	10:90
8	2	50:50
9	2	90:10
10	Local paint (water based paint)	-

3. Results and Discussion:

3.1. Morphological Properties of TiO_2 NPs

TEM images of TiO_2 NPs in anatase and rutile phase is illustrated in (Fig.8) for various magnifications. Fig 8 (a, b) indicates that the size of anatase NPs is in the range of 3-30 nm having uniform more or less spherical shape, in agreement with the results reported by [38]. This shape and size homogeneity of TiO_2 NPs will influence the characteristics of the local paint when added. As explained previously, the anatase phase NPs can be utilized in paint due to the photocatalytic properties of TiO_2 that lead to self-cleaning surfaces and materials. Fig. 8 (c, d) shows TEM image of TiO_2 NPs in the rutile phase, with higher size in the range of 35-75 nm and having elliptical shape. However, it has been noticed that sometimes both of phases suffer from particles aggregation. To prevent this, polyethylene glycol (PEG) is added to the mixture of the two phases as a dispersant material.

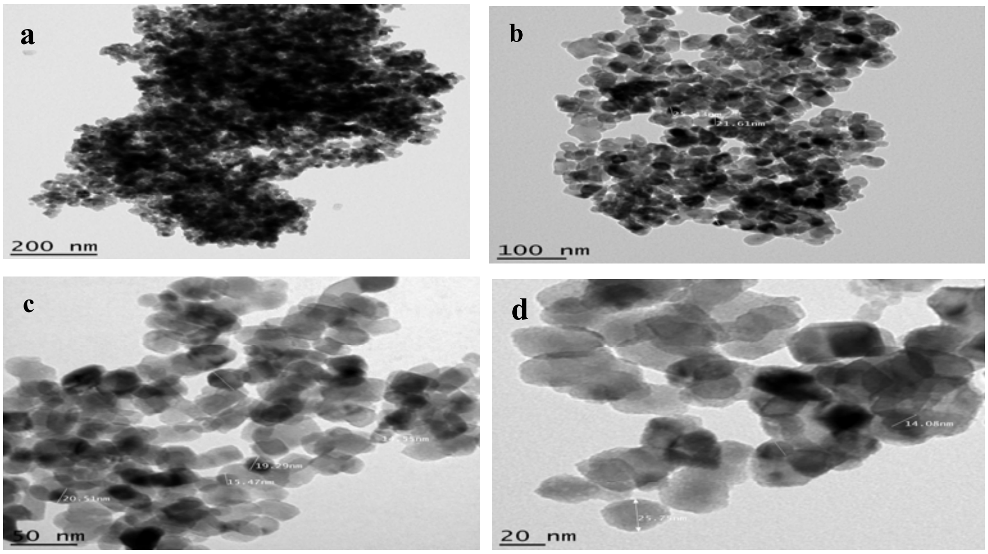


Fig. 8. Shows Transmission Electron Microscope (TEM) images TiO_2 nanoparticles , anatase phase before laser ablation treating with different magnifications, respectively.

3.2. Washability and Contrast properties of TiO_2 NPs

The purpose of testing local paint after the addition of the as-synthesized TiO_2 NPs, the washability test which is one of the important measurements widely used in paint application to test the resistance of many materials to scrub, abrasion, and washing. Additionally, the local paint before and after the addition of the mixture of TiO_2 NPs in anatase and rutile phases in addition to PEG as dispersant material. The results show that the coated films stand 3000 blow brush in washability instrument with mixture of NPs, note that the Iraqi Standard bearing the number 985 for the same local paint bears 500 blow brush. In other words, the films with added mixture of NPs have increased the washability at a rate of 2500 blow brush. (Fig. 9) shows washability machine. Contrast measurement is an easy to use opacity reflectometer instrument for the measurement of the opacity or luminous reflectance, of a gray scale sample. This is suitable for the evolution of coating hiding power. Contrast results were investigated for the local paint samples mixed with TiO2 NPs and PEG by, installing a Morris plate for hiding power horizontally, coating the sample to a uniform thickness of 50 μm, leaving it to settle for 2 h and coating again with the same amount moving the brush perpendicular to the first direction of movement. After leaving the sample to dry horizontally for 24 h, luminous reflectance is calculated for black and white parts for Morris plate to hiding power, respectively, using a reflectance device when the incident angle is 45° and the receiving angle is zero. The results for the contrast test for samples are in the range of 0.97-0.99. Note that for the Iraqi Standard bearing the number 985 for the same local paint, assay contrast for the white color is 0.9. These results show clear enhancement of local paint contrast properties after adding the mixture of TiO_2 NPs [2].

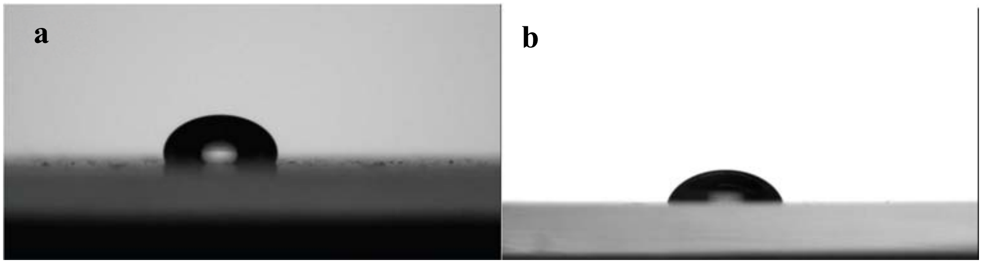
Fig. 9. Washability Machine.

3.3. Hydrophilic & Hydrophobic Surfaces (contact angle) properties of TiO_2

In recent years, there has been a considerable amount of work in order to develop contamination resistant coatings. As a commercial product, their potential is huge and their market truly global. Due to their wide range of possible applications, from window glass and cement to textiles, self-cleaning coatings may become an important labour-saving device. Self-cleaning coatings are classified into two types:

- super- hydrophobic;
- super - hydrophilic.

Both are clean themselves through the work of water. Hydrophobic coatings clean themselves by rolling droplets of water that carry away any dirt, whilst hydrophilic coatings clean themselves by sheeting water to remove dirt from the surface. However, Hydrophilic coatings have the ability to chemically break down the absorbed organics in sunlight or UV [39] .When the contact angle increases to more than 90°, the surface is hydrophobic, but when the surface contact angle is less than 90°, the surface is hydrophilic. In the present work, with UV irradiation and TiO_2 NPs, the surface contact angle converts from hydrophobic to hydrophilic. It is an important to remove organics and contaminants. There was an increase in contact angle up to 104±2, resulting in hydrophobicity. Due to its low surface energy, hydrophobicity depends on both the surface roughness and the chemical composition that can lower the surface energy sufficiently [40]. The hydrophilic surface is excellent for self-cleaning. With increasing surface energy, the most photocatalytic phase is anatase through its polymorphic structure as shown in (Fig. 10).



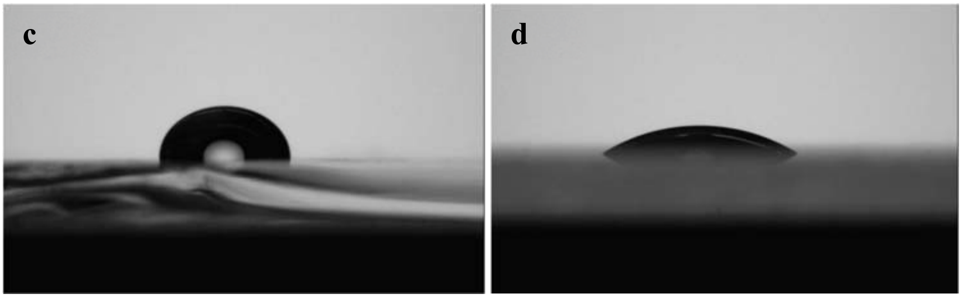


Fig. 10. Water contact angles of a 5 μL on surfaces treated with :**(a)** bulk formulation and APTES before irradiation**, (b)** bulk formulation and, APTES and TiO2 NPs before irradiation**, (c)** bulk formulation and APTES after UV irradiation,**(d)** bulk formulation, APTES and TiO2 NPs after UV irradiation.

3.4. The antibacterial activity of TiO_2

Photocatalytic TiO_2 antimicrobial effect reaction was first discovered by [41]. They investigated the effectiveness of the photocatalytic oxidation under UV irradiation against numerous microorganisms of Gram-positive bacteria (*Lactobacillus acidophilus*), yeast (*Saccharomyces cerevisiae*), Gram-negative bacteria (*Escherichia coli*) and green algae (*Chlorella vulgaris*). Since then, a series of investigations on photocatalytic disinfection have been intensively conducted on a wide range of microorganisms such as viruses, fungi and many species of bacteria [42,43, 44].UV light irradiation of TiO_2 activates valence band electrons to be transferred to the conduction band leaving behind a positively charged hole. The activated charge carriers react with atmospheric oxygen and water molecules to produce reactive oxygen species (ROS). Biocidal action of TiO_2 photocatalyst is frequently ascribed to OH• radicals and other reactive oxygen species (ROS) [45,46] which is the driving force behind the antibacterial activity of TiO_2 [47,48] .In particular, some studies have proved that the cell membrane is the fundamental site to be attacked by reactive photo-generated oxygen species, leading to lipid peroxidation [48,49]. The combination of cell membrane damage and more oxidative attack of intracellular components eventually caused cell death. Other studies have propose that the photo oxidation of coenzyme A (a coenzyme derived from pantothenic acid, important in respiration and many other biochemical reactions) will leading to cell respiration inhibition and finally cell death [48]. Generally, disinfections by titanium oxide are (3) times stronger than chlorine and (1.5) times stronger than ozone [50].

Have been prepared thin layers of (TiO_2) with a high photocatalytic activity and antibacterial properties for use as a self- cleaning transparent coatings for windows in outdoors applications. In this study Titanium dioxide (TiO_2) nanoparticles were prepared by sol-gel process using Titanium Tetrachloride ($TiCl_4$) as a precursor, and calcined at different calcination temperatures (400, 600, 800, and 1000) °C [51] .The synthesized nanoparticles were characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Ultraviolet spectroscopy (Uv-Vis), Atomic Force Microscopy (AFM). Self-cleaning properties were studies through two important tests; hydrophilicity by measuring the Water Contact Angle (WCA) and photocatalytic activity by using potassium permanganate ($KMnO_4$) as a model organic pollutant. Secondly, a thin film coating of TiO_2 nanoparticles was deposited by spin coating. The antimicrobial activity of TiO_2 nanoparticles was assessed quantitatively against two types of bacteria, (*Pseudomonas aeruginosa)*, and *(Staphylococcus aurous)*. As shown below in (Fig. 11) and (Fig. 12) [52].

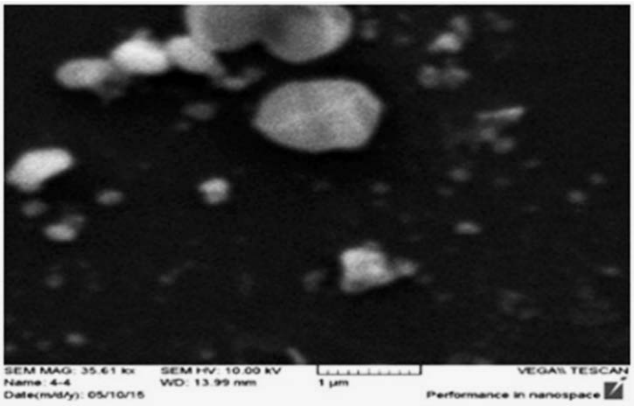


Fig. 11. SEM images of S. aureus cells in contact with TiO_2 nanocoating prepared at calcination temperature 1000°C

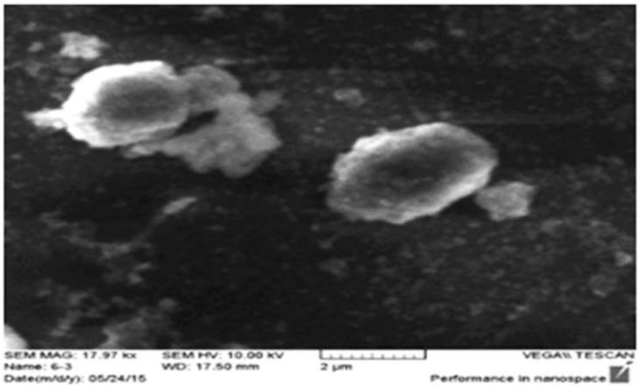


Fig.12 SEM images of P. aeruginosa cells in contact with TiO_2 nanocoating prepared at calcination temperature 800°C .

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