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Research Article

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Application of Nano Technology in the Self-Cleaning Finishing of Textiles: A Review

Zaid H. Mahmoud[1] and Ehsan Kianfar[2*]

[1]*Chemistry department, college of sciences, university of Diyala, IRAQ*

[2]*Young Researchers and Elite Club, Gachsaran Branch, Islamic Azad University, Gachsaran, Iran*

[*]Corresponding author
Ehsan Kianfar, Young Researchers and Elite Club, Gachsaran Branch, Islamic Azad University, Gachsaran, Iran.

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Abstract
Production of self-cleaning surfaces is possible with two methods of super hydrophobicity and photocatalytic decomposition of pollution. The basis of photocatalytic self-cleaning is the chemical decomposition of polluting substances using the photo-oxidation/reduction reaction due to incident radiation. Titanium dioxide or Titania is one of the most widely used materials in this field. The photocatalytic effect can lead to the destruction of organic compounds in the cell wall of bacteria and molecules of odor-causing compounds. Therefore, as a result of finishing with photocatalysts, in addition to the self-cleaning property, properties such as antimicrobial and anti-odor properties are also created in the surfaces. If the surfaces completed with titanium dioxide are exposed to light radiation, yellowing due to light and optical decomposition of the surface will also be prevented. In recent years, a lot of research has been done on self-cleaning textiles. This property, inspired by the characteristics of some plants and animals, has provided a new field in the production of high-performance textiles. There are two main approaches for the production of these textiles, in this session, the creation of surface roughness is discussed to create super-water-repellent and self-cleaning textiles.

Keywords: Textile, Self-Cleaning, Nano Photocatalyst, Nano Technology, Super Hydrophobicity, Pollution

1. Introduction

In recent years, researchers have turned to producing textiles with new properties [1-3]. Some of these properties are inspired by nature, among which we can mention the creation of self-cleaning properties on different surfaces, including textiles [4-7]. There are two different approaches to this type of completion. In the first approach, the self-cleaning fabric is a super-hydrophobic surface [8-11]. In the second approach, nanoparticles such as titanium dioxide are used as a nanometer coating on the textiles, and these nanoparticles, in the presence of water, oxygen and sunlight, cause the stains created on the textile to break down [12-17]. The set of operations and steps performed on fabric in order to increase its quality is called "textile finishing"[18-20]. In the production of textile products, finishing refers to all the steps that yarn, fabric and textiles go through to have a better appearance and higher performance [21-24]. The finishing operation is applied after the production of the textile product [25-28]. Finishing the surfaces with the aim of creating self-cleaning properties can be implemented with the following two approaches [29-32]: In the first approach, the textile becomes super-hydrophobic to create self-cleaning properties. In the second approach, nanoparticles such as titanium dioxide (in anatase phase) are used as a nanometer coating on textiles [33-36]. In the presence of water, oxygen and sunlight, these nanoparticles cause the stains created on the fabric to disappear.

2. Self-Cleaning and Super Waterproof

This property is obtained by chemical and geometric modification of the textile surface. The creation of Nano and micrometer roughness by using a hydrophobic coating causes the contamination of the textile surface to easily slip and separate from the hydrophobic textile in the presence of water, and in this way the surface of the textile remains clean [37-40]. The idea of creating such a product was inspired by the natural structure of the lotus leaf, and then various surfaces of nanoscale scales were created and evaluated by humans [41-43].

2.1. Measuring the Wettability of Surfaces

Usually, the level of surface wettability is evaluated by measuring the static contact angle of a drop of water in contact with the surface. As seen in Figure 1, the angle between the surface and the curvature of the droplet that is in contact with the surface is considered as the contact angle (CA). A contact angle of more than 90 degrees indicates that the surface is hydrophobic, a contact angle of less than 30 degrees indicates that it is hydrophilic, and an angle of more than 150 degrees indicates that the surface is superhydrophobic [44-46]. It is worth mentioning that although the use of materials such as fluorocarbon compounds in the finishing of textiles creates a contact angle of about 120 degrees and these surfaces are water-repellent and easy to clean, they are not classified in the group of self-cleaning surfaces [47-50].

Figure 1: Measurement of stable contact angle in hydrophilic, hydrophobic and superhydrophobic surfaces [2-3].

2.2. Natural Superhydrophobic Surfaces

At present, more than 200 types of natural hydrophobic surfaces have been identified, which always remain clean due to the chemical compounds on the surface or their specific morphology [51-53]. The concept of self-cleaning is inspired by the lotus leaf. It is said that despite growing in the swamp, it never gets dirty. As shown in Figure 2, the presence of micrometer ridges in the structure of this leaf causes large amounts of air to be trapped between these ridges when in contact with water. On the other hand, the presence of natural wax on this leaf causes the super-hydrophobic properties of this surface [54-57]. Among other examples of natural super-hydrophobic surfaces, we can mention rice plant leaves. This leaf has a structure similar to a lotus, with the difference that in the lotus, the surface hairs are uniformly distributed on the surface; However, in rice leaves, these hairs are arranged only parallel to the edge of the leaf [58-61]. Due to the special arrangement of the villi, the water drop slips easily in the direction of the villi with a contact angle of 4 degrees, but in the direction perpendicular to the villi, it slips with difficulty and at an angle of 120 degrees, and that is why this leaf It has the same directional or non-directional super-water repellency(figure3). Among other cases of superhydrophobic surfaces in nature, we can mention the leaves of Goshfil and the leaves of Indian star.

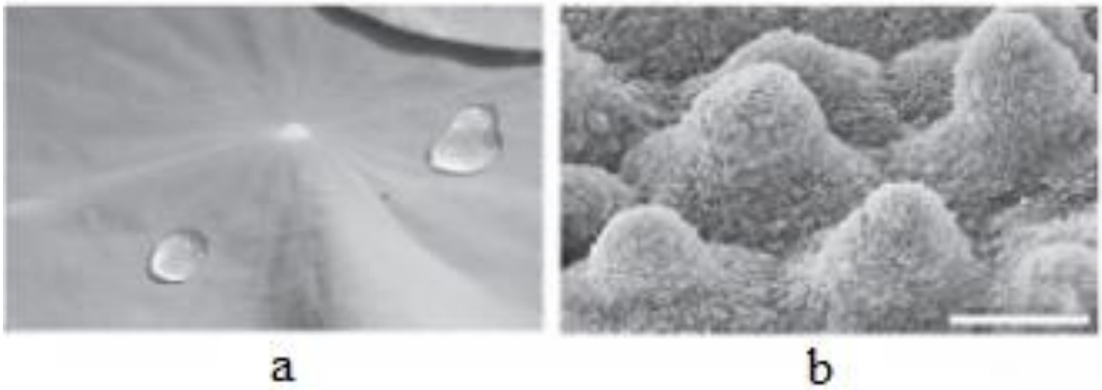

Figure 2: Hydrophobic structure of lotus leaf (a), electron microscope image of nano and microstructure protrusions in lotus leaf (b)[4].

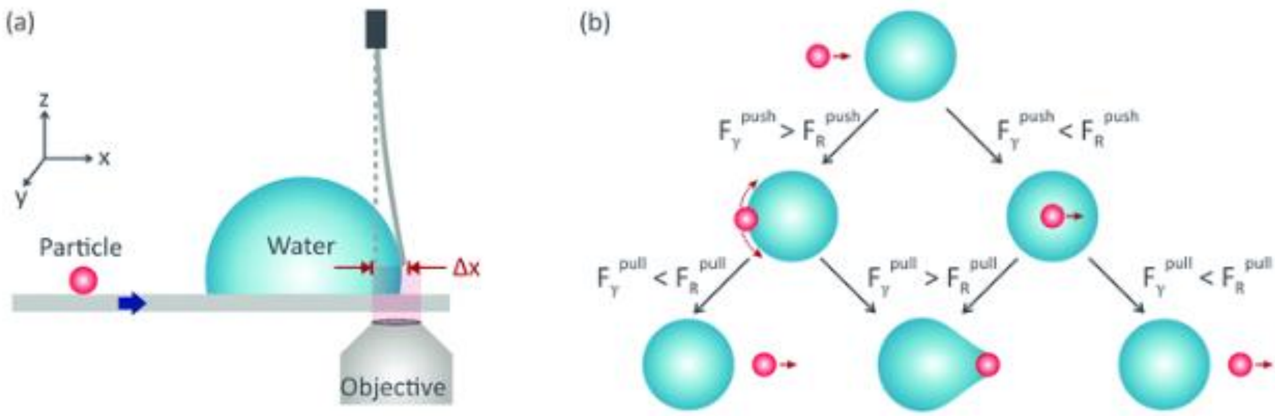

Figure 3: pollutants are removed from different surfaces by a drop of water [4].

3. Finishing the Waterproofing of Textiles

Although the concept of super-hydrophobicity is relatively new and dates back to the late 90s, concepts such as water repellency of textiles in the textile industry are more than 50 years old [62-66]. Most of the superhydrophobic finishing in textile engineering is done by hydrogels, mineral nanocomposites and colloidal solutions and by various methods such as padding, spraying, electrospinning, plasma, etc. on textiles (figure 4 and table 1). The surface of textiles is different from other solid materials such as metal sheets or glass surfaces in terms of flexibility and micrometric structural unevenness caused by fibers and fabric structure. The mentioned cases enable the ability of textiles to be super-waterproof by creating secondary nanometer roughness. Researchers propose two methods to produce superhydrophobic surfaces [67-70]:

• Making the surface rough by using materials with low surface energy.
• Modifying the surface of an uneven field using materials with low surface energy [5].

From simple methods such as padding and surface coating to more complex methods such as self-assembled layering of composite layers, nanometer coating of textiles is used [6]. In these methods, nanoparticles, nanorods or holes, carbon nanotubes, silica particles, zinc oxide nanorods and silver nanoparticles are used. Although it is not so difficult to create super water repellency in self-cleaning textiles; But the most important challenge is maintaining these characteristics during consumption. New preparation methods such as laser and plasma are very effective in increasing the stability of this feature in textiles [71-75]. In order to produce super-hydrophobic cotton fabric, metal salts, finishing with silanes, gas coating and layering are used. The use of metal salts such as silver and zinc oxide will give the fibers other properties such as antibacterial and conductivity in addition to superhydrophobic properties. Table 1 lists some finishing methods to produce self-cleaning textiles.

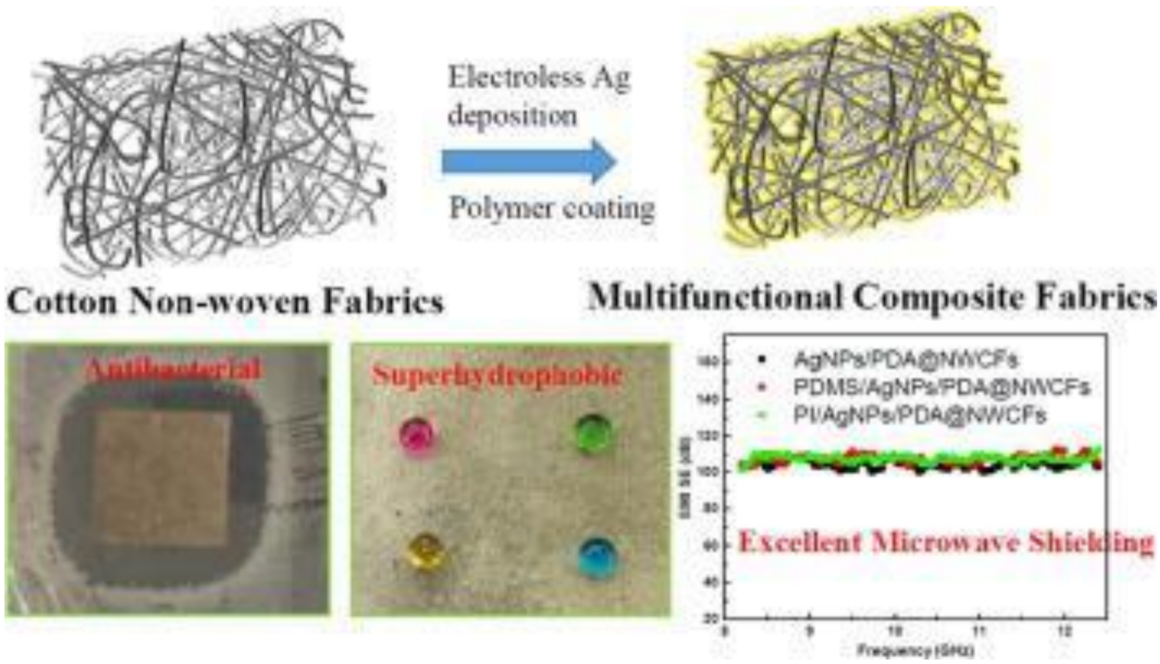

Figure 4: Microscopic image of cotton fibers and cotton supplemented with polymer nanoparticles to create surface roughness [7].

artificial fiber	cotton
Creating a silicone coating on the surface of polyester microfiber fabric	• Using carbon nanotubes to create nanoscale roughness. • Finishing layer by layer using silica nanoparticles and fluoroalkyl silane.
Covering synthetic fibers with electrospun mesh containing surface tension reducing materials	• The use of coating of silica nanoparticles with amine groups. • Finishing layer by layer with polydimethyldiallyl ammonium chloride and negatively charged silica nanoparticles.
Fluke coating of nylon 66 fibers on polyester fabric	• Perfluorocarbon coating using plasma enhanced chemical vapor deposition (PECVD). • Making the surface uneven by metals and then coating with hydrophobic materials.

Table 1: Different methods of producing self-cleaning super waterproof textile [5-7].

4. Self-Cleaning and Decomposition of Pollution Agents

Although creating self-cleaning properties was done by making surfaces superhydrophobic until years ago, further research showed that it is possible to use optical decomposition of organic compounds such as pollutants and microorganisms by semiconductor materials and convert them into carbon dioxide and water [76-79]. Created with proper self-cleaning properties. In this case, there is no need to superhydrophobic the surface [80-82]. For example, in research conducted by a group of Japanese researchers, a thin film of titanium nanoparticles was placed at a temperature of 5000C, and as a result of this process, a superhydrophobic surface was created. Although this coating became more complete when exposed to water and oil, it still had good self-cleaning properties [83-85]. Titanium dioxide or titania is one of the most widely used materials in the field of finishing self-cleaning textiles. In addition to this substance, the properties of other nanoparticles such as bismuth vanadate and benzophenone are being investigated by researchers. The most important challenge in performing this type of finishing is the low surface energy of the textiles, which makes the adhesion between the nanometer coating and the textile background difficult [86-89]. To solve this challenge, it is suggested to use methods such as low temperature sol-gel and a new generation of polymeric binders. Due to the many properties of coating with TiO_2, the use of this technology has attracted the attention of researchers of various sciences [90-93]. Figure 5 shows the photocatalytic activity of TiO_2 particles.

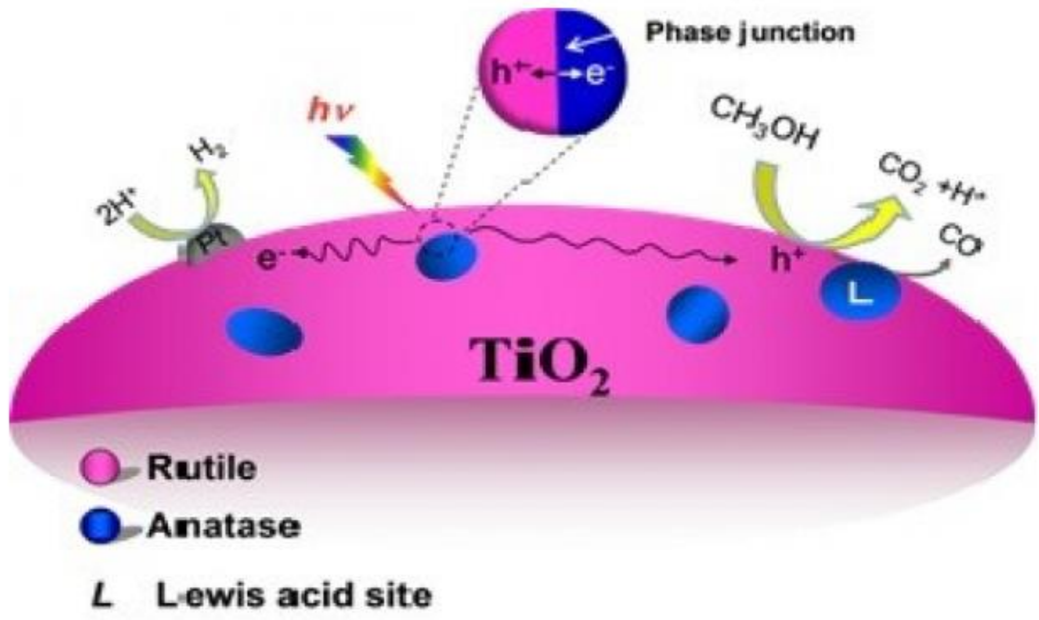

Figure 5: Photocatalytic activity of TiO2 particles in the presence of sunlight [7].

4.1. Photocatalytic Principles of Tio_2

Photocatalyst is a light-sensitive substance that oxidizes strongly in the presence of light rays. The self-cleaning property can be created by coating the surface with the photocatalytic oxide of an intermediate metal. In addition to acceptable photocatalytic properties, titanium dioxide is considered one of the best materials for creating this property for various reasons, including relatively cheap price, chemical stability, non-toxicity, and good biocompatibility. Titanium dioxide leads to self-cleaning properties in materials in the following two ways [94-96]:

- Photocatalytic oxidation

- Superhydrophobic property

The basis of the photocatalytic property of this semiconductor is the need for moderate energy to transfer an electron from the valence circuit to the conduction circuit. The electrons of the photocatalyst material are in the unexcited and basic state in the valence circuit (VB)[97-100]. When the surface is exposed to light, the electrons absorb energy and move to the conduction circuit (CB) (see Figure 6). The potential required to create electron/hole pairs in this material is +2.53 V, which allows the oxidation of water molecules and absorbed hydroxide ions and can lead to the formation of hydroxyl radicals with high oxidizing ability ˙(OH)). The electron transfer potential from the conduction layer is -0.52 V, which is not enough to react with absorbed oxygen molecules to create highly reactive superoxide radical ions (O-2). The radicals created during the mentioned reactions are able to perform photoelectrochemical reactions to decompose organic compounds such as pollutants, stains, microbes and other compounds into carbon dioxide and water [36]. Another reason for the self-cleaning property of titanium dioxide, which was discovered by accident in 1995, is the superhydrophobic property of this material. If this material is combined with a certain percentage of silicon dioxide, it leads to the creation of superhydrophobic properties when exposed to light [101-103]. In this case, the electrons cause the reduction of the Ti (IV) cation to (Ti (III) and the holes oxidize the O-2 anions. As a result of this phenomenon, some oxygen atoms are removed from the surface. And oxygen-free sites are created on the surface of the particles. Since water molecules can be placed in these vacancies, the surface of the particles becomes hydrophilic [37]. covers it with a continuous film and causes the surface to be washed away and this effect remains for several days after irradiation and gradually returns to the original state Figure 7 shows how photocatalytic self-cleaning surfaces work. The most important advantage of TiO_2 is the occurrence of photocatalytic and superhydrophobic effects on the surface at the same time. The self-cleaning property due to superhydrophilicity is often Self-cleaning and anti-fog mirrors are used in automobiles, but they have not been used in the field of textiles. Figure 8 shows the application of TiO_2 particles in automobile mirrors.

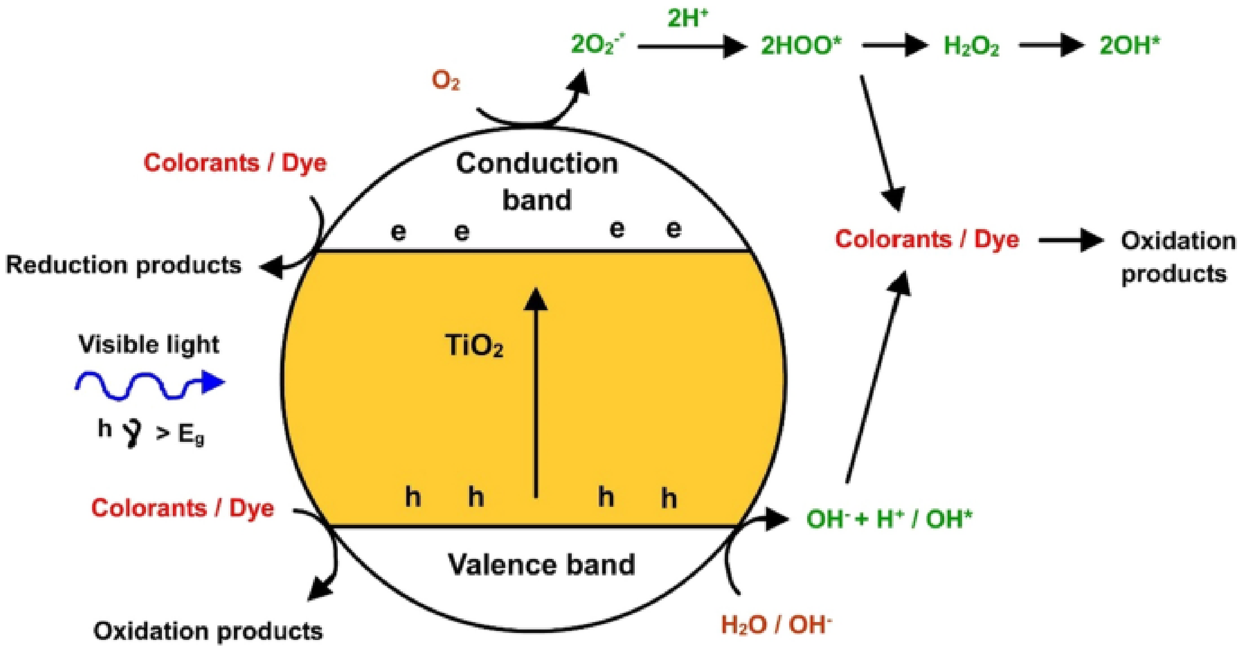

Figure 6: Schematic of the photocatalytic phenomenon of titanium dioxide [7].

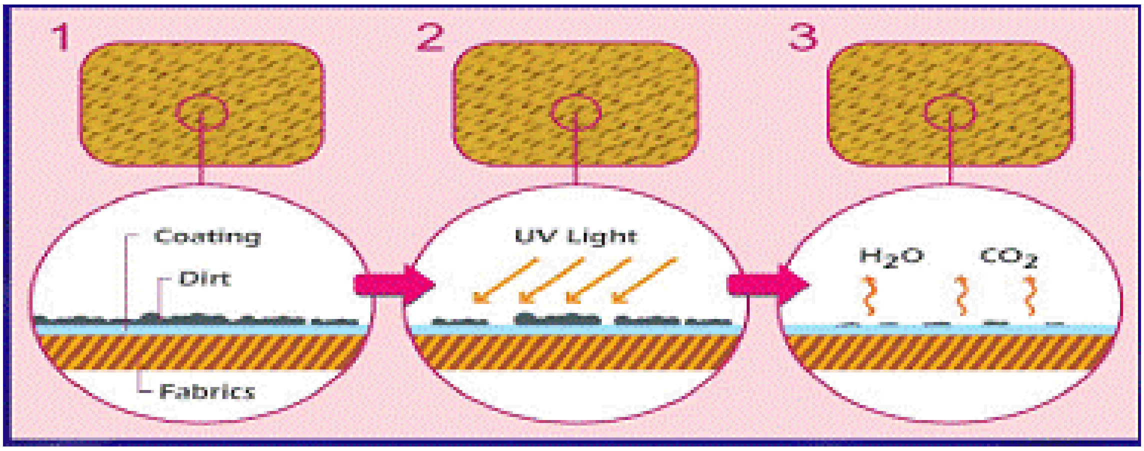

Figure 7: photocatalytic self-cleaning textiles work [7].

Figure 8: Application of TiO_2 in self-cleaning and anti-fog glass (a) and mirror (b)[7].

4.2. Factors Affecting the Photocatalytic Properties of Tio_2

Several factors influence the photocatalytic activity of titanium dioxide, some of the most important of which are shown in Figure 9. These factors include the size of the particles, the shape of the crystals, the specific surface area, the type and percentage of porosity, and the general structure of the particles (layered or core-shell or composite structure). Titanium dioxide crystal exists in three phases: anatase, rutile and brookite [104-106]. Meanwhile, brookite phase is less known as a photocatalyst and anatase phase has the most photocatalytic properties. Researchers have considered the combination of anatase and rutile to have the most photocatalytic properties. The photocatalytic property of anatase TiO_2 strongly depends on the morphology of the particles. If these particles are used in nanometer dimensions, the photocatalytic property will increase due to the spread of electron/holes before recombination (electron-hole recombination) and the increase of the specific surface area per unit of mass and volume [107]. Research has shown that titanium dioxide particles in the anatase phase with a size of 10 nm have the highest photocatalytic activity due to the best balance between surface charge and particle size [38].

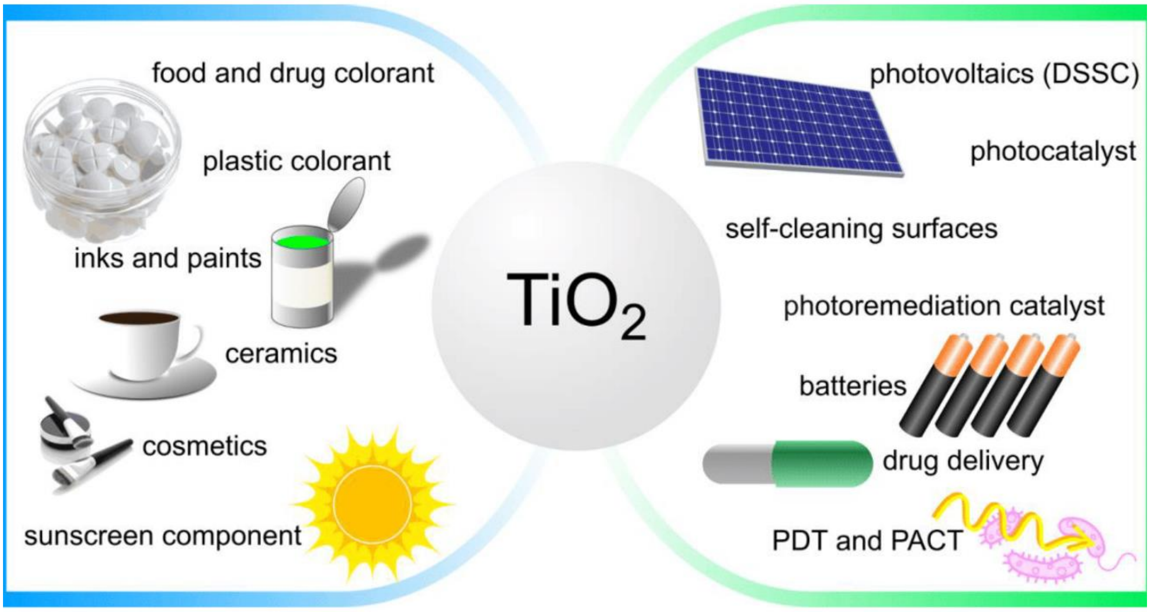

Figure 9: Factors affecting the photocatalytic properties of titanium dioxide [4].

4.3. Tio$_2$ Coating Applications

Finishing textiles with TiO_2 nanoparticles, in addition to creating self-cleaning properties, by breaking down odor-causing organic molecules and breaking down microorganisms, will create features such as anti-odor and antimicrobial properties. Protection against ultraviolet rays is one of the properties created in textile coated with titanium dioxide [39].

4.4. Self-Cleaning Finishing of Textiles Using Tio$_2$

Self-cleaning fabrics are used in many cases, including work clothes and military uniforms, household and urban furniture, carpets, curtains, tents, agricultural textiles, filters, etc. An example of these fabrics is shown in Figure 10. To improve the stability and adhesion between the base material and the photocatalyst coating, physical methods such as plasma irradiation or UV radiation under vacuum are used to functionalize the surface. But in chemical methods, polycarboxylic acid-based cross linkers are used [40].

Figure10: An example of a self-cleaning garment with Nanotechnology textiles [6].

4.5. Cotton Textile Finish
Cotton textiles have a weak bond with TiO_2 particles. Various methods have been developed to finish cotton textiles using titanium dioxide, the most important of which are the following [4-11].

4.6. Sol-Gel Method
The sol-gel method is suitable for textiles and polymers with low thermal resistance. In this method, most TiO2 and SiO2 particles are used simultaneously to take advantage of their synergistic effect in creating self-cleaning properties [12].

4.7. Surface Preparation Method with Radiation
In this method, plasma with ultraviolet rays is used to create negative functional groups (including carboxylic, percarboxylic, epoxide and peroxide) on the surface of textiles. The purpose of this work is to deposit Ti4+ positive ions present in TiO_2 particles on the surface of textiles with negative surface charge and create a strong ionic bond between positive particles and negative textile [13].

4.8. Method of Mixing Tio_2 with Metals
In this method, TiO_2 particles are coated with metals such as silver and gold. One of the most important advantages of this mixture is to increase the photocatalytic property of titanium dioxide, to create self-cleaning property in visible light due to strengthening the absorption of ultraviolet rays, and to improve the stabilization of TiO_2 particles during the washing of textiles [14].

4.9. Creating Chemical Cross-Links
In this method, polycarboxylic acids are used to create chemical cross-links between cotton and TiO_2 particles, but there are also limitations, the most important of which is the creation of a transparent and non-uniform layer on cotton fabric with the property of self-cleaning in visible light and the possibility of yellowing in the fabric. In case of baking at temperatures higher than 210 0C [15].

4.10. Woolen Textile Finish
The use of titanium dioxide in the finishing of woolen textiles, in addition to creating self-cleaning properties, improves properties such as hydrophilicity, antimicrobial and anti-yellowing due to light radiation. The use of ultraviolet radiation and uniform coating of wool with titanium dioxide/silicon dioxide nanocomposite are among the methods of increasing hydrophilicity and creating self-cleaning properties in these fibers. The presence of titanium dioxide crystals as an absorber of ultraviolet rays can also reduce the amount of yellowing of wool fibers due to light radiation. On the other hand, using the combination of silica and silver nanoparticles increases the hydrophilicity and antimicrobial properties of wool fibers. Since the thermal and chemical resistance of protein fibers is low, some special operations are required to complete these fibers with titanium dioxide. Chemical preparation methods of wool fibers are used for better adhesion of TiO_2. For example, we can mention the acylation of the wool surface using succinic anhydride. Oxidation of the wool surface with potassium permanganate and the use of butane tetracarboxylic acid (BTCA) as a binder can increase the stability of nanoparticles and their absorption by wool fibers [12-13].

4.11. Finishing Polyester Textiles
The use of argon or oxygen plasma with radio frequency (RF) is one of the methods of functionalizing the polyester surface before finishing with colloidal TiO_2 nanoparticles. Textiles completed with this method have antibacterial properties against E.Coli bacteria, are anti-ultraviolet rays, and stain decomposition. Similar results regarding the effect of textile preparation by plasma method have been reported for wool/nylon and polyester fabrics. TiO_2 suspension and colloid is poured on the mentioned textiles at a temperature of 1000C. In this method, colloidal TiO_2 as the initial layer is covered with another layer of TiO_2 with larger particle size. This provides the best color removal effect. The deposition of colloidal TiO_2 particles on textiles provides suitable areas for placing the larger crystals of the second layer. This method stabilizes the completion of nanoparticles and maintains the expected properties after photochemical dyeing of stains on textiles [14].

5. Comparing the Self-Cleaning Properties of Textiles with Superhydrophobic Methods and Tio_2 Particles
The effect of photocatalytic self-cleaning with TiO_2 has several major advantages over self-cleaning with the superhydrophobic method [15-19]:
• The ease of using TiO_2 compared to superhydrophobic surfaces.
• More durability and strength of surfaces completed with TiO_2.
• Multipurpose finishing using TiO_2 (self-cleaning, anti-bacterial, anti-odor and UV absorber).
• The stability of washing, abrasion and a more suitable environment of textiles completed with TiO_2.

6. Challenges of Developing Superhydrophobic Surfaces
Despite the great efforts and research in the field of manufacturing superhydrophobic fibers with self-cleaning properties, this field often has challenges related to wear and lack of stability of properties. The nanoscale fluffy structure of the fibers is fragile and can be easily damaged by pressure or light abrasion. For this reason, it seems necessary to create structures that are more stable against the acting forces. Another problem with these surfaces is their tendency to absorb pollutants such as oily substances. Harmful substances penetrate the fiber structure and are difficult to remove. The above-mentioned drawbacks make it difficult to use these fabrics for a long time.

7. Conclusion
• In this article, the topic of self-cleaning using super hydrophobicity was mentioned. Creating nanometer roughness is a good way to create hydrophobic surfaces. In the case of textiles, one of the main challenges in the development of this method is the use and instability of nanometer roughness.
• The development of self-cleaning surfaces is an active field in research. The concept of self-cleaning is directly related to concepts such as surface wettability, surface chemistry and physics, nanotechnology and mechanics. Although several methods have been proposed to produce self-cleaning textiles and create nanometer roughness in the surfaces, there is still a need to provide simpler methods that require fewer operating steps

and lower temperatures. Many physical and chemical methods are often used to increase the adhesion of TiO2 particles to the fabric. One of the most important of these methods is surface functionalization with chemicals or ultraviolet rays or plasma, and creating chemical cross-links on the fabric.

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