

Application of TiO₂ Nanoparticles for Obtaining Self-Decontaminating Smart Textiles

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The worldwide use of pesticides together with the possibility of chemical warfare agent's usage in military actions, terrorist attacks or in accidents, increased the risks of chemical contamination occurrence and consequently stipulated the need for the development of new protective materials and equipment with improved properties. Present day protective gear and incorporated materials afford only physical protection/barrier against toxic chemicals. Current research activities are thus directed towards the design of the so-called "smart textiles", which are capable of "self-decontamination", *i.e.* decomposition of toxic chemicals. This goal can be achieved by metal oxide nanoparticles incorporation onto textile substrates. For this purpose, TiO₂ nanoparticles have shown as the most promising, because of the easiness of their synthesis, low price and low toxicity. In this article we described the low temperature methods of TiO₂ nanoparticles synthesis (for a special application on textiles), different ways of their deposition on different types of textiles and the methods for testing the properties of thus obtained textiles.

Key words: photocatalysis, TiO₂, textile, textile materials, self-decontaminating materials, synthesis, chemical contamination.

Introduction

CHEMICAL contamination can be manifested through the use of chemical warfare agents (CWAs) in military actions, in case of accidents and also in terrorist attacks. And there are also increased risks of chemical contamination by pesticides, widely used toxic chemicals. The future soldier will be expected to carry more weight, utilize more technologies and withstand more extreme environment conditions. This is why today, in modern armies, there is a need for multifunctional materials and devices. Traditional protective clothes comprise suits and over garments based on permeable materials, usually made of activated carbon liners or based on insulating rubber materials. Although this kind of protective gear affords excellent protection against different kinds of toxic chemicals (especially CWAs), it has some major drawbacks. Some of them are bulk, increased weight and, consequently, a lack of breathability, which induces heat stress in soldiers and other users [1-4]. Moreover, this kind of materials represents only a physical barrier against chemical agents: the toxic chemicals are retained within the material, so further steps of post-use decontamination procedures and adequate disposal are needed. Because of all stated above, there is an increasing need for the development of more effective protective materials for these purposes, which will not only represent a barrier against toxic chemicals, but will also perform a decontamination (decomposition) of toxic chemicals. These

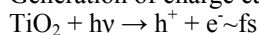
kinds of products are often called "smart textiles."

One way to achieve self-decontaminating properties of textiles is to employ nanotechnologies, especially metal oxide nanoparticles (MONPs) with photocatalytic activities. This can be achieved in two fundamentally different ways. One way is *de novo* synthesis of nanofibers by the electrospinning process [5]. Electrospinning is a cheap and relatively simple technique of producing nanofibers. It consists of introducing high voltage into a polymer solution through a small syringe, thus obtaining fibers with nm radius. Nanofibers of desired properties can be obtained by adding nanoparticles into a polymer solution. For example, with the addition of Al₂O₃, TiO₂ and MgO nanoparticles, fibers with self-decontaminating properties can be obtained. The other way for MONPs employment in textile industry is referred to special ways of woven textile substrates finishing. TiO₂ nanoparticles have proved to be the best for this purpose, because of the easiness of their synthesis, low cost and low toxicity.

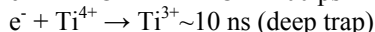
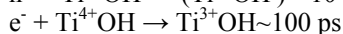
Evidence for the low toxicity of TiO₂ nanoparticles comes from cosmetics industry, with the 20-year long history of human use in sun screen preparations. There are a lot of studies which prove that micro- or nano-sized TiO₂ particles are not (photo)mutagenic or (photo)genotoxic to humans. Above all, there is no difference between micro- and nano TiO₂ in recognition, distribution and elimination from the body [6].

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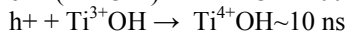
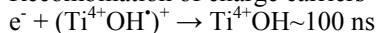
Generation of charge carriers:



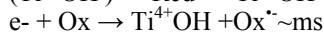
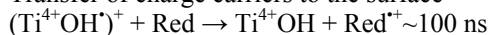
Trapping of charge carriers



Recombination of charge carriers



Transfer of charge carriers to the surface



Scheme 1. Mechanism of photocatalysis by TiO₂

Moreover, other properties of textiles could be modified with the use of TiO₂ nanoparticles, such as: hydrophobicity/hydrophilicity, UV protection, antibacterial properties and anti-wrinkle resistance. In this article, we have described the methods of the TiO₂ nanoparticles synthesis at low temperatures for a special application on textiles, different ways of their deposition and the methods for testing the properties of thus obtained textiles.

Photocatalytic properties of TiO₂ nanoparticles

TiO₂ exists in amorphous and crystalline forms. The amorphous form is photocatalytically inactive. There are three natural crystalline forms of TiO₂: anatase, rutile and brookite. Anatase and rutile have a tetragonal structure, while the structure of brookite is orthorhombic. Brookite is less common than the former two crystal polymorphs and is far more difficult to obtain. The elementary repeating unit of anatase and rutile is TiO₆²⁻ octahedron, but the pattern by which they are interconnected is different. There are also five synthetic, not naturally occurring polymorphs of TiO₂: TiO₂(B), TiO₂-R, TiO₂-H, TiO₂-II, TiO₂-III [7].

Anatase and rutile are photocatalytically active, while brookite has never been tested for photocatalytic activity. Pure anatase is more active as a photocatalyst than rutile, probably because it has more negative potential on the edge of the conductive band, which means higher potential energy of photogenerated electrons and also because of a larger number of -OH groups on its surface. However, it is interesting that the coupling of different crystalline phases of TiO₂ results in the increase in photocatalytic activity. For example, Degussa P25, the most commonly used commercial photocatalyst is a mixture of anatase and rutile and shows much higher photocatalytic activity than pure anatase or rutile.

Photocatalysis represents a photo-induced chemical reaction accelerated in the presence of the catalyst. This implies that both light (of certain energy) and a catalyst are necessary for a chemical reaction to occur. TiO₂ is a semiconductor and its molecular orbitals can be approximated with bands, out of which the valence band (highest occupied, HOMO) and the conductive band (highest unoccupied, LUMO), separated by the energy gap (not allowed electronic states), are the most important. The mechanism of TiO₂ photocatalysis involves few stages (Scheme 1). When TiO₂ particles absorb light (photons) with energy higher than or equal to the energy gap which separates the valence band and the conduction band ($E \geq 3$ eV, UV-A region of the EMG spectrum), electrons are

excited to the conduction band, and positively charged holes remain in the valence band. Generated charge carriers can recombine nonradiatively or radiatively (emission of heat energy), or migrate to the surface of the photocatalyst, and get trapped at certain places of the crystal lattice, subsequently reacting with e⁻ donor or e⁻ acceptor molecular species adsorbed at the photocatalyst surface. The competition between these two processes determines the overall efficiency of the photocatalyst. The electrons and the holes generated in TiO₂ nanoparticles are localized in different defect sites of the material. Electronic paramagnetic resonance (EPR) experiments have shown that e⁻ are trapped as two Ti(III) centers, while the holes are trapped as radicals concentrated at oxygen atoms at the photocatalyst surface [8].

The mechanism of oxidation and reduction of molecular species involves the generation of superoxide anions and hydroxyl radicals. The conduction band e⁻ reacts with adsorbed oxygen leading to the formation of superoxide anions. The holes in the valence band react with water and generate hydroxyl radicals, or react directly with adsorbed organic molecules. Also, hydroxyl radicals can oxidize wide a variety of organic molecules (contaminants, pesticides, warfare agents). This process in large excess of photocatalyst finally leads to the complete mineralization of organic molecules yielding CO₂ and H₂O molecules.

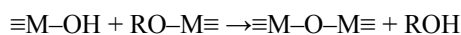
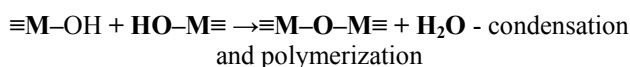
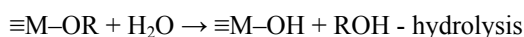
There are a number of papers describing the decomposition routes of chemical warfare agents and their simulants; thorough review of them is beyond the scope of this article. We will mention just a few illustrative examples. Obee and Satyapal [9] have studied photocatalytic decomposition of a nerve agent stimulant, dimethyl methylphosphonate (DMMP), on a TiO₂ coated glass substrate. They found that direct oxidation by valence band holes involves the P-O bond cleavage, since an intermediate oxidation product was methyl phosphonic acid. They also found a phosphate ion and carbon dioxide which are indicative of DMMP complete oxidation. Apart from direct oxidation by valence band holes, hydroxyl radical attack is another of DMMP oxidation pathways. It can proceed through two different reaction pathways: hydrogen abstraction and addition-elimination [10]. Vorontsov and coworkers [11] studied the TiO₂ photocatalytic decomposition of sulfur mustard analog chloroethylethylsulfide (CEES) in a gaseous phase. According to the found degradation products, it was concluded that the degradation of CEES involves, as the main step, the C-S bond cleavage with subsequent hydrolysis and oxidation of terminal carbon atoms. It should be emphasized here that the routes for TiO₂ photocatalytic decomposition of chemical warfare agents are different in aqueous, non-aqueous and gaseous phases, but in large excess of photocatalyst, it always gives products of complete oxidation. It was shown that the TiO₂ photocatalytic activity is influenced by a variety of factors: crystal structure, surface area, nanoparticles size distribution, porosity and a number and density of hydroxyl groups on the TiO₂ surface.

Synthesis of TiO₂ nanoparticles for their application on textile substrates

Since the discovery of TiO₂ nanoparticles, major efforts have been devoted to the development of methods for their synthesis, and numerous, fundamentally different ways of preparation have been postulated [12], some of them being:

sol-gel, sol, [13] hydrothermal and solvothermal methods [14, 15], micelle and inverse micelle methods [16], direct oxidation methods [17], chemical [18] and physical vapor deposition [19] methods and also electrodeposition [20], sonochemical [21] and microwave deposition methods [22]. However, when we take into consideration the application of TiO₂ nanoparticles on textile substrates it should be kept in mind that the low-temperature methods for the synthesis of highly crystalline TiO₂ nanoparticles are highly appreciated. Textile substrates are usually dipped into a reaction mixture, without the isolation of nanoparticles; after deposition they are processed at temperatures below 100°C to further induce the crystallization and to remove a solvent. Therefore, the wet chemistry methods such as sol-gel or hydrothermal methods are used to obtain textiles with self-decontaminating properties. As these methods are the most promising ones, we shall discuss them in more detail.

The sol-gel synthesis is the most promising alternative for the TiO₂ nanoparticles preparation, since it has numerous advantages: low temperatures, versatility of performance, and the homogeneity of products at the molecular level. The sol-gel method [23] is performed by the hydrolysis of a titanium precursor, usually titanium(IV)chloride or titaniumtetraisopropoxide (TIP) in a mixture of water and alcohol in acidic conditions. It involves the reaction of hydrolysis of a corresponding Ti precursor and a subsequent polymerization reaction (Scheme 2) leading to the formation of the liquid sol phase. The products of these reactions are influenced by: rate of hydrolysis, amount of water, ratio of TiO₂/water, applied temperature and reaction time. The large excess of TIP and low hydrolysis rates lead to the formation of Ti-O-Ti polymeric chains, while the formation of Ti(OH)₄ is favored in the presence of medium amounts of water and high hydrolysis rates. It was also found that the rate of particles coarsening is increased with increasing temperature, because the viscosity of the solution and TiO₂ solubility depends upon temperature. The average radius of a TiO₂ nanoparticle is linearly increased with reaction time. Complete polymerization and loss of solvent leads to the formation of the solid gel state. If the solvent is removed under supercritical conditions, a very porous material is obtained, named aerogel.



Scheme 2. Sol-gel synthesis of TiO₂ nanoparticles

The sol-gel method usually gives amorphous nanoparticles, which are converted to crystalline TiO₂ by heating at temperatures above 400°C. However, this process usually induces agglomeration of nanoparticles, decreasing the number of surface hydroxyl groups, and the surface area - properties that are important for a photocatalytic activity. Some research groups developed methods for TiO₂ nanoparticles preparation at temperatures below 100°C, without the need for subsequent heat treatment [24-27]. This kind of reactions is always performed in acidic conditions, in the presence of acetic, nitric or perchloric acid. Andersson and Bard [24] obtained needle-shaped anatase nanoparticles at temperatures 60-70°C, with the average radius of 8 nm, and at 90°C

nanoparticles were agglomerated to form irregular structures. Gopal [25] and Tang [26] obtained rutile nanoparticles in acidic conditions with the average size of 50nm, at temperatures of 40 - 50°C. Sol-gel TiO₂ nanoparticles preparation methods at low temperatures are of the outmost importance for the application in textiles.

Different types of amines acting as surfactants can be employed as shape controllers in sol-gel reactions. Amines employed for this purpose are: triethanoleamine, diethylenetriamine, ethylenediamine, trimethylenediamine, and trithylenetetramine. For example, it was found that the shape of TiO₂ nanoparticles changes from cubical to ellipsoidal at pH above 11, with triethanolamine as a shape controller.

Hydrothermal methods also employ a step of hydrolysis of titanium precursor (usually alcoxide) but also involve heating the reaction mixture in steel vessels (autoclaves) with or without Teflon liner. The temperature and pressure conditions are controlled. The temperature can be elevated above the boiling point of water (usually around 150°C), so the applied pressure is the pressure of vapor saturation. Because of high temperatures applied in the hydrothermal method, nanoparticles are isolated from the reaction mixture, and after the calcination step, they are resuspended in order to be applied on textile substrates.

Today, efforts in the synthesis of TiO₂ nanoparticles are made in order to increase their quantum efficacy and modulate their optical properties – absorbance shift towards the visible region of spectrum, in order to make them more suitable for practical self-decontaminating purposes.

Deposition of TiO₂ nanoparticles on textile substrates

A very important segment of the application of nanotechnologies in the textile industry is resolving the problem of binding nanoparticles to the fabric. The central problem is to assure tight binding of nanoparticles to the surface of textiles in order to increase the durability of the desired properties. This also ensures that nanoparticles are not released in the environment, fulfilling also the ecological requirements [28]. The obtained films must be colourless and optically transparent, so that there is no disturbance of the original colour of the fabric, and finally, the mechanical properties must remain intact [29].

In order to apply TiO₂ nanoparticles, the maximum chemical compatibility between nanoparticles and textile surface should be achieved. The literature stated several methods used for this purpose. These are the following: a method that uses covalent linking agents, a layer by layer method (using electrostatic interactions), and methods for the introduction of reactive functional groups onto textile surface which applies RF, MW or UV plasma or hydrolytic enzymes. In the following text, typical procedures and methods for TiO₂ nanoparticles deposition onto textile substrates will be discussed.

The dip-pad-dry-cure process is often used to create bonds between TiO₂ and a fabric. Qi *et. al.* examined the colorant decomposition activities of TiO₂-treated cotton fabric by the dip-pad-dry-cure process, before and after 10 and 20 washings. The obtained results showed that after 20 washings, self-cleaning properties were not significantly impaired in comparison to the situation after 10 washings, which may be due to the creation of the covalent bond between the titanium layer and the surface of cotton which is the result of dehydration reaction of the hydroxyl groups

of cellulose and titanium [30, 31].

Some authors in their studies use SiO₂ as a binder since it prevents textile from degradation during the photocatalytic activity of TiO₂. The composite TiO₂-SiO₂ layer should prevent the effect of daylight radiation on cotton fibres. TEM and SEM pictures of thus treated textiles show that TiO₂ nanoparticles are captured by the silica network [32]. Some authors, in order to make the TiO₂-SiO₂ layer, deposited it on the textile by soaking cotton in a 1:1 solution of colloidal TiO₂ and SiO₂ Ludox SM-30. The sample was then dried in air at 100°C for an hour. The results of high-resolution transmission electron microscopy (HRTEM) and infrared spectroscopy show that the corrosion of the upper layers of cotton would occur due to the effect of daylight on the TiO₂ particles, if there were no SiO₂ as a binder [33].

Cotton is a polysaccharide with many free hydroxyl groups on its surface. Succinic acid was used as a linking agent between cotton and TiO₂ nanoparticles. It has two carboxyl groups of which one forms the ester bond with the hydroxyl cellulose group and the other forms electrostatic interactions with TiO₂. Besides succinic acid, other non-toxic, low cost saturated poly-carboxylic acids were used, such as 1,2,3-propanetricarboxylic acid and 1,2,3,4-butanetetracarboxylic acid. Samples of cotton were immersed in an aqueous solution of the linking agents (6%, w/w) in the presence of NaH₂PO₂ as a catalyst (4%, w/w) for 1 h. After drying that lasted for 3 min at the temperature of 80°C-90°C, the textiles were cured at different temperatures for 2 min (115°C < T < 210°C). The characterisation of the ester link between linking agents and cellulose fibers was performed by the attenuated total reflection infrared spectroscopy (ATR-IR) [34]. In the case of both anatase and rutile crystal forms, the bond between cotton and TiO₂ is strong enough and can withstand the washing effect. In some studies, a citric acid was also used as a linking agent for cellulose and TiO₂ [35].

Wool and silk, which have keratinous structure, are of considerable use in the textile industry both as independent materials and as additions to other fibres depending on the application [34, 36]. By the deposition of TiO₂ nanoparticles on this kind of fibers, the self-decontaminating textiles could be obtained. Since these functionalized fibres are often not stable, it is necessary to further stabilize them. TiO₂ has a great affinity for the hydroxyl and carboxyl groups [37-41], but there are fewer than 50% free of them in the keratins, and a special treatment must be approached in order to increase their number [42]. The acylation of wool by succinic acid anhydride increases the number of carboxylic groups. Resulting fibres showed enhanced binding of TiO₂ nanoparticles and thus more effective self-cleaning properties.

The composition abundance of carboxyl groups makes alginate very useful for the application on various types of fabrics. It is a natural polysaccharide extracted from brown algae [43]. It is a polymer of 1,4-linked β-D-mannuronic and α-L-guluronic acid and provides additional carboxylic groups, as additional binding sites for TiO₂. In a combination with zinc oxide, it provides a satisfactory microbial protection, as well as UV radiation protection when applied to the coloured cotton fabrics [44]. Mihailovic *et al.* applied TiO₂ nanoparticles with alginate on polyester fabrics in order to create a stronger bond between the fabric and TiO₂, which resulted in improving the self-cleaning properties of this material [45].

The layer by layer deposition method was also used for TiO₂ nanoparticles application onto textile substrates. This method consists of alternate immersion of substrate in two solutions of opposite polarity. Thus a multi-layer film is obtained, based on electrostatic interactions between layers. This process can be repeated many times, depending on a desired thickness of the multi-layer. Grandcolas *et al.* [46-47] deposited WO₃-modified titanate nanotubes on military textile (50% cotton-polyamide) by this method. They used polyethyleneimine as a positively charged polyelectrolyte solution. The obtained textiles showed excellent self-decontaminating properties in the visible part of spectrum. The advantages of this procedure are reflected in its low cost of preparation and a very thin layer which is uniformly deposited on the fabric.

Krogman *et al.* [48] used an automated spray technique of applying the layers, which is very efficient and fast, regardless of the substrate's nature. They used hydroxylized plastic as a substrate; consequently the same procedure could be used on cotton, because the cotton already has hydroxyl groups. It should be emphasized once more that, in this manner, the obtained layer is mechanically stable as a result of strong electrostatic interactions between charged species.

The textile surface can also be functionalized by radiofrequency (RF) and microwave (MW) plasmas, as well as by UV irradiation. This process takes place at low pressures, in the air, leaving the textile intact, while only the surface layer is transformed, of 1-20 nm thickness [49]. The radiation effect from these areas creates -COO⁻ and -O-O⁻ groups on the surface, to which is then a positively charged nanoparticle attached. In the reaction between active oxygen species (¹O₂, O, O⁻, O⁺), created by an effect of RF plasma in the air and the fabric surface, a large number of functional groups (C-O, C=O, -O-C=O, -COH, -COOH) is formed. In addition to these groups, the literature also mentions the possibility of epoxide, percarboxylate and peroxide groups formation [50]. The main difference between RF and MW field is their irradiation time. In the MW, the field is significantly shorter and ranges in the interval of 5-45s, depending on the fabric, while, as stated above, in the RF field it goes to 30min. Since the activation of the surface by the vacuum UV radiation field takes place with much lower energy, the result is only a formation of atomic and excited oxygen species. A better control of occurred surface modification is thus obtained as well as its greater uniformity. The depth of modified layer is about 10 nm, *i.e.* about 50 atomic layers [51].

The interaction between the activated textile surface by RF, MW plasma and UV irradiation and TiO₂ nanoparticles is electrostatic in its nature, since the textile surface is negatively charged as a result of the activation and formation of COO⁻ and -O-O⁻ groups on the surface. It should be noted that TiO₂, in this case, can be bound only to the parts of the textile surface which have been subjected to radiation, while they wash-off from the others. Also, it is necessary to apply TiO₂ immediately upon activating the surface since the oxygen species react with air and are slowly deactivated, which will only reduce the effectiveness of the overall process [52].

Low temperature plasma (LTP) can also be applied for the functionalization of fabric. This procedure is applied in case of polyesters, due to the fact that it weakly binds TiO₂ for a lack of functional groups that could chemically bind TiO₂. As well as in the case of other plasmas, the LTP also affects the substrate surface layer while the rest of the

material remains intact [49]. These changes on the surface depend on the composition of the gas phase and the parameters of the apparatus, and significantly affect the titanium adhesion. Two negative functional groups (COO⁻ and -O-O⁻), are the most responsible for the improved binding of TiO₂ nanoparticles to textile surface, and thus its improved self-cleaning properties. The direct current glow discharge plasma proved to be the best of all used plasmas, for the purpose of increasing the reactivity of the polymer surface [52].

Fabric functionality can be also increased when treated with enzymes. The textile surface is hydrolyzed and its number of functional groups is thus increased. Montazer and Seifollahzadeh [53] treated polyester and wool with protease-Savinase and lipase-Lipex enzymes in the ultrasonic bath, with butane tetra-carboxyl acid as a cross-linking agent. Lipase is used to functionalize polyesters since it has the ability to hydrolyze carboxylic esters [54-56]. On the other hand, protease is used for the wool surface functionalization, since it hydrolyzes peptide bonds, in order to reduce the felting tendency and increased dyeing efficiency [57]. The cross-linking agent also has a purpose of enhancing the nano-particles adsorption and stabilization on the fabric surface. The same authors in their study compare the hydrophilic properties of a fabric prior to the enzymatic treatment, with the enzyme on the surface, and with TiO₂ bound to the modified fabric. Logically, the best water adsorption properties are obtained for the modified fabric to which TiO₂ is attached, since nano TiO₂ has a property to "force" water droplets to be at a small angle to the surface, to quickly spread on it and then dry. The SEM images show that the enzyme is located on the surface of the material to a thickness of a nanometer to a picometer. After the enzymatic treatment, when the incorporation of TiO₂ is performed, the SEM images clearly show the formed active layer. In this manner, treated fabrics also display good microbiological protection, as well as good self-cleaning properties.

In the conclusion, there are several different ways to introduce reactive functional groups onto textile surface and to attach TiO₂ nanoparticles to textile substrates, but to the best of our knowledge, to date no comparative study of self-decontaminating, mechanical and other properties of differently TiO₂ modified textiles has been undertaken. So we cannot state here which method gives optimal results.

Testing the functional properties of TiO₂ modified textiles

Since the described modification procedures alter surface properties and impart textile functions, different test methods are used to assess the properties and functionality of TiO₂-modified textile materials. The testing of fiber mechanical performances is necessary to provide confirmation that the modification procedure does not negatively change the original features of host fibers, while the testing of material UV-protective, antibacterial and self-cleaning properties is a good criterion for the evaluation of photocatalytic activity introduced by the presence of TiO₂.

The mechanical properties of TiO₂-treated fabrics are usually evaluated through measurements of the tearing strength [29, 58, 59], tensile strength [29, 58, 60-62], bending rigidity [29] and air permeability [29, 58, 60, 62]. Measurements of tearing and tensile strength are commonly used methods to evaluate the effect of TiO₂ treatment on fabric resistance to tearing and stretching force, while

bending rigidity serves as an objective measure of the features which are decisive for fabric handle properties and it is related to fabric stiffness and difficulty of fabric deformation under bending. The air permeability of the fabric is the rate of air flow passing perpendicularly through a known area under defined air pressure differential between the two surfaces of a material [29]. It is mainly dependent upon the fabric thickness and porosity and it is used for the assessment of changes in the material weight, volume and confort properties [60].

Photocatalytic self-cleaning fibers are able to clean themselves when exposed to light, but they also possess antibacterial, deodorizing and UV blocking functions. Thus, several testing methods can be used for the evaluation of the photocatalytic activity of TiO₂-modified textiles.

The design of an experimental setup for the photocatalytic activity assessment through accelerated decomposition of different compounds comprises the selection of an adequate light source, a model compound and a type of a photocatalytic reaction vessel.

The choice of the light source in terms of its form, emitted wavelengths and light intensity depends on the type and shape of the examined material, as well as on the objective of the examination. Since textiles are flexible, a cylindrical lamp could be used inside the reactor and material can be wrapped around, or a plate samples can be placed perpendicularly to the beam of the lamp located outside the reactor. The effects of the wavelength and of the light intensity can be controlled by using filter solutions, solid optical filters and grids. In order to avoid heating effects due to the infrared fraction of the emission, a water jacket can be placed in the light beam [62, 63]. The photocatalytic reaction rate depends in a complex way on the light intensity received at the catalyst surface [64, 65], which could be adjusted by varying the distance between the lamp and the surface of the examined material and measured by the UV radiometer [66,67]. In experiments where the objective was to investigate photocatalytic activity under daylight, a tungsten iodide lamp with a cut-off filter to remove the radiation below 420 nm or a Xenon lamp with water and glass filters to cut off IR and UV irradiation, respectively [69], were used as visible light sources.

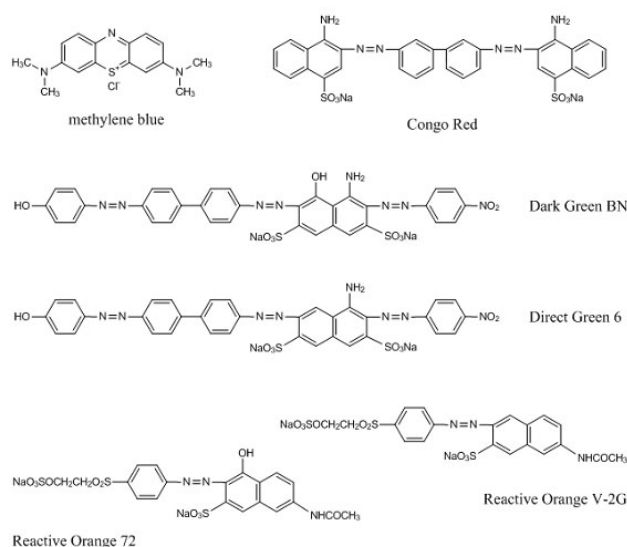


Figure 1. Structures of some synthesized dyes applied as model compounds for photocatalytic activity assessment

A broad range of organic pollutants which are used to assess the photocatalytic efficiency of TiO₂-coated materials

can be classified into three categories: dyestuffs, organic compounds and gases [70]. Dyes, both natural and synthesized, are commonly used as model pollutants, mostly because their degradation can be easily monitored by spectroscopic measurements. As a source of the natural colorant stains, sour cherry juice, tea [59], red beet sap [32], coffee [29, 51, 71], blueberry juice [72], red wine [29, 31, 51, 62, 71, 73], curry [29], and some others have been used. Methylene blue has a widespread application as a synthesized organic dye because it is mainly nontoxic, does not absorb the light in the UV-A region and exhibits strong absorption in the visible light ($\lambda_{\max}=664\text{nm}$; $\varepsilon_{664}=7.4\times 10^4\text{M}^{-1}\text{cm}^{-1}$) [70]. However, methylene blue is an inappropriate substrate for a photocatalytic activity test in the visible region, because its visible light absorption has the influence which should be excluded for the evaluation of a real photocatalytic activity of materials [74]. Some of the other synthetic dyes, for example trisazo dyes Direct Green 6 [59] and Dark Green BN Green 6 [75], diazo dyes Congo red [76] and Acid Blue 113 [53], monoazo dyes Reactive Orange 72 [59], Reactive Orange V-2G [75], Acid Orange 7 [77] and methyl orange [68, 78], or a fluorescent dye Rhodamine B [77], have also been applied for a photocatalytic activity assessment (Fig. 1).

Besides dyes, different organic compounds have been used as model compounds for the evaluation of photocatalysts degradation efficiency and among them are acetic acid [74], phenol [69], acetone, di-n-butylsulfide [73], and ammonia [79]. The screening method for odor reduction capacity of textile samples with photocatalytic properties using formaldehyde as a basic analyte was proposed by A. Ritter *et al.* [80].

Some papers investigated the photocatalytic efficiency of TiO₂-modified materials intended for use as self-decontaminating military textiles by using real chemical warfare agents (CWAs) or their simulants as model compounds. M. Grandcolas *et al.* [46,47] used blistering agent yperite (mustard gas, 2,2'-dichlorodiethyl sulfide) in the examination of the self-decontaminating properties of layer-by-layer functionalized textiles based on WO₃-modified titanate nanotubes. Because of safety issues associated with a high toxicity of CWAs, in many cases photocatalytic degradation was tested in compounds that mimic their chemical and physical properties (Fig.2). These include diethylsulfide (DES) [46, 81] and 2-chloroethyl ethyl sulfide (2-CEES) [11, 47, 82] which are simulants for yperite due to similarities in structure, chemistry and physical properties, and S-2-ethylthioethyl O,O-dimethyl phosphorothioate (Demeton-S), acting as a simulant for the nerve agent VX (O-ethyl S-(2-diisopropylamino)ethyl methylphosphonothioate), since both have low vapor pressure and both contain an oxidizable, electron-rich heteroatom [82]. Dimethyl methylphosphonate (DMMP) [9, 46, 47] and diethyl methylphosphonate (DEMP) [10] were also used as nerve agents simulants. The degradation of DMMP and DEMP as model compounds for hazardous pesticides and CWAs is a convenient method to estimate their reactivity towards TiO₂ photocatalysis, because the phosphorus-fluorine and phosphorus-sulfur bonds in a nerve agent sarin and organophosphorus pesticide malathion should be more labile than the phosphorus-carbon and phosphorus-oxygen bonds in these simulants, which are consequently less reactive than warfare agents and pesticides [10].

Different types of reaction vessels have been used for the examination of the photodegradation process, depending mostly on the chosen model compound and on the photocatalytic experiment setup.

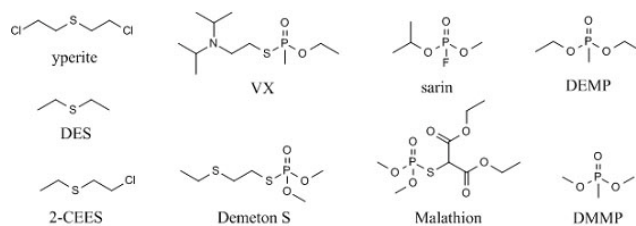


Figure 2. Structures of model compounds used for examination of photocatalytic activity of self-decontaminating military textiles

In most cases, the application of synthesized dyes as model compounds for the assessments of the photocatalytic activity of TiO₂-modified textile was conducted in a simple batch type reactor, where colorant decomposition activities were studied in the beakers that contained a colorant solution and the immersed pieces of fabrics samples. The evaluation of colorant decomposition was usually done by spectroscopic measurements of the retained colorant concentration (in solution or on the fabrics samples) as a function of irradiation time [71, 72, 77, 78, 83, 84]. Even less demanding procedures were based on stain removal tests, where natural colorants were dropped on the surface of the examined fabric samples and the decomposition was observed after a defined time of light irradiation by eye visible stain discoloration [71, 72, 83]. On the other hand, the mineralization of organic stains can also be quantitatively monitored by the amount of CO₂ generated during photocatalytic decomposition, as it was done by A. Bozzy *et al.* [51]. This procedure is, however, to some degree more demanding with respect to the reaction vessel construction.

When investigations were intended to assess different factors that affected the photocatalytic decomposition efficiency, more complex constructions and some specially engineered reactors were used, which were usually continuous-flow. Y. Dong *et al.* [79] have investigated the ammonia removal efficiency by nano-TiO₂ finished cotton fabrics in a specifically designed 2.5 L fixed-bed glass reactor which was a part of the photo degradation and testing system. The UV lamp was axially positioned inside the reactor, and the TiO₂-finished fabric was wound and fixed on its inner wall. Gaseous ammonia was emitted from specially made wall pieces, which are used to stimulate the indoor concrete wall of typical room and placed in an environmental chamber. The ammonia and clean dry air were mixed in a gas mixer and passed through the reactor. The temperature and humidity of the mixed gas flow were controlled, and the concentration of gaseous ammonia in the air from the reactor was determined by an NH₃ gas detector.

Besides the photocatalytic degradation capabilities, the permeability to toxic chemical agents is another important feature of self-decontaminating military textiles. K.C. Krogman *et al.* [48] used a specially designed and engineered stainless steel permeation cell (Fig.5) to conduct the desired reactive mass transfer tests on a sample coated with highly reactive layer-by-layer (LbL) films, intended for the application on fibers worn by military personnel. A coated sample was sandwiched between two sides of the cell. One side was the enclosed vapor space of a known volume above the sample and it contained saturated concentration of CWA simulant CEES. Through the other side, a stream of ultrapure carrier gas was passed under the sample at a flow rate that was large enough to ensure negligibly small partial pressure of the simulant. The

exposed cross-sectional area of the sample through which mass transfer was allowed to occur was specified by the cell geometry and chosen so as to eliminate edge diffusion effects. The mass flux of CEES through the sample was determined by measuring the flow rate of the carrier gas and the concentration of CEES in the contaminated stream, which was analyzed using a total hydrocarbon analyzer equipped with a flame ionization detector.

Many research papers are focused on photocatalytic activity assesment by the examination of the antimicrobial properties of TiO₂-modified textile materials, since a powerful oxidizing effect of TiO₂ upon the light irradiation leads to the destruction of a broad spectrum of microorganisms, such as bacteria, viruses and fungi. These examinations were done by studying the antibacterial efficiency of textile materials against Gram-negative bacteria *Escherichia coli* [45, 53, 61, 72, 85] and *Klebsiella pneumoniae* [30], Gram-positive bacterium *Staphylococcus aureus* [31, 61, 71, 83, 85-87], airborne bacteria and fungi [88] or bacteria isolated from the active sludge [78]. The antibacterial efficiency was usually quantitatively evaluated on the basis of the percentage of bacterial reduction in comparison with control samples [53, 72, 86,87], or by a comparison of the number of viable cells as a function of contact time with tested materials [31,71,78,83], or it was simply examined by measuring or observing the zone of cells growth inhibition after defined the incubation period [30, 61, 78, 85, 88].

The presence and functionality of TiO₂ deposited on the textile surface can be indirectly determined by studying the UV absorption property of the coated materials, since UV absorption is a natural attribute of TiO₂ [58, 87]. The UV blocking function of textiles was usually evaluated by the determination of the ultraviolet protection factor values (UPF) [30, 45, 58, 60-62, 83, 87, 89]. The UPF is the ratio of UV radiation measured without the protection of the fabric compared to that with protection. According to the Australian/New Zealand Standard AS/NZS 4399:1996, the UPF rating system indicates how much the material reduces UV exposure and classifies clothing into broad protection categories: good (UPF 15-24), very good (UPF 25-39) and excellent (UPF 40-49). A textile material must have a minimum UPF of 15 to be rated as UV protective [60-62]. UPF tests are conducted using a spectrophotometer or a spectroradiometer and serve as a measure of the UV protection provided by clothing fabrics.

Conclusions

TiO₂ modified textiles obtained by the finishing procedures described above represent the best solutions so far for obtaining the so-called "smart textiles" with self-decontaminating properties. However, in order to incorporate these materials in modern protective equipment, a few problems should be solved. The first problem is related to TiO₂ nanoparticles properties. They should have high quantum efficacy (with the lower degree of recombination of photogenerated charge carriers), in order to improve the rate of photocatalysis, *i.e.* decomposition of toxic chemicals. Furthermore, the application of doped TiO₂ nanoparticles with absorption in the visible part of the spectrum should be considered, so that photocatalysis can take place in natural solar light. The second problem is related to the tight binding of TiO₂ nanoparticles to different kinds of textile substrates (cotton, wool, polyester and polyamide). The binding methods, as described above,

usually take advantage of covalent or/and electrostatic interactions. The methods for the introduction of reactive functional groups on textile surface are also described. The development and improvement of these procedures will ensure the tight binding of TiO₂ nanoparticles, and consequently the durability of self-decontaminating textiles. The development of these procedures should assure retaining desirable mechanical and comfort properties of textiles. Solving these problems will ultimately enable obtaining highly durable, comfortable, self-cleaning textiles, with decontamination rates in time scale of minutes, in the visible spectrum range.

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Primena nanočestica TiO₂ za dobijanje samodekontaminirajućih pametnih tekstila

Široka upotreba pesticida u svetu, zajedno sa mogućnošću upotrebe bojnih otrova u vojnim akcijama, terorističkim napadima ili akcidentnim situacijama, povećala je rizik od pojave hemijske kontaminacije i shodno tome uslovila potrebu za razvojem novih zaštitnih materijala i opreme sa poboljšanim karakteristikama. Današnja zaštitna oprema kao i materijali inkorporirani u nju pruža samo fizičku zaštitu – barijeru protiv toksičnih hemikalija. Zbog toga su današnje istraživačke aktivnosti usmerene ka dizajnu takozvanih „pametnih tekstila“ koji mogu da vrše samodekontaminaciju odn. razlaganje toksičnih jedinjenja. Ovaj cilj se može postići inkorporacijom nanočestica metalnih oksida na tekstilne supstrate. Za ovu svrhu nanočestice TiO₂ su se pokazale najboljim, zbog lakoće njihove sinteze, niske cene prekursora i niske toksičnosti. U ovom radu smo opisali metode za sintezu nanočestica TiO₂ na niskim temperaturama (za specijalnu upotrebu na tekstilu), različite načine njihovog nanošenja na različite tipove tekstila, kao i metode za testiranje osobina ovako dobijenih tekstila.

Кључне речи: fotokataliza, nanočestice, titandioksid, tekstil, tekstilni materijali, samodekontaminirajući materijali, metoda sinteze, hemijska kontaminacija.

Применение наночастиц TiO₂ для получения обеззараживающих умных текстилей

Широкое применение пестицидов в мире, наряду с возможностью использования отравляющих веществ в военных действиях, в терактах или в аварийных ситуациях, повышают риск химического загрязнения, и следовательно, вызывают необходимость разработки новых защитных материалов и оборудования с расширенными функциями. Сегодня защитное и безопасное оборудование и материалы включены в него обеспечивают только физическую защиту - барьер против токсичных химических веществ. Таким образом текущая деятельность исследований направлена на разработку так называемых «умных текстилей», которые могут выполнять обеззараживание т.е. разложение токсичных соединений. Эта цель может быть достигнута путём включения наночастиц оксидов металлов на текстильные подложки. Для этого наночастицы TiO₂ оказались лучшими, потому что у них простота синтеза, низкая стоимость прекурсоров и низкая токсичность. В этой статье мы описали методы для синтеза наночастиц TiO₂ при низких температурах (для специального применения на ткани), различные способы их применения – нанесения на различные виды тканей, а также и методы для тестирования свойств таким способом полученных текстилей.

Ключевые слова: фотокатализа, наночастицы, диоксид титана, текстиль, текстильные материалы, обеззараживающие материалы, методы синтеза, химические загрязнения.

Application des nano particules TiO₂ pour obtenir les textiles intelligents auto purifiants

La grande utilisation des pesticides dans le monde entier, la possibilité d'emploi des poisons de combat dans les actions militaires, les attaques terroristes ou les situations d'accidents ont augmenté le risque de la contamination chimique. Tout cela a stipulé le besoin du développement de nouveaux matériaux de protection et de l'équipement aux caractéristiques perfectionnées. L'équipement actuel de protection ainsi que les matériaux y incorporés n'assurent que la protection physique – barrière contre les toxines chimiques. A cause de cela les recherches actuelles sont centrées sur la conception des soi-disant «textiles intelligents» qui sont capables d'accomplir une auto décontamination c'est-à-dire la décomposition des matières toxiques. On peut réaliser ce but par l'incorporation des nano particules des oxydes des métaux dans les substrats de textiles. A cet effet les nano particules TiO₂ sont les plus adéquates à cause de la facilité de leur synthèse, un bas prix et une petite toxicité. Dans ce travail on a décrit les méthodes pour la synthèse des nano particules TiO₂ à basses températures (pour l'emploi spécial chez les textiles), les différentes façons de leur déposition sur les différents types de textiles et les méthodes pour tester les propriétés des textiles obtenus de cette manière.

Mots clés: photo catalyse, nano particules, titane dioxyde, textiles, matériaux textiles, matériaux auto purifiants méthode de synthèse, contamination chimique.