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VAN YUZUNCU YIL UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCES
MECHANICAL ENGINEERING DEPARTMENT

APPLICATION OF UPC (UP CONVERSION) MATERIALS ON SELF-CLEANING TEXTILE

M.Sc. THESIS

PREPARED BY: Ali Mohamed Hassan EMHAMED
SUPERVISOR : Assist. Prof. Dr. Halil Ibrahim YAVUZ

VAN-2018

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ACCEPTANCE and APPROVAL PAGE

This thesis entitled **"APPLICATION of UPC (UP CONVERSION) MATERIALS on SELF-CLEANING TEXTILE"** prepares by ALI MOHAMED EMHAMED under supervision of Assist. Prof. Dr. HALİL İBRAHİM YAVUZ in the department of Mechanical Engineering has been accepted as a M.Sc. Thesis.

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Member: Prof .Dr. Bekir Özçelik (Çukurova Üni) — Signature: ....

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Director of institute

THESIS STATEMENT

All information presented in the thesis was obtained according to the ethical behaviors and academic rules frame. And also, all kinds of statement and source of information that does not belong to me in this work prepared in accordance with the rules of theses, were cited to the source of information absolutely.

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Alı Mohamed EMHAMED

ABSTRACT

APPLICATION OF UPC (UP CONVERSION) MATERIALS ON SELF-CLEANING TEXTILE

Emhamed, Ali Mohamed
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There has been an increasing consideration in nanotechnology during the present decade due to its enormous potential in applying and creating novel materials for enhanced properties and applications. This study aims to study the behavior and effect up conversion materials with Titanium dioxide to increase light efficiency, and effect of adhesion of nanoparticles by a Sol – Gel dip coating method on the textiles. The growing interest towards self-cleaning coating technologies is due to their high potential in commercial products and their ability to reduce cleaning labor costs. For example, a fabric with self-cleaning properties would save cost in fabric cleaning and extend the lifetime of the textile. In this study, photo catalytic self-cleaning and activities of the thin films were investigated, All samples drying at temperatures (60-90-120 °C) in vacuum drying oven with a time factor , there is no effect on the samples when the effect of a change in the temperature of drying on (Flat and Denim) textiles. Depending on the samples tested under Sun test and the number of hours can be deduced more hours of sun test light it will give more activity photo catalytic. Dip coating method were observed a very effective method in porous materials and it is a simple method. SEM analysis were connected $TiO2/Er^{3+}$ in test. It was demonstrated that the weave structures of treated textures were held stable and did not watch shrinkage of the cotton. XRD analysis the upconversion luminescence of ER^{3+} was showed the best performance.

Keywords: Nanotechnology, Self Cleaning, Up-conversion Materials.

ÖZET

YUKARI ÇEVRİMLİ MALZEMELERİN KENDİ KENDİNİ TEMİZLEYEN KUMAŞLAR ÜZERİNDE UYGULAMASI

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Geliştirilmiş özellikler ve uygulamalar için yeni malzemeler uygulama ve oluşturma konusunda yetkili bir potansiyele sahip olduğu için, mevcut on yıl boyunca nanoteknolojide artan bir düşünce olmuştur. Bu çalışma, ışık etkinliğini arttırmak için Titanyum dioksit ile dönüşüm malzemelerinin davranışını incelemek ve etkileşimde bulunmak ve nanopartiküllerin bir sol - jel daldırma kaplama yöntemi ile yapışmasının tekstiller üzerindeki etkisini amaçlamaktadır. Kendi kendini temizleyen kaplama teknolojilerine yönelik artan ilgi, ticari ürünlerde yüksek potansiyelleri ve temizlik işçiliği maliyetlerini azaltma kabiliyetlerinden kaynaklanmaktadır. Örneğin, kendini temizleyen özelliklere sahip bir kumaş, kumaş temizlemede maliyetten tasarruf ederek tekstil ömrünü uzatabilir. Bu çalışmada, fotokatalitik kendiliğinden temizleme ve ince filmlerin aktiviteleri incelenmiş, faktörü ile Vakum kurutma fırında sıcaklıklarda (60-90-120 °c) kurutma Tüm numuneler, (Flat and Denim) Tekstil kurutma sıcaklığında bir etkisi yoktur. Örnekleri güneş testi altında test ve rakamlar aracılığıyla saat sayısına bağlı olarak daha fazla etkinlik fotoğraf katalitik verecek güneş test ışığı daha saatlerce anlaşılabilir olabilir. Daldırma kaplama yöntemi gözenekli malzemelerde çok etkili bir yöntem gözlendi ve basit bir yöntemdir. SEM analizi test TiO_2/Er^{3+} bağlandı. Bu işlenmiş dokuların dokuma yapılar istikrarlı tutulur ve pamuk daralma izlemek değildi gösterilmiştir. XRD analizi ER^{3+} ' nın dönüşümlü lüminesans en iyi performansı gösterdi.

Anahtar kelimeler: Nanoteknoloji, Kendini Temizleyen, Fonksiyonel tekstiller.

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SYMBOLS AND ABBREVIATIONS

Some symbols and abbreviations used in this study are presented below, along with description.

μm	Micrometer
3D	Three displays
ATR- IR	Attenuated total reflection with infrared
C	Carbon
°C	Celsius degree
CO_2	Carbon dioxide
Cu TCPP	Cutcpp Tetrakis carboxyphenyl porphinatocopper
E	Electron
Er^{3+}	Erbium
H	Hour
h^{+}	Electron hole
Ho^{3+}	Holmium
HRTEM	High-resolution transmission electron microscopy
Hv	Light
Min	Minute
NIR	Near-infrared spectroscopy
Nm	Nanometer
NPs	Nano Particles
O	Oxygen
Pr^{3+}	Praseodymium
RE	rare earth
SEM	Scanning electron microscope
Si O_2	Silicon dioxide
Ti O_2	Titanium dioxide
Tm^{3+}	Thulium
UC	Up-conversion
UV-Vis	Ultraviolet–visible spectroscopy

UV	Ultraviolet
Xe lamp	Xenon lamp
XRD	X-ray diffraction
$YAlO^3$	Yttrium aluminum trioxide
Yb^{3+}	Ytterbium
Λ	Wavelength

1. INTRODUCTION

Nanotechnology has benefited the most in the production of these functional textiles. Nanotechnology is a scientific discipline that researches the materials of the future with superior features. These superior features are found on the nanometer scale. it is predicted that the demand for composite materials formed by combining textile fibers and materials with other polymers and materials will increase to a great extent. Future wearers will increase the production and use of multifunctional intelligent (interactive) textile products that can provide other services, especially in the health and safety.

The original idea of self-cleaning textiles envisioned a scenario where tablecloths and suits shrug off coffee, tea, and other stains where large awnings, tents and other architectural structures stay spotlessly clean without requiring any washing or cleaning. Due to the remarkable developments made in this field during the last few decades, a phenomenon first observed in the lotus leaf and so named the lotus effect. However, subsequent research established that a surface can also be made self-cleaning by photocatalytic breakdown of organic compounds such as adsorbed dirt, contaminants, pollutants or microorganisms into carbon dioxide and water, by metals having semiconductor properties.

In many applications, the use of textiles is limited due to their soiling and wetting behavior . To overcome this limitation, textiles are improved with a variety of finishes of different product classes. Recently, products have been invented that make use of the Lotus Effect and implement self-cleaning properties to a textile surface. The successful realization of this effect leads to a significant reduction in the cleaning requirement of such surfaces.

The lotus effect, is achieved by chemical and geometrical modification of a surface. By creating micro and Nano scale roughness accompanied by a hydrophobic coating, dirt on the surface can be removed by water droplets as they bead up and roll off the hydrophobic surface, thus keeping the surface clean (Daoud et al., 2011). Photocatalytic self-cleaning, on the other hand, is based on chemical breakdown of dirt through photo oxidation and photo reduction reactions in the presence of light (Fujishima and Zhang, 2006). Titanium dioxide or titania is the most frequently used substance in this field. Photocatalytic activity can break down the organic compounds present in cell walls of bacteria, as well as organic odor molecules present in the atmosphere, thus inducing a self-cleaning function as well as conferring antimicrobial and deodorization properties to treated surfaces.

Photocatalysis, that is the acceleration of chemical redox reactions thanks to the synergy of particular materials (usually semiconductor) and solar light, is one of the most promising tool for the handling of different problems in several areas of applied chemistry, including environmental science. In fact photocatalysis allows the photo-decomposition of both organic and inorganic polluting substances absorbed or deposited on photoactive surfaces by redox reactions induced by solar light.

Titanium dioxide (TiO_2) is one of the mostly used photocatalytic material in order to develop innovative materials and solutions in different fields: water and air purification, anti-bacterial and self-sterilizing surfaces, food industry, coating, paper production, cosmetics and building materials (Fujishima and Honda, 1972; Chen et al., 2009). In construction sector titanium dioxide has been used to realize self-cleaning treatments in a large number of building elements, as cement mortars, exterior tiles, paving blocks, glasses, paints, finishing coatings, road-blocks, concrete pavements (Chen et al., 2009; Bondioli, 2009). Its widespread use is attributed to its main features: high catalysis efficiency, chemical stability, inexpensiveness, non-toxicity, compatibility with traditional construction materials (Fujishima and Zhang, 2006; Chen et al., 2009), As TiO_2 treated surfaces absorb light they provide protection to surfaces against photoyellowing and photodegradation. Because of such multifunctional properties imparted by TiO_2 coatings, this technology is receiving increasing attention in research as well as commercial processes in the last few years (Fujishima, 2000)

Photocatalytic properties under UV light have been developed. However, the large band gap of TiO_2 requires an excitation wavelength that falls in the UV region. Since, the solar light reaching the earth consists of only 5% UV and almost 43% visible light, application of UV-based TiO_2 photocatalysis is limited. To utilize the visible region of the solar spectrum for catalysis, the optical properties of titanium is therefore, indispensable. In this regard, TiO_2 can be modified by many methods, such as up conversion materials.

The sol-gel method is a ceramic production method that has been studied over the last two decades and is used as a shortening of the word solution-gelation. The sol-gel method is a chemical method and is described as "Sol-gel Method" because it contains a sol as starting material and the gel is obtained using this sol. The method is one of the most important techniques for the formation of different functional coatings and has advantageous properties. For example; easy coverage of large areas, homogeneity of highly mixed oxide films, and accessibility to nanocrystalline materials.

Dip coating is an industrial coating process which is used, for example, to manufacture bulk products such as coated fabrics and specialized coatings for example in the biomedical field and also use to create thin-film coatings. The dip coating methods are simple methods for nanoparticle deposition.

Due to the advances in nanotechnology applications, interest in self-cleaning surfaces is increasing. These coatings find many different areas of application such as windowpanes, cements, textiles and coting. For example, self-cleaning coatings used in textiles can reduce the cost of cleaning while extending the life of textile products as it reduces the number of washings. In this study, it was aimed to achieve a self-cleaning cotton fabric and textiles coated by dip coating method UPC/TiO_2, and effect of dip coating method nanoparticle deposition on the textiles. The thin films having various UPC/TiO_2 ratios were synthesized by SOL-GEL method. Photocatalytic self-cleaning and activities of the thin films were investigated through this study. And the other aimed from this study is Investigation of the effect up conversion assist TiO_2 photo catalytic Materials on self-cleaning textiles.

2. LITERATURE REVIEW

2.1. History of Self Cleaning

Over thousands of years of natural selection, living organisms including all plants and animals on our earth are evolutionarily optimized functional systems. One of their most fascinating properties is the ability of self-cleaning which means that the surfaces can repel contaminants such as solid particles, organic liquids, and biological contaminants by the action of rolling-off water drops. This kind of self-cleaning surfaces has both the ability of super hydrophobicity and self-cleaning properties, and with lotus leaf as the typical representative, therefore is known as “Lotus effect” (Nosonovsky, 2008; Latthe, 2014) During the past few decades, a large number of studies have been conducted to a full understanding of the functions, structures, and principles of self-cleaning surfaces. By now, many different synthesis technologies have been developed to design and fabricate self-cleaning surfaces. (Lee, 2009; Bixler, 2014) Today, a great variety of self-cleaning surfaces based on lotus effect have also been commercialized with the range from window glasses to solar cell panels (Parkin, 2005).

To achieve self-cleaning properties nature uses an efficient method, which has been perfectly realized on the leaves of the lotus plant (Barthlott, 1997). Besides this species, self-cleaning properties can be found on a variety of other biological surfaces, such as cabbage, reed and nasturtium. The main function of nanostructured super hydrophobic surfaces in nature is probably the protection against pathogenic organic contamination like bacteria or spores. These are regularly removed from the leaves by rainfall.

Although discovered already in the 1970s, Barthlott and his team in the 1990s identified the reason for the self-cleaning properties and named it the ‘Lotus Effect’. It is based on the specific properties of micro- and nanostructured super hydrophobic surfaces, which are always completely cleaned by rainfall: the contact area of water and dirt particles is largely minimized by the double structured surface. This in combination with hydrophobic chemistry results in extremely high contact angles that let water drops roll off at the slightest inclination, in so doing, taking up all adherent particles and removing them, leaving behind a clean and dry surface.

On many of these surfaces even high-viscous liquids drip off. The Lotus Effect is based on a minimization of the contact area of hydrophobic surfaces by an overlapping double structure approximately 100 nm to approximately 100 μm in size. Because of this active principle, the Lotus Effect differs from the ‘soil-repelling’ and ‘soil-release’ function. As the Lotus Effect depends only on physicochemical characteristics it is independent of the living system and can be transferred into technical systems. The first commercial products with the Lotus Effect were wall painting and roof tiles.

In order to reveal the roles of the roughness and waxes covered over the entire surface of lotus leaf on the self-cleaning property, many scientific research workers carried out extensive researches. Neinhaus and Barthlott investigated nearly 300 kinds of plant leaf surface, and indicated that this self-cleaning property is caused by both the rough structure and the hydrophobic epicuticular waxes (Barthlott, 1997).

Figure 1. Leaves and flowers of Lotus (Özdoğan et al., 2006).

Lotus leaves have self-cleaning properties. As shown the image shows the surface of a Lotus leaf (Fig. 1) Persistent stains applied by researchers were easily removed by rain droplets and rolled off the leaf. By the discovery of the hydrophobic and nanostructured surface of this leaf, lots of end uses, particularly as coatings for buildings, aircraft, cars and textiles (Özdoğan et al., 2006).

Self-cleaning technology has developed since the late 20th century, and some achievements have led to practical application (Bixler, 2013). As we know that, the self-cleaning property of lotus leaf is based on the combine of its roughness surface and low surface energy wax (Cheng, 2013). Therefore, we can obtain two ideas for preparation of self-cleaning surfaces inspired by the Lotus effect but not constrained by lotus leaf structure. First, to construct micro- Nano composite hierarchical structure on an initial hydrophobic surface, and second, to modify low surface energy materials on the micro-nano composite hierarchical structure surface.

2.2. Historical Background of Photocatalysis

Photo oxidation of an organic substance, chlorazol sky blue, through photosensitization of titanium dioxide at λ= 365 nm was first reported by Goodeve and Kitchener in 1938 (Goodeve et al., 1938). Later on, Kato and Mashio, (Fujishima and Honda, 1972) extended the study to tetralin and 2-propanol using titanium dioxide and zinc oxide in 1964. Shortly thereafter, a breakthrough was brought in 1964 (Filimonov, 1964). Shortly thereafter, a breakthrough was brought in by Honda and Fujishima who, inspired by photosynthesis in plants, investigated photo electrolysis of water (water splitting) with light energy. They discovered that water can be decomposed into oxygen and hydrogen through photo electrochemical reaction in the presence of ultraviolet-visible light using rutile titanium dioxide as the anode and platinum as the counter electrode in aqueous electrolyte solutions. In 1972, the conception of solar-activated electrochemical photolysis of ware demonstrated that titanium dioxide semiconductor could be used as an environmental friendly photocatalyst for solar-assisted energy conversion (Fujishima and Honda, 1972).

Influenced by Frank and Bard, who were the first to investigate the decomposition of toxic cyanide in water by photocatalysis with titanium dioxide in

1977 (Frank et al., 1977) the detoxification of organic pollutants using titanium dioxide powder without plasticization, by way of a photocatalytic process under ambient condition, has attracted worldwide attention. In the middle of 1980s, the fanaticism of using titanium dioxide electrode as a tool for hydrogen production was shifted due to a number of challenges, such as instability, low efficiency and lack of reproducibility. Simultaneously, scientific studies on titanium dioxide as a multifunctional photocatalyst had started. Later on, research on photocatalysis focusing on pollutant removal blossomed particularly in the treatment of wastewater and polluted air. Nevertheless, titanium dioxide photocatalysis was not commercially attractive due to the low quantum efficiency caused by immature synthesis technologies and thus almost none of these developments had been commercialized (Hashimoto et al., 2005).

Since the discovery of photocatalysis, scientists mostly focused on exploring the potential of titanium dioxide in environmental applications, while the feasibility and compatibility between titanium dioxide, photocatalytic technologies and substrate substances had been overlooked. Until 1990s, there was an increasing interest in the concept of photo-induced self-purification materials through the incorporation of photocatalysts in various substrates in order to introduce a function of disinfection, primarily for water and air treatments (Watanabe et al., 1993). Knowing its potential in maintaining cleanliness of a surface, the utilization of titanium dioxide coating as self-cleaning surface was explored. The first photocatalytic self-cleaning ceramic was realized by (Fujishima and Heller, 1995) concurrently in early 1990s. Many researchers and investors conceived similar ideas to explore a number of self-cleaning products, such as self-cleaning lamp covers, self-cleaning glasses, self-cleaning window blinds, self-cleaning tents, etc. With more photocatalytic-products available, new application areas have been exploited. In 1995, Fujishima research group, accidentally discovered that titanium dioxide possesses a high photo-induced hydrophilicity after light irradiation, which widened the application of the photocatalyst as surface coating. Ever since, industrial products using photocatalytic surface functionalization treatment are marked as hydrophilic self-cleaning coating. Three years later, the photocatalytic antimicrobial property of titanium dioxide-coated materials was ascertained, in which Escherichia coli could be completely decomposed by titanium dioxide under UV irradiation.

In the twenty-first century, advanced photocatalytic technologies have been continually pursued. However, the application has greatly been limited due to the high temperature required in the application process. Until 2004, with the aid of an advanced bottom up nanotechnology approach and the sol–gel process, Daoud and Xin first fabricated self-cleaning cotton through in situ nucleation and growth of anatase titanium dioxide at low temperature and ambient pressure. Since then, numerous photocatalytic self-cleaning surface functionalization processes have been proposed for low thermally resistant materials. Photocatalyst-substrate adhesion, coating homogeneity and photocatalytic efficiency are greatly dependent on the base substrates. With further improvement of the photocatalytic self-cleaning coating techniques, (Daoud, 2004) the application of homogenous titanium dioxide coating in different types of materials with reproducible photoactivity has become possible. On the other hand, many endeavors have been devoted to improve the photocatalytic properties of titanium dioxide. Methods such as dye/surface sensitization, selective ion doping, composite semiconductor coupling, surface chelation have been widely explored, particularly in (1) extending the effective absorption range of titanium dioxide from ultraviolet to visible-light region; (2) suppressing the recombination of the generated electron–hole pairs through enhancing the charge separation; and (3) modifying the quantum efficiency of the heterogeneous photosensitive catalysts. (Chatterjee and and, 2005) To date, attempts are still being dedicated to produce stable visible light photocatalysts with efficient photochemical reactions in diverse applications (Linsebigler at al., 1995).

$$TiO_2 + hv \longrightarrow e- + h+ \qquad (1)$$
$$e- + h+ \longrightarrow Tio_2 \qquad (2)$$
$$e- + O_2 \longrightarrow O2- \qquad (3)$$

(Linsebigler at al., 1995)

2.3. General Remarks About Upconversion Materials

Upconversion was first observed, in the 1960s, by Auzel and independently by Ovsyankin and Feofilov. The phenomenon has been reviewed (Auzel, 2004). It was not for another 30 years that it started to come into its own, when nanotechnology began to take off. Luminescent lanthanide nanoparticles have been proved to be extremely useful for bioimaging, biolabels, and bioassays.

Upconversion is an optical process that involves the conversion of lower-energy photons into higher-energy photons, as in figure 2. It has been extensively studied since mid-1960s and widely applied in optical devices. Over the past decade, high-quality rare earth-doped upconversion nanoparticles have been successfully synthesized with the rapid development of nanotechnology and are becoming more prominent in biological sciences (Chen and Zhao, 2012).

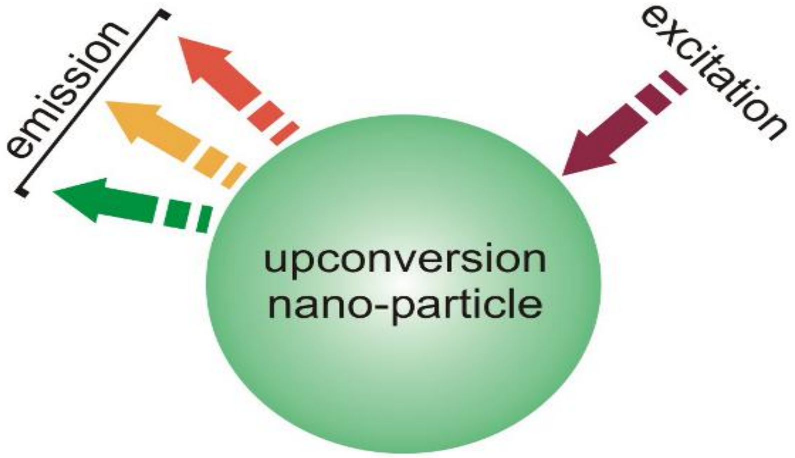

Figure 2. Basic function of the Upconversion materials (Jun et al ., 2015).

Upconversion materials have been employed as energy relay materials in dye sensitized solar cells to broaden the range of light absorption. However, the origin of the enhancements can be induced by both upconversion and size-dependent light scattering effects. (Zhou et al, 2014) Manipulation of upconversion (UPC) emission is of particular importance for multiplexed bio imaging (Jun et al ., 2015).

2.4. Basic Structure of Upconversion Nanoparticles

The basic structure of upconversion nanoparticles (UC) consists of transition metal, lanthanide or actinide, dopant ions embedded in the lattice of an inorganic crystalline host. of these dopant ions, the trivalent lanthanides are predominantly used because most of them (except lanthanum, cerium, ytterbium and lutetium) have multiple metastable states, making them well-suited for UC. Although a single lanthanide ion is sufficient to produce the UC effect, co-doping is usually favored as most lanthanide ions have low absorption cross sections leading to weak emission. To enhance UC efficiency, co-doping between two different lanthanide ions, the first serving as an absorber and other acts as an emitter, is generally performed to exploit the energy transfer UC process. Ytterbium (Yb^{3+}) ion is often used as the absorber ion due to its larger absorption cross-section in the near-infrared (NIR) region. Conversely, erbium (Er^{3+}), thulium (Tm^{3+}) and holmium (Ho^{3+}) ions are frequently used emitter ions due to their equally spaced energy levels that facilitate photon absorption and energy transfer in UC processes (Wang , 2009).

Another important component of UC is the host materials, which determines the optical properties and emission efficiency. The desired host materials should have close lattice matches with the dopant ions and low lattice phonon energies to minimize energy losses and maximize irradiative emissions. Halide-based compounds are mostly used due to their low phonon energies but the hygroscopic nature of the heavier halides makes the fluorides a more popular choice (Wang, 2009).

2.5. Fundamental Processes Leading to Infrared Upconversion

The mechanism concerning infrared upconversion phenomena in Yb^{3+}-. sensitized materials was once extensively investigated during the period when the devices were of interest as possible display devices. Although the upconversion phenomena are apparently very complicated, the underlying fundamental processes involved are relatively simple and their physical nature has been well explored. The fundamental processes include optical absorption, radiative and nonradiative decays and energy transfer.

The optical absorption process in rare earth ions in solids has been thoroughly discussed on both experimental and theoretical grounds. As to irradiative decay processes, calculations were made for decay rates of rare earth ions in certain crystal lattices (Weber, 1967). There is a relation, Fiichtbauer- Ladenburg equation, connecting the irradiative decay process with optical absorption process. Nonradioactive decay processes are dependent upon the host material and level characteristics. However, it is generally known that the nonradioactive decay rate decreases approximately exponentially with increasing energy gap to the next lower level (Weber, 1967 ; Riseberg et al., 1968).

It is widely accepted that the resonant energy transfer between the same or closely matched energy levels in rare earth ions is very rapid. The process is known to be due to exchange or multiple interaction between neighboring ions (Curie, 1963). Hence the excitation energy is considered to be shared by a number of Yb^{3+} and Er^{3+} ions due to rapid energy transfers before losing energy by means of radiative or nonradiative decays. Energy transfer between levels having considerable energy mismatch can take place in the form of phonon-assisted energy transfer. The energy transfer rate in this case is considered to be small and to decrease exponentially with increasing energy mismatch. However, since phonon-assisted energy transfer is a unidirectional process, efficient net energy transfer may often take place.

2.6. Main Applications of Upconversion Materials

Potential applications of upconversion materials include lasers, novel display technologies, solar cells, and biophysics. In this section, describe of uses upconversion materials in these applications.

2.6.1. Lasers

One of the first historical applications of upconversion materials was in the area of solid-state compact lasers emitting in the visible. Early lanthanide based upconversion lasers only operated at low temperatures, making the systems impractical.

Most of the currently studied upconversion lasers are based on heavy-metal fluoride fibers which tend to have poor chemical, thermal and mechanical properties. The development of highly efficient and stable materials that can up convert at room-temperature with low excitation density thresholds is required (Paschotta, 2000).

2.6.2. 3D volumetric displays

Lanthanide-doped transparent heavy metal fluoride glasses were synthesized and shown to have good infrared to visible upconversion properties at room-temperature. A two-laser excitation system combined with a mechanical scanning system was used for the selective excitation of a voxel of sample, at the crossing point of the two laser beams. Red, green and blue emissions could be obtained in glass layers doped with Pr3+, Er3+ and Tm3+. By rapid spatial scanning of the transparent upconverting material, the position of the excited voxel could be moved within the volume of the sample, thus allowing 3D images to be drawn. potential applications of 3D volumetric displays include computer assisted design, medical imaging, television and art.

2.6.3. Solar-cells

The use of up converting materials is being considered in the photovoltaic industry for the development of high-efficiency solar cells. The largest losses in the traditional silicon solar cells arise from the mismatch between the wavelengths in the solar spectrum and those that can be efficiently used by the solar cells. In particular, the solar photons with energies below the band gap of the silicon semiconductor are not absorbed and do not contribute to energy conversion, while a portion of energy above the band gap is also lost. Significant improvements in solar cell efficiencies can therefore be expected by combining luminescent upconversion and down-conversion layers that would shift the energies of these otherwise wasted photons to the spectral range that can be used by the solar cells (Trupke, 2006).

2.6.4. Bio-imaging

Upconversion nanomaterial's could be used as probes for single molecule imaging in biological cells. For bio imaging , nanoparticles (having diameters below 50 nm after functionalization) with high brightness and continuous emission are required. In addition, they need to be resistant to photo bleaching and have a minimal spectral overlap with the cellular auto fluorescence. Current imaging methods use organic dyes or fluorescent proteins. The use of such probes is problematic because of their sensitivity to photo bleaching which limits the imaging times. Another major drawback is that these probes are usually excited by UV light, often resulting in tissue photo-toxicity and limited observation depth (due to poor light penetration) (Wu, 2009).

2.7. TiO_2

TiO_2 titanium, is an inert, nontoxic, biocompatible and abundant transition metal oxide. Rather than other semi-conductor metal oxides, TiO_2 plays an important role in permanent disinfection and photo-degradation of unwanted and toxic organic substances from contaminated air and water due to its inert structure, photo-stability, high efficiency, water insolubility and low cost.

Titanium is a very well-known and well-researched material due to the stability of its chemical structure, biocompatibility, physical, optical, and electrical properties. Its photo catalytic properties have been utilized in various environmental applications to remove contaminants from both water and air (Li et al., 2008). Titanium-based photo catalytic systems are used for a variety of applications such as decomposition of unwanted and toxic organic compounds, destruction of pollutants from contaminated water and air and killing of harmful bacteria and cancer cells (Comparelliet al., 2005). The unique feature of the photo catalytic process is that it breaks down the pollutants and harmful organic compounds into simple molecules such as carbon dioxide and water (Vijay et al., 2009). Due to its stability in harsh environments, titanium dioxide TiO_2 is a ceramic that has the potential to be the material of choice for gas sensors that operate at temperatures above 400 °C (Seeley et al., 2009).

Anatase is the most popular crystalline phase used in photo catalytic processes due to having a more negative conduction band edge potential (higher potential energy of photo-generated electrons) rather than rutile (Yu, 2008). Yet there are studies in literature that show that rutile phase or mixture of rutile and anatase phases has higher photo catalytic activity than a pure anatase phase .TiO_2 has a wide application area. It can be used as white pigment in paint (especially rutile type), paper (Macwan et al., 2011) rubber, plastics and cosmetics industry and optical coatings, dye-sensitized photo electrochemical cells and gas sensors are the examples of applications of TiO_2. Furthermore, TiO_2 thin film photo catalysts prepared on glass, tile, various architectural materials and cotton fabrics have been described as promising antibacterial, self-cleaning and deodorization systems (Wu, 2011).

2.8. Photo Catalytic of TiO_2

Ever since 1977, when Frank and Bard first examined the possibilities of using TiO_2 to decompose cyanide in water (Frank, 1977), there has been increasing interest in environmental applications (Fujishima, 2000). TiO_2 is close to being an ideal photo catalyst in several respects. For example, it is relatively inexpensive, highly stable chemically and the photo generated holes are highly oxidizing.

As has been pointed out by Heller, all of the extensive knowledge that was gained during the development of semiconductor photo electrochemistry during the 1970 and 1980s has greatly assisted the development of photo catalysis (Heller, 1981). In particular, it turned out that TiO_2 is excellent for photo catalytically breaking down organic compounds. For example, if one puts catalytically active TiO_2 powder into a shallow pool of polluted water and allows it to be illuminated with sunlight, the water will gradually become purified. Ever since 1977, when Frank and Bard first examined the possibilities of using TiO_2 to decompose cyanide in water (Frank et al., 1977), there has been increasing interest in environmental applications. These authors quite correctly pointed out the implications of their result for the field of environmental purification. Their prediction has indeed been borne out, as evidenced by the extensive global efforts in this area (Frank et al., 1977; Heller, 1981; D.F. Ollis, 1993).

2.9. Improving Photocatalytic of TiO_2 by Addition of Upc Materials

Since the discovery of the semiconducting properties of TiO_2 (band-gap energy (Fujishima and Zhang, 2006), great research efforts have been directed to a better exploitation of solar energy in photocatalysis. However, despite the great number of photocatalyst formulations proposed, most of them are only active under ultraviolet (UV) radiation, which is only a little fraction (5%) of solar light. To be of practical use for photocatalysis, the photo-response of the transition metal oxides should be within the visible light (43%) of the electromagnetic radiation reaching the planet’s surface.

Different approaches to improve the exploitation of sun lighting photocatalytic processes have been proposed, especially oxide semiconductors doping (Khan et al., 2002) or titania photosensitization (Zhao et al., 2005). However, both approaches still suffer from disadvantages. Moreover, titania photo-sensitization with organic dyes still presents major limitations for applications in photocatalysis, due to the poor stability of the dye, which can undergo desorption, photolysis and oxidative degradation, and fast back electron transfer, resulting in low quantum yield for the photocatalytic reaction (Zhao et al., 2012) .

Good visible photocatalytic activity results were found on N-doped TiO_2, both under visible irradiation and under solar simulated radiation in the removal of several pollutants such as emerging contaminants (Vaiano et al., 2015). The photocatalytic performance of a semiconductor material is mainly limited by its intrinsic optical properties as the occurrence of the photocatalytic reaction requires an excitation source with energy equal or greater than the band gap of the semiconductor (Yang et al., 2014). So, a main issue emerged, since the photocatalytic activity is related to the light propagation inside the overall volume of photoreactors (Vaiano, 2014). Therefore, since the improving of the photo-catalytic reactivity is correlated to an efficient irradiation of the catalytic surface, the chance to get this improvement by modifying a photocatalyst with light carriers such as emitting phosphorescent particles (generally known as phosphors) has been successfully verified to confer additional radiation emission or to decrease the optical path of irradiation towards the photocatalyst (Wu et al., 2013). A reasonable consequence of such an approach for the intensification of the photocatalytic process seems to be the use of up-conversion phosphors able to convert low-energy into high-energy photons (Wang, 2009). Few examples report the use of inorganic up-conversion phosphors in a photocatalytic system. To this purpose, active carbon supported un doped TiO_2 catalyst (C-TiO_2) was modified with $Er^{3+:}YAlO_2$ up-conversion phosphors that convert visible light into UV light able to photoexcite TiO_2 (Dong et al., 2015). It is worthwhile to high light that the photocatalytic tests were carried out with a visible light source that is not able to activate un doped TiO_2.

Moreover, in order to utilize visible light directly, C-TiO_2 catalyst was modified by blue, green and red color emitting inorganic up-conversion phosphors through calcination assisted solvothermal method. The characterization data demonstrated that such photocatalysts could be excited by UV, visible and NIR light simultaneously. In this case, all the composites exhibited excellent induced Rhoda mine B degradation activity under the irradiation of 980 nm NIR laser, although uncoupled phosphors and C-TiO_2 TiO_2 showed no destruction ability . However, it is very important to underline that only 35% of dye decolonization has been achieved after 5 h of irradiation (Wu et al., 2014). Recently, triplet–triplet annihilation up-conversion luminescence has emerged as an efficient process with anti-Stokes shift upon excitation by low power light intensity . When compared to rare-earth up-conversion phosphors, the organic ones have several advantages including more intense absorption coefficient of sensitizer and higher quantum yield (Rachford and Castellano, 2010).

2.10. Application of TiO_2 for Self Cleaning

Self-cleaning applications using semiconducting powders or thin films have become a subject of increasing interest especially in the last 10 years. The self-cleaning property has been known to be a mutual effect between photocatalysis and hydrophobicity. The photocatalysis property help decompose the organic substances that come into contact with the surface and thus prevent them from building up. The hydrophobicity makes the cleaning more effective as the water spread over the surface rather than remaining as droplets which help collect the dirt better, make the surface dry faster, and moreover, prevent the undesirable water streaking or spotting on the surface. (Guan, 2005) TiO_2 is one of the most widely used materials for self-cleaning application because its thermo stability and photocatalytic properties (Cui et al., 1993; Parra et al., 2004). The ability to engineer the TiO_2 to have super hydrophilic property on surfaces is also an advantage, Compared with traditional advanced oxidation processes the technology of photocatalysis is known to have some advantages, such as ease of setup and operation at ambient temperatures, no need for post processes, low consumption of energy and consequently low costs. (Bahnemann, 1994)

The heterogeneous photocatalytic oxidation with TiO_2 meets the following requirements what could make it competitive with respect to other processes oxidizing contaminants:

• A low-cost material is used as photocatalyst.

• The reaction is quite fast at mild operating conditions (room temperature, atmospheric pressure).

• A wide spectrum of organic contaminants can be converted to water and CO_2.

• No chemical reactants must be used and no side reactions are produced.

2.11. Sol Gel

The goal of sol-gel processing is to control the structure of a material on a nanometer scale from the earliest stages of processing. For pure silica powders, fibers, and even monoliths. The potential of improved properties due to ultra-structural processing, control of higher purity, and greater homogeneity has been realized. Other engineering advantages of the lower temperature chemically based sol-gel processing such as net-shape casting, fiber pulling, and film coating have also reached economic potential. (Hench and West, 1990). The sol-gel method requires lower temperatures (100-400 °C) than conventional methods, especially in thin film coatings in inorganic construction. The most technologically important application area of the sol-gel method is thin film formation.

The method of application of the method can be given in three approaches first, a colloidal sol is prepared and the particles are soldered. The particles are then dried. According to the second approach, the colloidal particles on the left are connected to form a gel. This gel is then dried and heated to obtain the crystallized material gel is formed by polymerization of each oligomer units. The polycondensation and hydrolysis of organometallic compounds such as alkoxides leads to gelation.

Applications of sol-gel technology in textiles, water, oil and soil repellency, , bio catalytic properties, biocompatibility properties, electrical conductivity, dyeing resistance. Furthermore, in the textile industry of sol-gel technology; in the production of photochromic, electro chromic and thermo chromic textiles, in the development of fastness, in the modification of barrier properties; has the potential to be used in the production of antimicrobial fabrics in the production of super hydrophobic fabrics with improved filtration, adsorption, selectivity and crease.

In the textile industry it is possible to obtain very different properties of textile materials by coating with sol-gel technology. For this purpose, extensive researches have been made in recent years. Different sol-gel matrices such as inorganic, organically modified, hybrid sol-gels and interpenetrating polymer networks have been used for encapsulation. Perhaps each type of sol-gel has its own advantages and disadvantages Inorganic sol-gels are good in optical transparency; chemical robustness but brittleness and low porosity are major limitations. Similarly organically modified sol-gels have good tunable porosity and electrochemical activities, but are relatively fragile and have limited optical transparency (Collinson, 2002). Sol-gels can be prepared with flexible rigidity, controlled porosity, and balance hydrophobicity and hydrophilicity, but poor optical transparency and structural collapse on drying are somewhat limiting factors.

2.12. Dip-coating

The wet chemical sol-gel processing paves the way to the versatility and ease of liquid film deposition techniques for a variety of inorganic and hybrid coating materials. Among the available deposition techniques, dip coating is the most widely used for industrial and especially laboratory applications which is essentially founded on the simple processing, the low cost and the high coating quality. Nevertheless, other techniques like spin coating, spraying or meniscus coating are practical as well for some applications which will be demonstrated in other chapters of this book. The industrial origins of dip coating trace back to the seminal works at Schott in the 1940s (Islich, 1982). And ever since the late 1950s it is used in the production of automotive rear mirrors. In the following years also large area optical coatings like antireflective and solar control glasses were coated using this technique.

Dip coating designates the deposition of a wet liquid film by withdrawal of a substrate from a liquid coating medium. The batch dip coating process can be divided into five stages: immersion, start-up, deposition, drainage, and evaporation (Fig. 3), but nevertheless the underlying chemical and physical processes are mostly overlapping. Starting with the immersion of the substrate, a coherent liquid film is entrained on withdrawal of the substrate from the coating fluid, which then consolidates by drying and accompanying chemical reactions. To obtain the final coating material, normally a further curing or sintering step is then necessary (Scriven, 1988).

The deposition step represents the actual sol-gel transition with concomitant processes of draining, evaporation and hydrolysis. In the experiment this becomes apparent in a receding drying line that is moving downwards with colorful parallel interference lines, leaving behind the consolidated gel film. In contrast to the bulk sol-gel process, the complete transition passes in only a few seconds or less if volatile solvents are used. Due to the evaporation and the result rig cooling furthermore a downward laminar flow of vapors forms out over the surface of the wet film, enhancing the drying and keeping the water content almost constant. In this stage of the deposition any turbulence or variation in the atmosphere will inevitably lead to in homogeneities in the film properties.

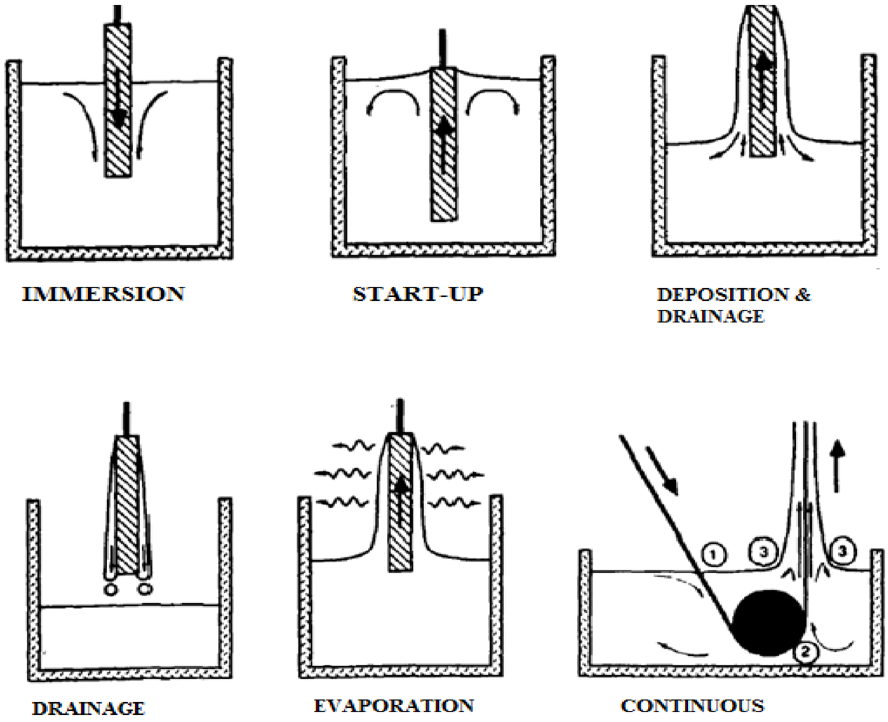

Figure 3. Fundamental stages of sol-gel dip coating (Scriven, 1988).

The continuous dip coating process separates immersion from the other stages, relegates startup to a very short episode, hides drainage in the deposited film and restricts drying to the deposition stage and afterward. So dip coating of a continuous sheet, is the process to consider first. The coating thickness can be controlled basically by the withdrawal speed and by the concentration and viscosity of the coating liquid. For a given coating system, however, there is normally an operational range that allows the preparation of smooth and homogeneous films. Dip coating is one of few techniques that allow a simultaneous double-sided coating of flat substrates which is of advantage especially in the production of optical filters . Typically, such films can be deposited with a single layer thickness ranging from only a few nanometers to approximately 200 nm for oxide coatings prepared from solutions of metal salts. Thicker films up to 1 μm thickness can be obtained from colloidal systems and even several microns are accessible with inorganic-organic hybrid materials.

2.13. Literature Summary

Afzal et al. (2013) self-cleaning properties have been investigated by conducting photocatalytic degradation of methylene blue, coffee and wine stains under visible-light irradiation. CuTCPP/TiO_2-coated cotton fabrics showed superior self-cleaning performance when compared to bare TiO_2-coated cotton. Furthermore, CuTCPP/TiO_2-coated fabrics showed significant photostability under visible-light as compared to free base TCPP/TiO_2-coated fabrics. The fabrics were characterized by FESEM, XRD and UV-Vis spectroscopy. An insight into the mechanistic aspects of the CuTCPP/TiO_2 photocatalysis is also discussed. Visible-light driven self-cleaning cotton based on copper (II) porphyrin/TiO_2 catalyst exhibits significant potential in terms of stability and reproducibility for self-cleaning applications.

Mendez-Ramos (2013) the study has explored the emerging and ground-breaking photonics approach to enhance the photocatalytic activity of one of the main semiconductor electrodes used in water-splitting reactions, titanium dioxide (TiO_2), the blue shifting of the incident radiation by means of a highly efficient up-conversion by a rare-earth (RE) doped luminescent material to assist in the harvesting of long wavelengths in unused portions of infrared light. the study present an up to 20% improvement of the photocatalytic action of the commercial benchmark TiO_2 efficient photocatalyst in the decomposition of methylene blue in water under Xe-lamp irradiation, and also an outstanding enhancement by a factor of about 2.5 of the photolytic degradation rate of this pollutant. Our results prove that the ultraviolet (UV) radiation that reaches the TiO_2 particles is increased by the addition of the RE-doped powder material into a slurry type photo-reactor, boosting both the photocatalytic and photolytic degradation rates. Thus, show the feasibility of handling and transforming the incoming infrared radiation, bridging the UV gap of the photocatalytic semiconductor.

Tung, (2011) the study , an overview of the development of photocatalytic self-cleaning fibers and their future prospects is presented. These fibers with their tremendous potential in a wide range of applications may bring about substantial benefits to mankind and the environment through the saving of natural resources consumed during washing and cleaning processes. Although more research is needed to ensure maximum efficiency of the technology at minimum impact on the safety of living organisms and the environment, the scope of this technology may also be extended to as yet unknown fields.

Qi et al. (2006) Nanocrystalline titanium dioxide has been prepared under ambient pressure and at temperatures close to or approaching room temperature using hydrolysis of titanium tetraisopropoxide in an acidic aqueous solution. A transparent thin layer of nanocrystalline titania has been produced on cotton textiles by a dip-pad–dry-cure process. These TiO_2 coated cotton textiles possess significant photocatalytic self-cleaning properties, such as bactericidal activity, colorant stain decomposition and degradation of red wine and coffee stains. Self-cleaning cotton may find potential commercialization in the textile industry.

Bozzi et al. (2005) found that the cleaning and reduction of red wine, coffee, make-up and oil stains in the study of self-cleaning with light under the sunlight with low temperature modified with TiO_2, gradually increased CO_2 during daylight illumination at 50% with the follow-up of the observed. UV activated textiles coated with TiO_2 for the bare-treated cotton were found to be the most active sample during the cleaning of coffee and red wine stains under daylight. The amount of self-cleaning which resulted in dirt cleaning was calculated for the evaluation of the photoactivity of the TiO_2 groups prepared in different experimental conditions.

Wu et al. (2009) prepared self-cleaning fabrics with TiO_2 nanoparticles prepared by low-temperature aqueous sol process. They adopted SEM, HRTEM, ATR-

IR and XRD as the characterization technique. They have produced anatase TiO_2 nanoparticles in sizes of 3-5 nm. They have shown that TiO_2 coated cotton fabrics are a distinct self-cleaning feature, such as antibacterial activity and photocatalytic degradation of dyes.

Guan, (2005) Self-cleaning glass can be realized utilizing photo-induced hydrophilicity of titanium dioxide. In order to understand the photo-induced hydrophilic self-cleaning effect, it is necessary to understand the relationship between the mutual effect of photohydrophlicity and photocatalysis. In the study, the relationship between hydrophilicity, photocatalysis and the self-cleaning effect is investigated. It is found that the TiO_2/SiO_2 surface can have more hydrophilic activity and less photocatalytic activity, or vice versa by adding different amount of SiO_2. It is the synergetic effect of hydrophilicity and photocatalysis that improves and maintains the self-cleaning effect. SiO_2 addition increases the acidity which results in the increase of the hydroxyl content in the composite films, with the consequence that the hydrophilicity and photocatalytic activity are increased during UV irradiation thus enhances the self cleaning effect.

Palamutcu et al. (2011) the study, morphologically well-defined TiO_2 nano particles (NPs), prepared by sol-gel method was coated on the cotton textile surface to develop self-cleaning, UV blocking and antibacterial cotton textile surfaces. Commercially available Degussa TiO_2 powder photocatalyst was used as benchmark for comparison. To evaluate the self-cleaning action of modified textile fabric, tea stains were introduced on the cotton fabric. Under sun-test illumination, decrease in the color of tea stain was followed over time for the determination of self-cleaning performance of the modified textile surface. The effects of TiO_2 treatments on the main functions of cotton fabric were investigated by the measurements of tensile strength, tear strength, wrinkle recovery angle and color fastness measurements. The modified cotton textiles with TiO_2 NPs and Degussa TiO_2 powder showed strong self-cleaning performance under illumination and tea stain was completely removed in 30 min. TiO_2 coating improved UV protection factor of cotton textile by three fold. According to the untreated cotton textile, the modified textiles with sol-gel based TiO_2 NPs and TiO_2 powder showed much stronger antibacterial performance against.

Veronovski et al. (2009) have worked on the development of titanium nanoparticle surfaces on artificial cellulose fibers that facilitate photocatalysis. One of the techniques is to place silica (SiO_2) as an intermediate element between the bound titanium nanoparticles and the underlying cellulose. Electron transmission microscopy (SEM) showed that TiO_2 nanoparticles were retained by the silica network. In this regard, silica can be used as an adhesive between TiO_2 nanoparticles and cellulose fibers. Differences between the surface morphologies of TiO_2 and TiO2-SiO_2 were determined using SEM. The changes in the surface properties of the fibers indicate the presence of TiO_2 and SiO_2.

3. MATERIALS AND METHODS

All experiments were carried out in the Mechanical Engineering Department laboratory, Faculty of Engineering University of Yüzüncü Yıl, Van, Turkey. During the period from April to November 2017.

3.1. Materials

Distilled water was used in all experiments ,Titanium (IV) butoxide reagent grade 0.97%, Ethylene glycol, izo propyl these materials were determined to confirm Dissolving up conversion materials in the solutions. Up conversion materials: Sodium yttrium fluoride ytterbium and erbium doped (99 %), Erbium chloride hexa-hydrate (99.9 %), Yttrium nitrate hex hydrate (99.8 %), erbium nitrate penta-hydrate (99.9 %), Niobium (V) ethoxide (99.95%) were Purchased from sigma Aldrich.

3.1.1. Material to be coated:

Textile In this study, 100% cotton woolen (Flat) textile type: 1595 / Denim textile type: A2994 from ORTA ANADOLU TEKSTIL A.S. Kayseri

3.1.2. Stain used in the staining test:

Tea, ketchup, coffee, methylene blue.

Nanoparticles are tiny, so Series Analytical Balance (figure4) was used in this work, it has high capacity semi micro ranges and Anti-static glass breeze break with a thin evaporated metal coating.

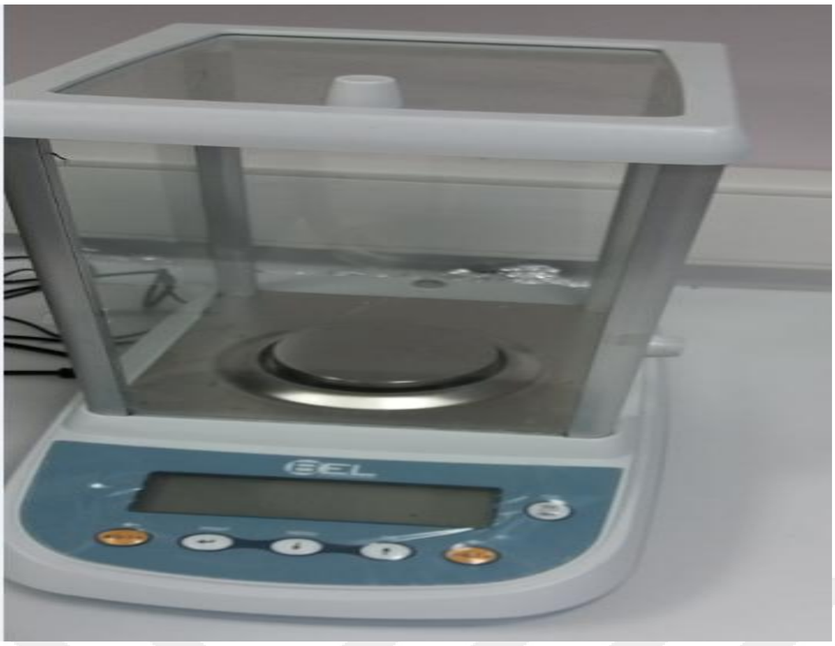

Figure 4. Series analytical balance.

Advanced vacuum drying oven (figure 5) was used in this work, The vacuum drying oven is specially designed for drying of material which is thermo-sensitive and oxidative easily. The laboratory drying oven can be filled with inert gas to dry some materials with complicated components. The laboratory drying oven has been widely used in pharmaceutics, electrical and chemical industry.

Figure 5. Advanced vacuum drying oven.

Calcination furnace (figure 6) is mainly intended for modifying ashes in various cereal products. Ash is the measurement of a mineral material remaining as a non-flammable remnants of the sample. Its temperature can be set to 300 °C up to 1100 °C depending on its implementation.

Figure 6. Furnace for calcination.

3.2. Synthesis of TiO_2, Colloidal Mixture

Titanium -isopropyl hydrolysis was performed by adding 4 ml of titanium butoxide and 50 ml of Ethylene glycol to 50 ml of Isopropyl which is catalyzed to Dissolving up-conversion materials , The mixture stirred and heated to 65 °C for 30 min by Reflux device as figure 7, then 5 ml of water was added to the TiO_2 mixture to improve the consistency of solution under stirring for 30 min at 65 °C, The mixture stirred and heated to 65 °C for 30 min. Finally, TiO_2 colloidal solution were obtained to dissolving up conversion materials, TiO_2 colloidal solution was kept at room temperature, before adding up-conversion materials. The samples having different UPC ratios. The experimental procedure is also depicted in Figure 8.

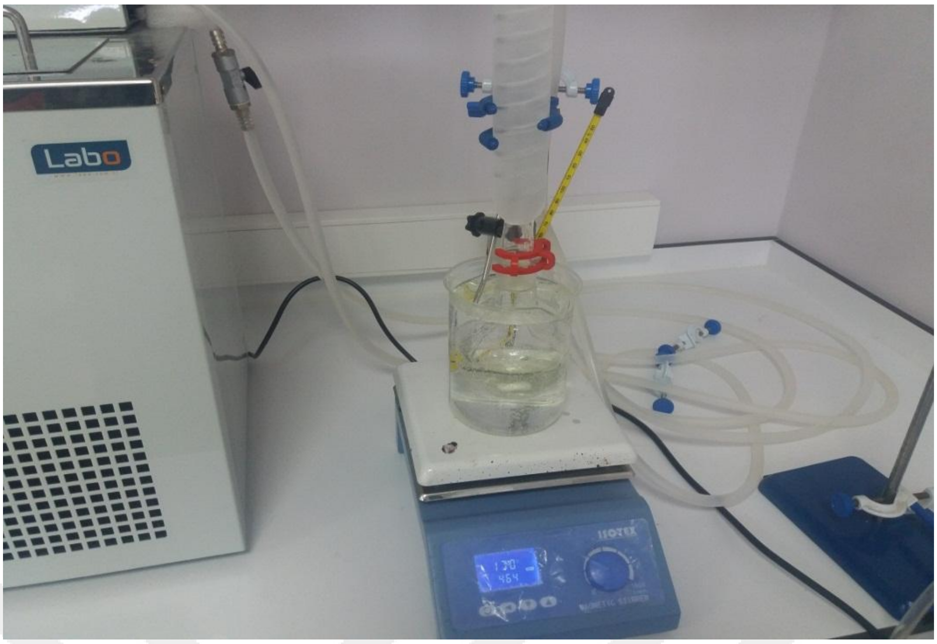

Figure 7. Synthesis of UPC/ TiO_2, colloidal mixture by reflux device.

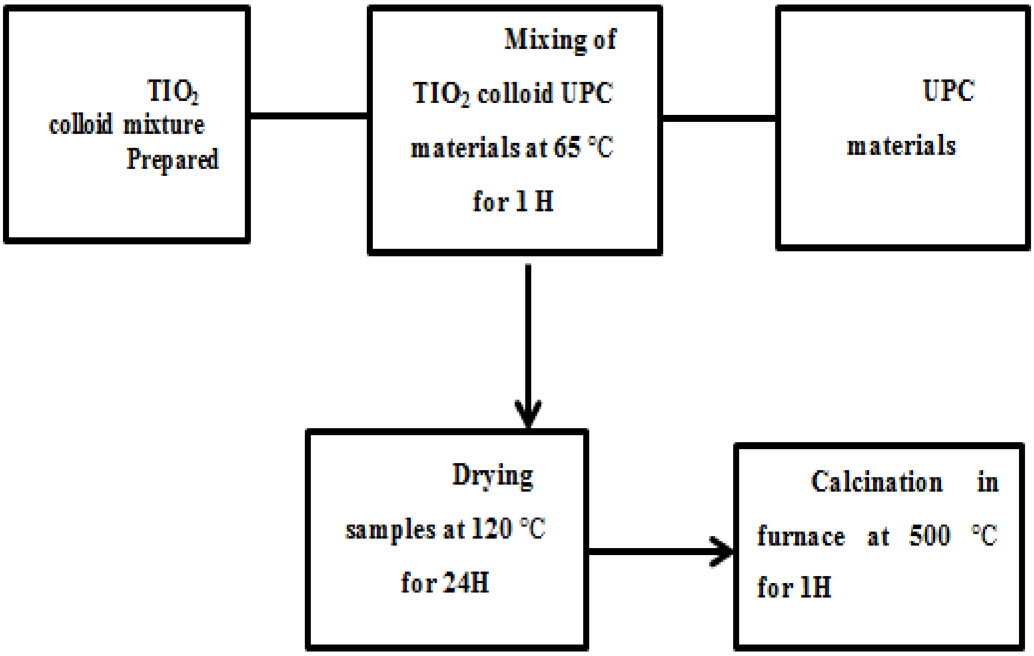

Figure 8. Synthesis Thin films of TiO_2/UPC photocatalyst coating.

3.3. Preparation of TiO_2/Upc Coating

The samples were classified into several methods according to the amount of nanoparticle and degrees of temperature of the SOL GEL dip coating method in the following tables.

Table 1. Amount of nanoparticle samples group A

No. simple	Tio_2 (ml)	Upc	Type of upc	Temperature
A1	14	0.0051	Erbium chloride	Room temp
A 2	14	0.0041	Yttrium nitrate	65 ℃

Amount of nanoparticle samples group A were mixed colloidal solution of 50 ml Ethylene glycol and Isopropyl alcohol on the reflux device for 1 h then 5ml water was added to solution for 30 min.

Table 2. Amount of nanoparticle samples group B

No. simple	Tio_2 (ml)	Upc (g)	Type of upc	Type of upc	Upc	Temperature
B1	10	0.01	Erbium chloride	Niobium	0.05	Room temp
B 2	10	0.01	Yttrium nitrate	Niobium	0.05	Room temp

Amount of nanoparticle samples group A were mixed colloidal solution of 50 ml Ethylene glycol and Isopropyl alcohol on the reflux device for 1 h then 5ml water was added to solution for 30 min.

Table 3. Amount of nanoparticle samples group S

No. simple	TiO_2 (ml)	upc (g)	Type of upc	water (ml)	Temperature
S1	5	0.001	Sodium yttrium	95	Room temp
S2	5	0.001	Erbium nitrate	95	65 ℃

3.4. Dip Coating Process

Samples are processed by dip coating use to create thin-film coatings

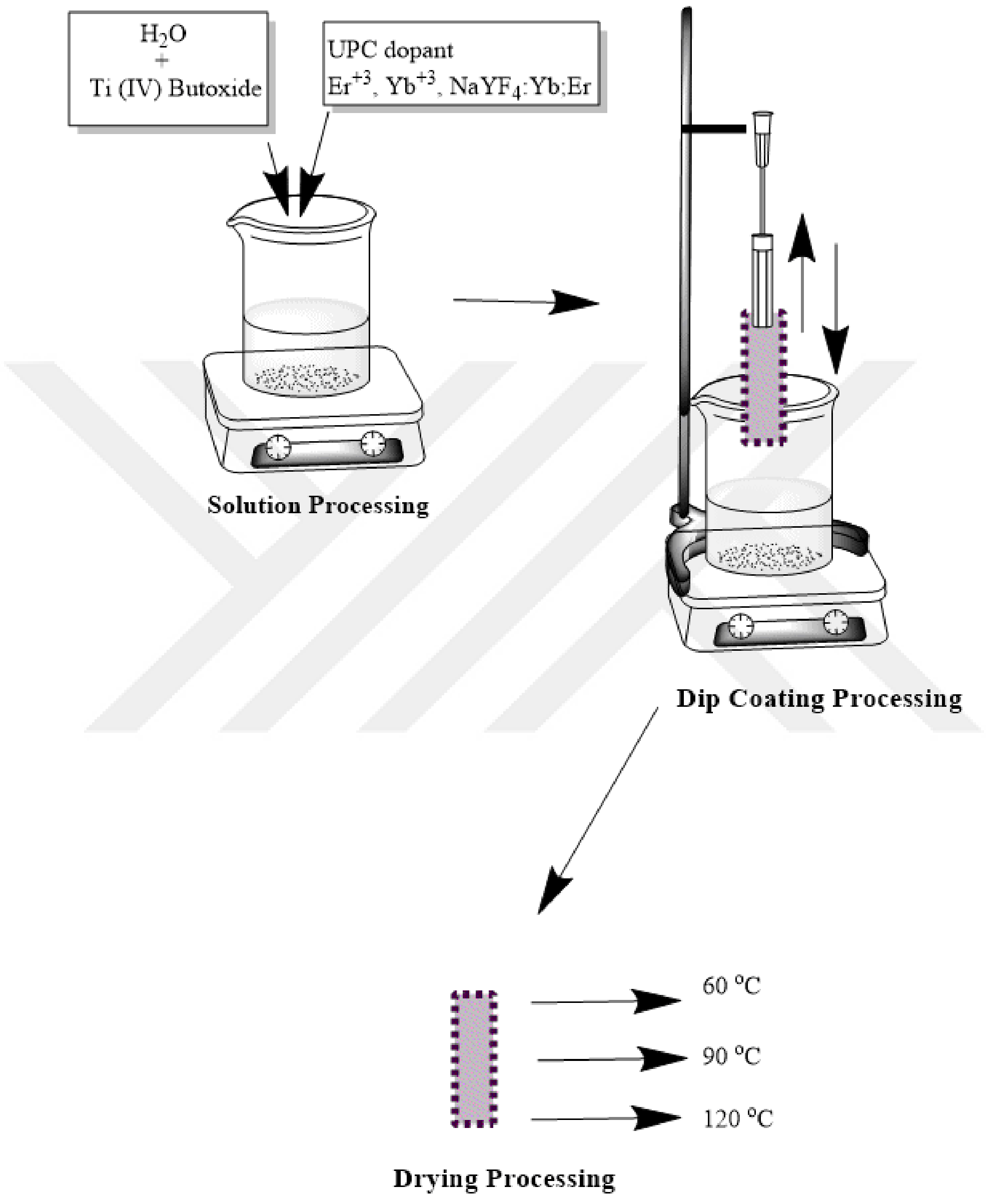

Figure 9. Description of coating process of textile by dip coating technique.

The textiles were cut to sizes 5x15 cm size cotton fabrics for dip coating process, The textiles were dipped in the solution coating, then textiles were putted in drying oven at 120 °C for 1 hour, for draying, A transparent thin layer of Nano crystalline

Upc/TiO_2 has been produced on cotton textiles. And take some of them Applied SEM and XRD analysis.

3.5. Staining Process

The nanoparticle coated sample is a test to measure the self-cleaning performance of textile surfaces First, methylene blue material, which is widely used as a stain material. However, ketchup, green tea, coffee were chosen as the staining material.

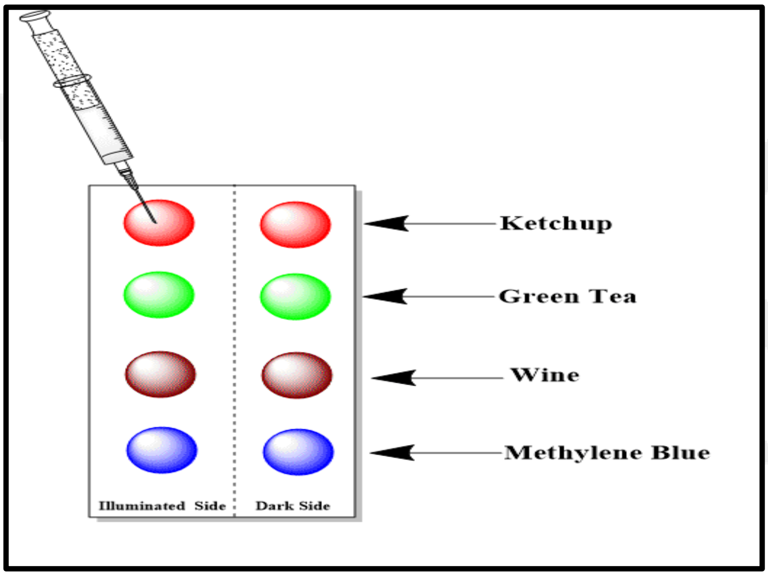

Figure 10. Staining process.

3.6. Suntest

Is a device that provides illumination approximating natural sunlight. The purpose of the solar simulator is to provide a controllable indoor test facility under laboratory conditions, used for the testing of solar cells, solar simulators used for photovoltaic testing, sun screen, plastics, and other materials and devices.

1x 1500 W air-cooled Xenon Lamps, Measurement and Control of Irradiance in the wavelength range or 300-420 nm / 340 nm.

Figure 11. Sun test device.

These samples of textile were exposed to UV radiation of 800 W/m2 in the Atlas SUNTEST solar simulator for different times. The stained fabrics were subjected to light fastness test at 3 periods (12,48,72) h.

4. RESULTS AND DISCUSSION

In this study, solution of TiO_2/UPC materials of different ratio nanoparticles were synthesized by sol-gel system and covered over materials as thin movies by dip coating method. It was observed that there was a difference in the color of single samples due to the increased accumulation of coating on the sample, due to the high viscosity of the coating solution, also the difference between the samples will be clarified in the effect of the time of the sun test and the effect of the temperature on the textile and the results of SEM and XRD and adhesion of nanoparticles coating on textiles.

4.1. Photocatalytic Self-cleaning Activity on Textile

The samples were classified based on the time of exposure and the temperature of drying of self-cleaning activity on (flat and Denim) textile.

4.1.1. Flat raw materials depending on the time of solar simulator testing

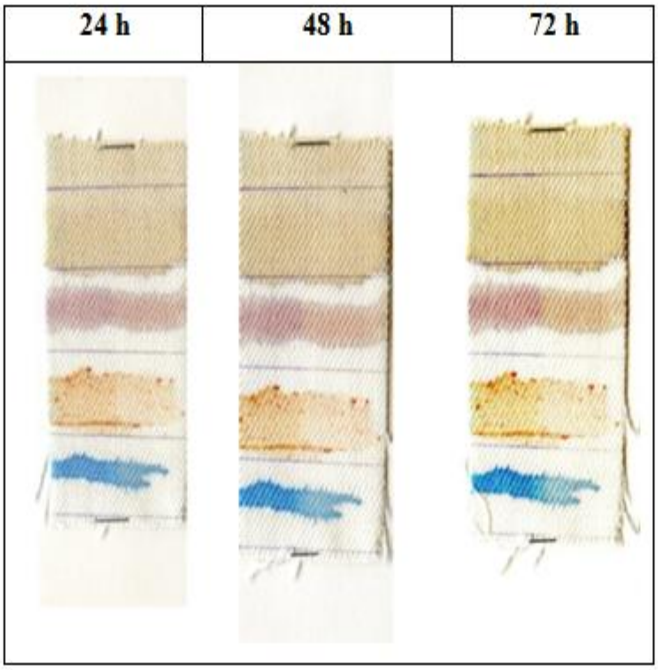

Figure 12. Number of hours solar simulator testing (Flat textile).

In Figure 10 shows the difference between the textiles samples from the self-cleaning area and therefore note that the higher the number of hours of exposure, the higher the photo catalytic and better result of self-cleaning.

4.1.2. Denim raw materials depending on the time of solar simulator testing

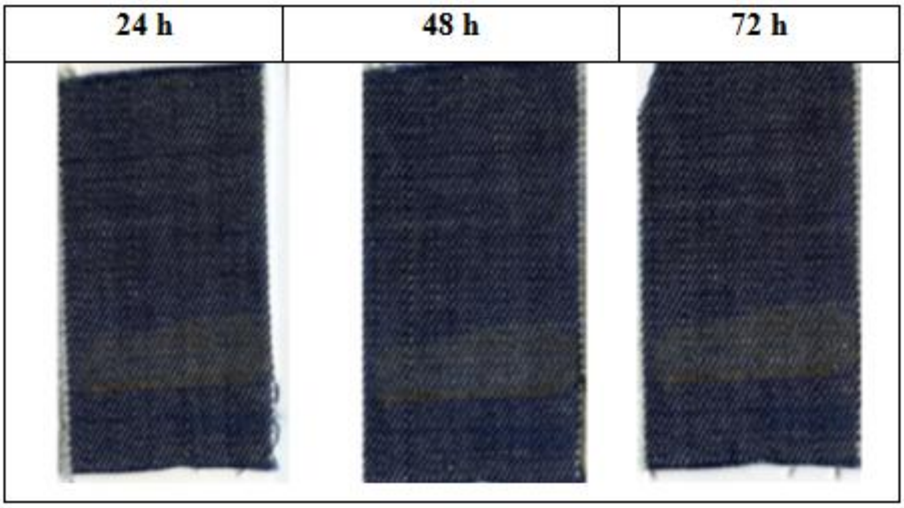

Figure 13. Number of hours solar simulator testing (Denim textiles).

Although the color was dark of Denim textiles in Figure 11 shows the difference between the textiles samples from the self-cleaning area and therefore observed that the higher the number of hours of exposure, the higher the photo catalytic and better result of self-cleaning.

4.2. Effect of Temperature of Drying on (Flat) Textiles

The samples applied were dried at 60 °C, 80 °C and 120 °C, to determine the effect of exposure to different temperatures and to show any change in samples.

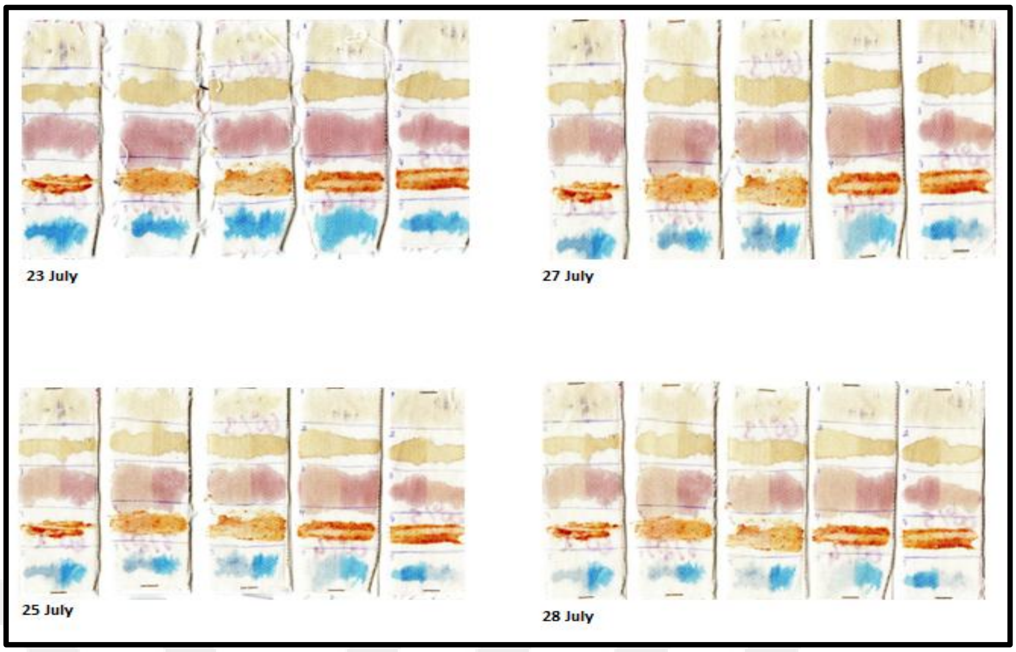

Figure 14. (Flat) textiles were dried at 60 °C.

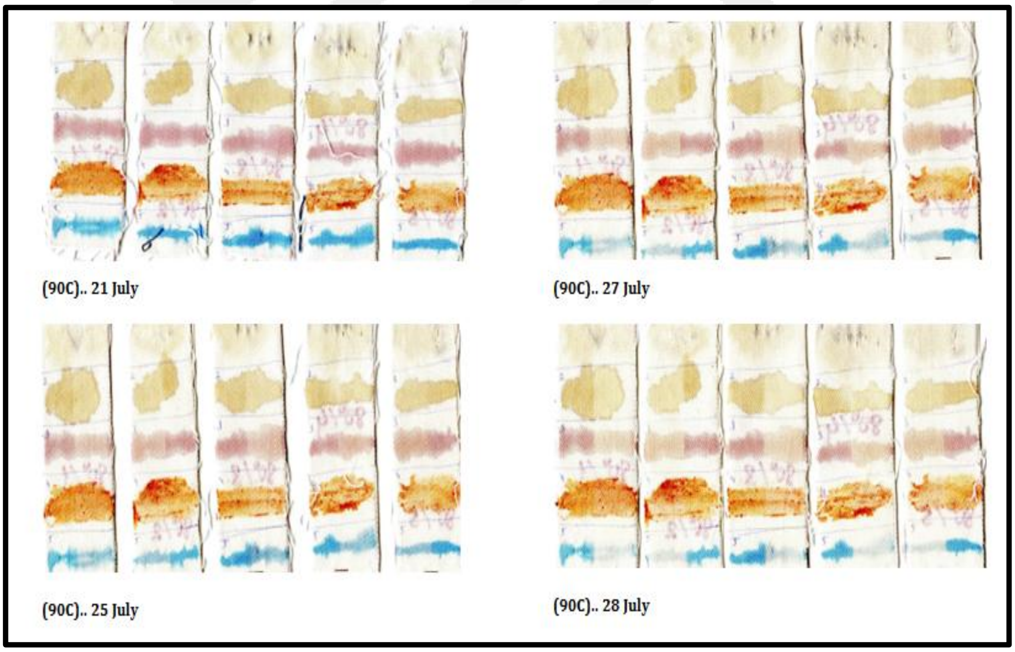

Figure 15. (Flat) textiles were dried at 90 °C.

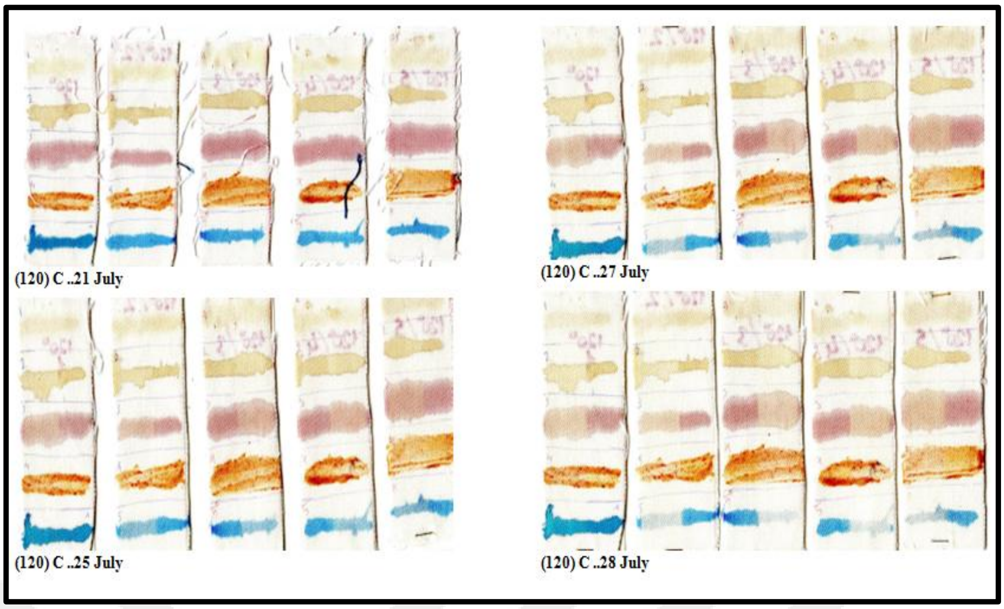

Figure 16. (Flat) textiles were dried at 120 °C.

Duo to previous figures show that there is no effect on the samples when the effect of a change in the temperature of drying on (Flat) textiles.

4.3. Effect of Temperature of Drying on (Denim) Textiles

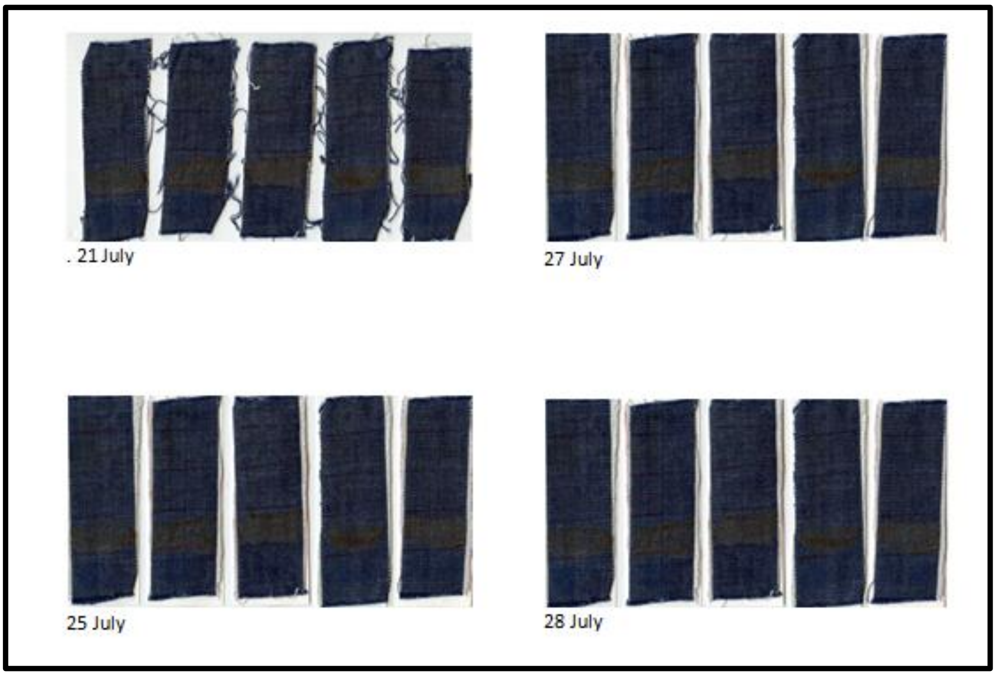

Figure 17. (Denim) textiles were dried at 60 °C.

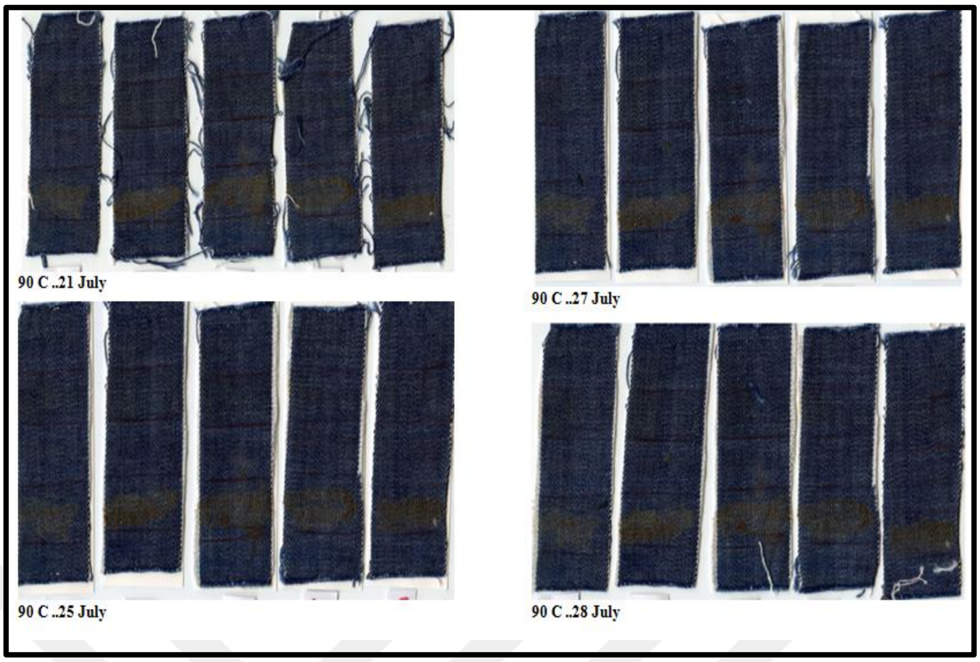

Figure 18. (Denim) textiles were dried at 90 °C.

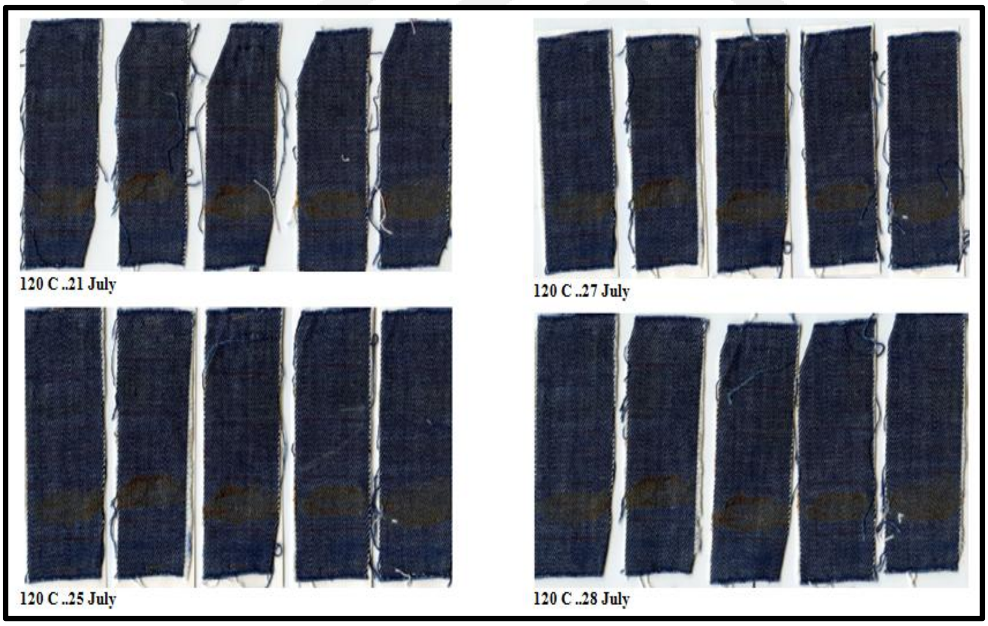

Figure 19. (Denim) textiles were dried at 120 °C.

Also previous figures show that there is no effect on the samples when the effect of a change in the temperature of drying on (Denim) textiles, this shows that the self-cleaning properties on the textiles are similar to the two types used.

4.4. Structure of Thin Film of TiO_2/ UPC

4.4.1. SEM results

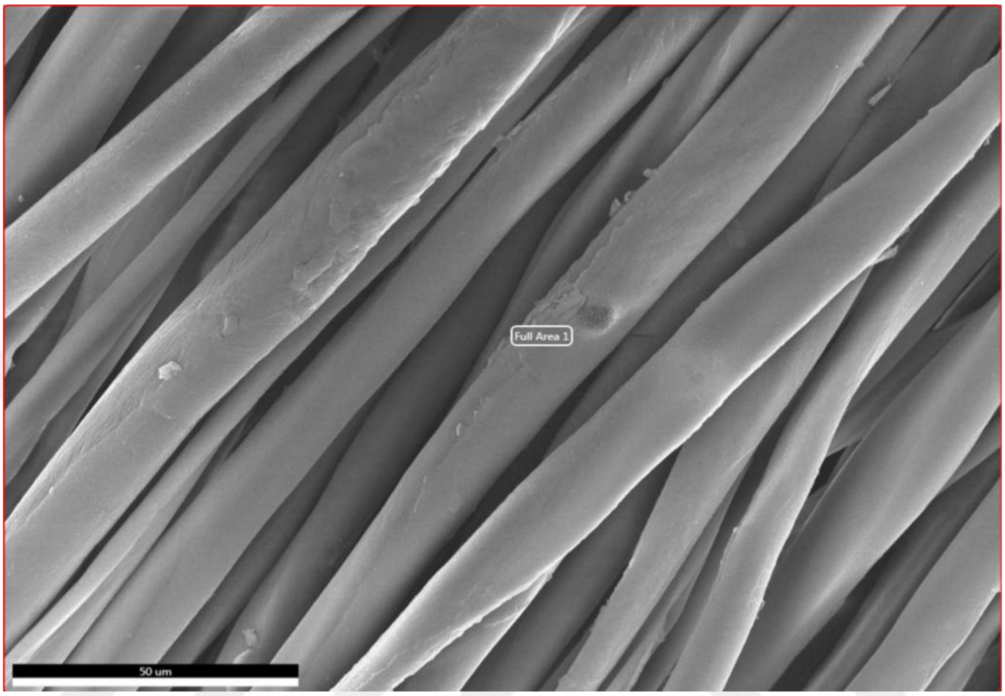

Figure 20. SEM of A0 simple.

Figure 20 shows the sample (A0) from (flat) textile, which can be accepted as RAW material, without any coating to explain the difference in adhesion of nanoparticles before and after coating. The SEM's maginification is 10K (50μm Scale Bar and 20KV with Field emission Gun). The figure illuminated to surface of cotton fibers clearly, some of cottons has a little insignificant dust particles. In addition, the cotton surface was seen as smooth and well oriented. Before coating of cotton fibers, some chemical pretreatment should be applied due to its surface restraining from UPC well coating. This pretreatment is simple process by textile dipping to hot water (80 °C) at 30 min.

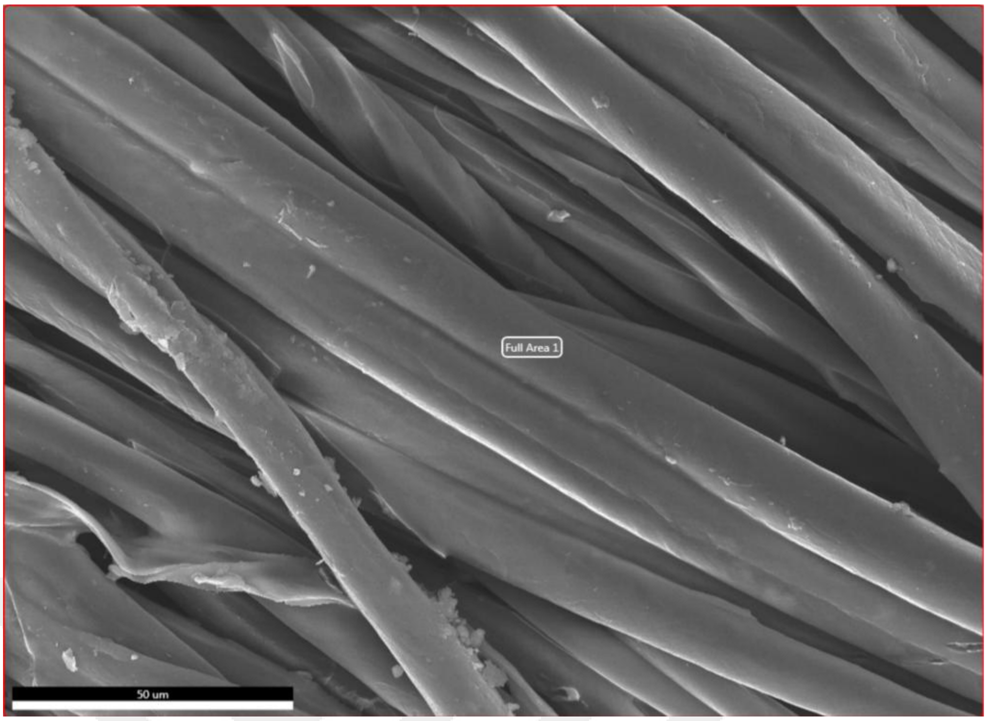

Figure 21. SEM of (A1) simple A1 (TiO_2 / Er).

After pretreatment by hot water (80°C), the first mixture applied raw cotton. The figure 21 represent Er doped TiO_2 **(TiO_2:Er)** samples on 10K magnification SEM image, which has taken under 50µm Scale Bar and 20KV with Field emission Gun. On the Er doped samples, Smooth and crack free coating has been observed in figure21. It should be Er enable TiO_2 coating to well oriented on cotton surface due to correct match crystal structure orientation (it can be explained in XRD Part). Also a little bit insignificant small particles was seen. The reason for the addition of Er is to increase the self-cleaning effect of TiO_2 in dark environments.

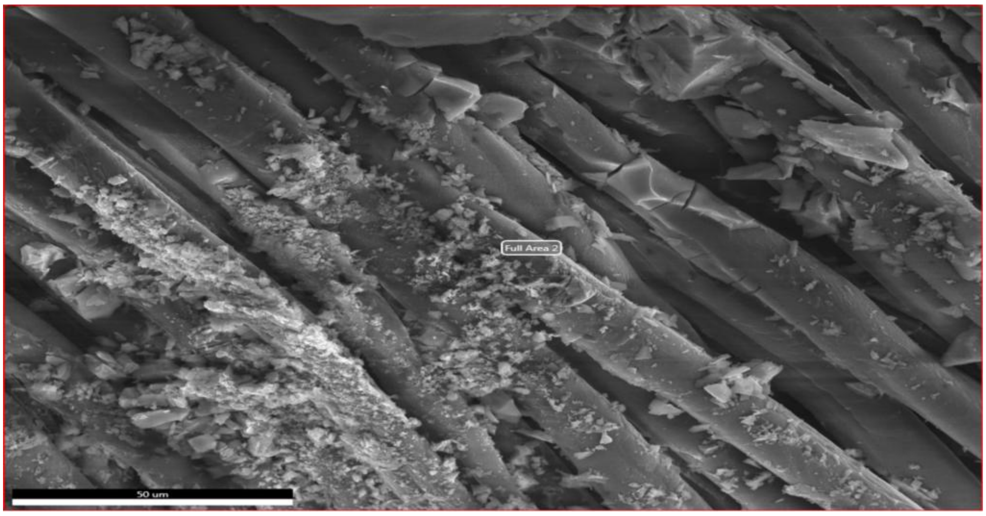

Figure 22. SEM of A2 simple Yb doped TiO_2.

The not well coating has been seen on Er doped TiO_2 sample. The excess particules and thick films has been seen on the (Figure 22). Compare of Er:TiO_2, the coating of TiO_2 are very bad when Yb doped is used instead of Er, which is seen in A1 sample. This coating can cause both a change in color on cotton and a bad effect after dyeing.

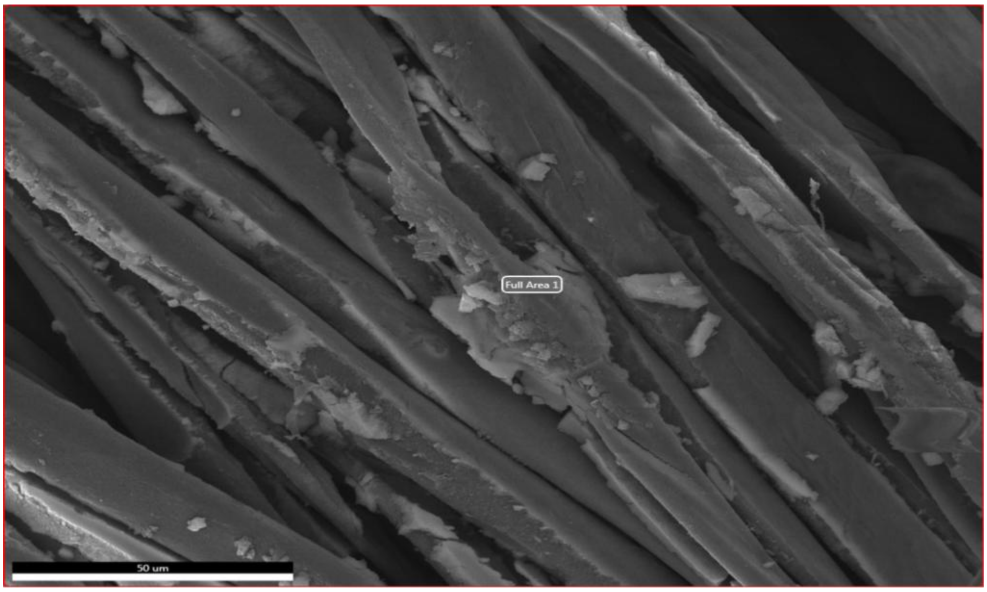

Figure 23. SEM of S1 simple NaYb:Er :Yb.

The SEM image of Sample **NaYb:Er :Yb** the not very good coating is also a news of bad self cleaning. Due to the bad wetting of Cotton by **NaYb:Er :Yb**, full-fledged particle modification appears to increase adhesion and coating production. However, there is a need to increase the physical bonding effect of the coating. Future work should be focused on this topic.

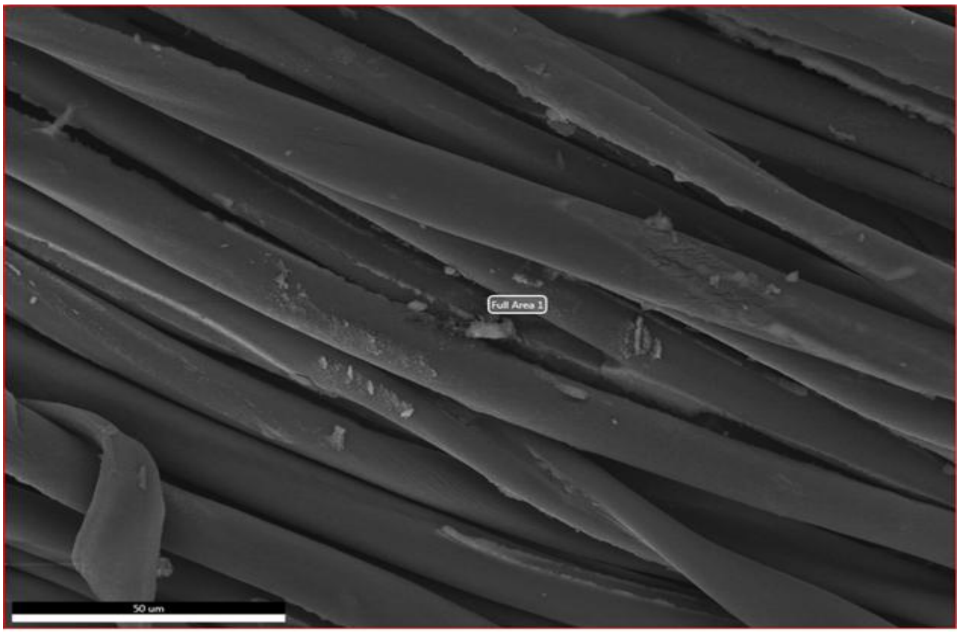

Figure 24. SEM of S2 simple. (Sol:TiO_2 Er)

It is seen that the wetting of the cotton TiO_2 is good but the holding is weak again. However, this prescription is hopeful in terms of performance (self-cleaning) and the way it is held.

4.4.2. XRD results

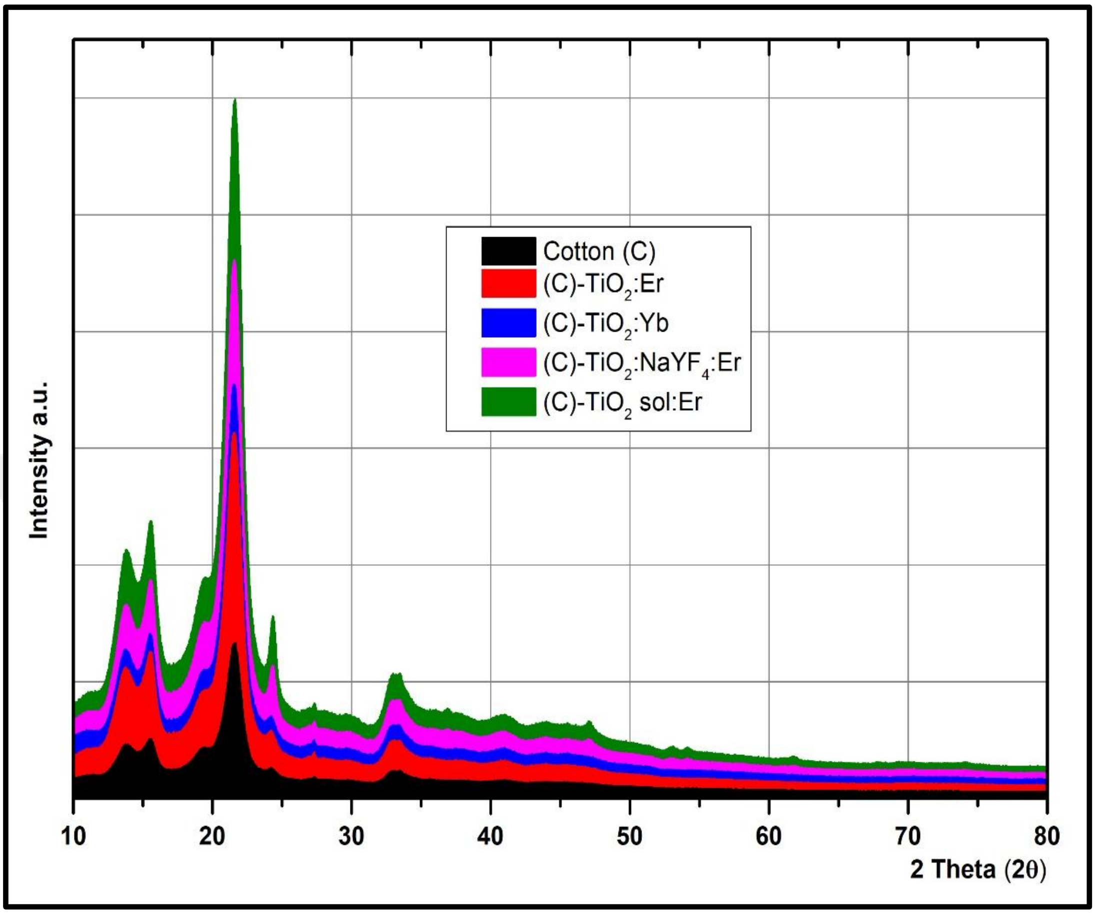

Figure 25. XRD of samples.

Figure 25 represent the XRD diffraction patterns of all samples. The cotton (C) samples has characteristic typical crystalline cellulose peaks like on 2 theta 14.5º, 16.2º, 22.3º, and 33.7º. Those peaks also are seen raw and modified cotton in perfect accordance with literature. And a lot of small oriented peaks are shown TiO2: Er doped materials. These peaks belongs to Anatase TiO2. There is no seen other phase of TiO2. The sharped peaks of samples at 22.3º as are seen in the figure belongs to direction of (002). Therefore, it is necessary that the coating should be wrapped around the group (100) direction of cotton and growth direction should be 100 direction without cotton. This is seen in the case of TiO_2: Er.

The radiance upconversion properties of the tempered UCP materials unfaltering state and time settled iridescence estimations. In laser control subordinate estimations of the upconversion iridescence force it was discovered that the green and red outflow of Er^{3+} indicated distinctive impacts of Tan on the quantity of required photons mirroring the distinctions in the populace courses of various vitality levels energy.

4.5. Effect of Dip Coating Method Nanoparticle Deposition on the Textiles

Current microscopy techniques incorporate by far most of breaks down that can be utilized to portray Nano composite coatings on materials. These dissects incorporate examining electron microscopy, transmission electron microscopy, nuclear power microscopy, filtering test microscopy. The example S2 (Sol:TiO_2 Er) was routinely set apart with covering ,a few strands began to connection to each other and framed a consistent film from nanoparticles and appearance of a thin layer and straightforward on the material, covering the structure of texture. Followed by the sample A1(TiO_2 / Er). the nanoparticles were less than the sample S2 (Sol:TiO_2 Er). In sample A2 Yb doped TiO_2. shows irregular coating very large accumulation of nanoparticles on textile . Due to the difference in the amount of nanotubes and the different temperature of the solution of SOL GEL dip coating. It is a simple and effective method for porous materials but is mainly based on the viscosity and synthesis of the solution.

5. CONCLUSIONS

Photo catalytic self-cleaning was investigated through this study, The solution of TiO_2/UPC materials Different amounts of nanoparticles was synthesized by SOL GEL method , and relied on dip coating methods as a basic way to coating textiles samples, and effect adhesion of nanoparticles on textiles. Depending on the samples tested under Sun test and the number of hours through of figures Can be deduced more hours of sun test light it will give more activity photo catalytic so self-cleaning it will be high efficiency.

All samples drying at temperatures (60-90-120 °C) in vacuum drying oven with a time factor , there is no effect on the samples when the effect of a change in the temperature of drying on (Flat and Denim) textiles. Although the color was dark of (Denim) textiles, self-cleaning has been achieved on (Denim) textiles, due to the similarity of the characteristics of the r between the textiles.

Dip coating method were observed a very effective method in porous materials and it is a simple method. Here we conclude that the high viscosity of the coating solution results in an irregular and accumulated coating as well as a change in the color of the cloth. Also conclude that the dip coating method requires low viscosity for the coating solution to allow for a coating solution run back and the saturation of the textile pores, so that the coating is not accumulated and it is regular

SEM was utilized to examine the nearness of stored Nano layers as well as join nanoparticles at first glance in the dip coating method, SEM pictures were connected for a superior comprehension of the consuming conduct of the treated with TiO_2/Er in S2 test. It was demonstrated that the weave structures of treated textures were held stable and did not watch shrinkage of the cotton texture in the wake of consuming. At higher amplification, the surface of the texture is more prominent.

XRD analysis the radiance upconversion properties of the strengthened UCNP materials were portrayed in enduring state and time settled iridescence estimations Upconversion luminescence of ER^{3+} was showed the best performance a broad band emission.

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APPENDIX

EXPANDED TURKISH SUMMARY
(GENİŞLETİLMİŞ TÜRKÇE ÖZET)

YUKARI ÇEVRİMLİ MALZEMELERİN KENDİ KENDİNİ TEMİZLEYEN KUMAŞLAR ÜZERİNDE UYGULAMASI

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İnsanların üç temel ihtiyacı vardır bunlar beslenme, barınma ve örtünmedir. Örtünmede ilk olarak hayvan postları kullanılmış ve teknolojinin ilerlemesi sayesinde günümüzde tekstil ürünleri kullanılmaya başlanmıştır.. Bireyler daha sonrasında ilk olarak kendileri üzerinde örtünmede ve süslenmede kullandıkları tekstil ürünlerini evlerini ve eşyalarını örtüp süslemede de kullanmaya başladılar. Aradan geçen zamanla beraber başlangıçta basit işler olan çuval yapımı ve yelken bezi yapımı gibi işlerden günümüzde daha karmaşık aşamalar gerektiren savunma sanayi ,sağlık , inşaat ve ziraat alanlarında tekstil ürünleri kullanılmaya başlanmıştır. Önümüzdeki 15-20 yıllık süreçte ise şuan için teknik tekstiller olarak bilinen tekstil ürünlerinin hakim olacağı bir pazarın oluşacağı tahmin edilmektedir, bu gelecek vaad eden ürünlerde farklı polimer malzemelerle tekstil ürünleri belli oranlarla karıştırılarak yeni kompozit malzemler elde edilecek ve kullanılıcaktır. İlerleyen zamanlarda bu teknolojik kumaşları giyen kimseler örtünme ve süslenmenin yanı sıra sağlık, güvenlik ve enformasyon ihtiyaçlarını da bu tekstil ürünlerinden karşılayabileceklerdir. Bu fonksiyonel tekstil ürünlerinin üretiminde en çok nanoteknolojiden yararlanılmıştır. Malzemede nano boyutta iyileştirmeler yapılarak elde edildiğinden bu ismi almaktadır. Bilindiği üzere malzemelerde nano boyuta inildiği zaman malzeme bilinen davranışlarının aksinde optik mekanik ve termal özellikler gösterebilmektedir. Gerek lif yapısının nano boyutta olması gerek kumaş üzerine uygulanan bitim işlemlerindeki maddelerin nano boyutta olmasıyla tekstil ürümlerinde fonksiyonel farklılıklar kazandırılmıştır.

GİRİŞ

Nanoteknoloji, fonksiyonel tekstiller üretiminde çok fayda sağlamıştır. Nanoteknoloji, geleceğin materyallerini üstün özelliklerle araştıran bilimsel bir disiplindir. Bu üstün özellikler nanometre ölçeğinde bulunur. tekstil elyaflarının ve malzemelerin diğer polimerler ve malzemelerle bir araya getirilmesiyle oluşan kompozit malzemelere olan talebin büyük oranda artacağı ön görülmektedir. Gelecekteki kullanıcılar, özellikle sağlık ve güvenlik alanında diğer hizmetleri sağlayabilen çok fonksiyonlu akıllı (etkileşimli) tekstil ürünlerinin üretimini ve kullanımını artıracaktır.

Temizlik tekstili, masa örtüleri ve takımlarının, büyük tenteler, çadırlar ve diğer mimari yapıların herhangi bir yıkama veya temizleme gerektirmeden temiz kalacağı kahve, çay ve diğer lekeleri silip bıraktığı bir senaryo öngörüyordu. Son yıllarda bu alanda yapılan olağanüstü gelişmelere paralel olarak, lotus yaprağında gözlenen ve lotus etkisi olarak adlandırılan bir fenomen vardır. Bununla birlikte, daha sonraki araştırmalar, yüzeyin yarı iletken özelliklere sahip metaller tarafından adsorbe edilmiş kir, kirletici maddeler, kirleticiler veya mikroorganizmalar gibi karbondioksit ve suya fotokatalitik olarak parçalanmasıyla kendiliğinden temizlenebileceğini ortaya koymuştur

Birçok uygulamada tekstillerin kullanımı kirlilik ve ıslanma davranışlarından ötürü sınırlıdır. Bu kısıtlılığın üstesinden gelmek için, tekstil ürünleri farklı ürün sınıflarında çeşitli kaplamalarla geliştirilir. Son zamanlarda, Lotus Efektini kullanan ve kendinden temizleme özelliklerini tekstil yüzeyine uygulayan ürünler keşfedildi. Bu etkinin başarılı bir şekilde gerçekleştirilmesi, bu yüzeylerin temizleme gereksiniminde önemli bir düşüşe neden olur.

Lotus etkisi, bir yüzeyin kimyasal ve geometrik modifikasyonu ile elde edilir. Mikro ve Nano ölçekli pürüzlülüğü hidrofobik bir kaplama eşliğinde oluşturarak yüzeydeki kir su damlacıklarıyla alınabilir ve hidrofobik yüzeyi dışarı atar ve böylece yüzeyini temiz tutar (Daoud vd., 2011). Fotokatalitik kendini temizleme, diğer taraftan, ışığın varlığında foto oksidasyon ve foto redüksiyon reaksiyonları yoluyla kimyasal kirlenme üzerine kuruludur (Fujishima ve Zhang, 2006). Titanyum dioksit veya titanium bu alandaki en sık kullanılan maddedir. Fotokatalitik etkinlik, atmosferdeki organik koku moleküllerinin yanı sıra bakteri hücre duvarlarında bulunan organik bileşikleri parçalayabilir, böylece kendiliğinden temizleme fonksiyonu oluşturur ve aynı zamanda muamele edilen yüzeylere antimikrobiyal ve koku giderici özellikler kazandırır.

Belirli materyallerin (genellikle yarı iletken) ve güneş ışığının sinerjisi sayesinde kimyasal redoks reaksiyonlarının hızlanması olan fotokatalizma, uygulanan kimyanın çeşitli alanlarında (çevre bilimi de dahil olmak üzere) farklı problemlerin ele alınmasında en umut verici araçlardan biridir. Aslında fotokatalizör, güneş ışığından kaynaklanan redoks reaksiyonları ile fotoaktif yüzeylere emilen veya biriken organik ve inorganik kirletici maddelerin foto-dekompozisyonunu sağlar.

Titanyum dioksit (TiO_2), su ve hava temizleme, anti-bakteriyel ve kendinden sterilize yüzeyler, gıda endüstrisi, kaplama, kağıt üretimi, kozmetik ve yapı gibi yenilikçi malzemeler ve çözümler geliştirmek için en çok kullanılan fotokatalitik malzemeden biridir. Malzemeler (Fujishima ve Honda, 1972; Chen vd., 2009). İnşaat sektöründe titanyum dioksit, çimento harçları, dış cephe kaplamaları, kaplama boyaları, camlar, boyalar, kaplama boyaları, yol blokları, beton kaldırımlar gibi çok sayıdaki yapı elemanlarında kendini temizleme işlemlerini gerçekleştirmek için kullanılmıştır (Chen vd,. 2009; Bondioli, 2009). Yüksek kataliz etkinliği, kimyasal stabilite, ucuzluk, toksik dışılık, geleneksel inşaat malzemeleri ile uyumluluk (Chen vd., 2009; Fujishima ve Zhang, 2006), TiO_2 ile muamele edilen yüzeyler hafifliği absorbe ettiği için fotoğraftan ve fotodragradasyondan korunmak için yüzeylere koruma sağlar. TiO_2 kaplamalar tarafından sağlanan bu çok işlevli özelliklerden dolayı, bu teknoloji son yıllarda araştırma ve ticari süreçlerde artan bir ilgi görmektedir (Fujishima, 2000)

UV ışığı altında fotokatalitik özellikler geliştirilmiştir. Bununla birlikte, TiO_2'nin geniş bant aralığı UV bölgesine düşen bir uyarılma dalga boyu gerektirir. Dünyaya ulaşan güneş ışığı sadece % 5 UV ve neredeyse % 43 görünür ışıktan oluştuğundan, UV bazlı TiO_2 fotokatalizasyonu uygulaması sınırlıdır. Güneş spektrumunun görünür bölgesini kataliz için kullanmak için, titanyumun optik özellikleri vazgeçilmezdir. Bu bağlamda, TiO_2, yukarı dönüştürme malzemeleri gibi birçok yöntemle modifiye edilebilir.

Sol-jel yöntemi son yirmi yıl içinde incelenmiş bir seramik üretim yöntemidir ve kelime çözümünün kısaltılması olarak kullanılır. Sol-jel yöntemi bir kimyasal yöntemdir ve başlangıç malzemesi olarak sol içerdiğinden "sol-jel yöntemi" olarak tanımlanır ve jel bu sol kullanılarak elde edilir. Yöntem, farklı fonksiyonel kaplamaların oluşumu için en önemli tekniklerden biridir ve avantajlı özelliklere sahiptir. Örneğin; büyük alanlarda kolay kapsama, homojenliği yüksek karışık oksit filmleri ve Nanocrystalline malzemelere erişilebilirlik.

Daldırma kaplaması, örneğin, biyotıp alanında kaplamalı kumaşlar ve özel kaplamalar gibi toplu ürünler üretmek ve aynı zamanda ince film kaplamaları oluşturmak için kullanılan endüstriyel bir kaplama işlemidir. Daldırma kaplama yöntemleri nanopartikül ifadesi için basit yöntemlerdir.

Nanoteknoloji uygulamalarındaki gelişmeler nedeniyle, kendiliğinden temizlenen yüzeylerde ilgi artmaktadır. Bu kaplamalar, pencere, çimentolar, tekstil ve birliktelik gibi birçok farklı uygulama alanını bulmaktadır. Örneğin, tekstillerde kullanılan kendinden temizleme kaplamaları, çamaşır sayısını azaltırken tekstil ürünlerinin ömrünü uzatarak temizlik maliyetini azaltabilir. Bu çalışmada, kendi kendine temizleme pamuklu kumaşı ve tekstiller üzerine daldırma kaplama metodu UPC/TiO_2 tarafından kaplanmış kumaşlar ve daldırma kaplama metodu nanopartikül elde etmek amaçlanmıştır. Çeşitli UPC/TiO_2 oranları olan ince filmler sol-jel yöntemi ile sentez edilmiştir. Fotokatalitik kendini temizleme ve ince filmlerin faaliyetleri bu çalışma ile araştırıldı.

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KONFERANS BILDIRILERI / CONFERENCE PAPERS	
	H.i Yavuz A.M.H.A. Emhamed Photocatalytic Self-Cleaning Properties of UPC Assist TiO2 Nanocrystalline ICCMMS 2017 CU, Adana Turkey

PATENTLER/PATENTS	
2018	Application of Self Cleaning Materials On Textile Surface(Under Rewiev)

ÖDÜLLER/ AWARDS	
Libyan schollar ship	**M.Sc 2014-2017**

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