



MARMARA UNIVERSITY
INSTITUTE FOR GRADUATE STUDIES
IN PURE AND APPLIED SCIENCES



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Ph.D. THESIS

Department of Chemical Engineering

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ÖZET

Cr, Zn, Ag KATKILARININ TiO₂'in FOTOKATALİTİK ÖZELLİKLERİ ÜZERİNE ETKİLERİ

Fotokatalitik özelliğinden dolayı kendi kendini temizleme uygulamalarında tercih edilen TiO₂, solar spektrumun çok az bir bölümünü oluşturan UV ışığı ile aktive edilebilmektedir.

Bu çalışmada Ag, Zn ve Cr katkılarının üç farklı konsantrasyonunun (0.5 %, 1 %, 1.5 %) SLS cam üzerinde oluşturulmuş TiO₂ filminin fotokatalitik aktivitesi üzerine etkilerinin incelenmesi amaçlanmaktadır.

Na⁺ göçünü engellemek amacıyla SLS camlar öncelikle SiO₂ çözeltisi ile kaplanmış daha sonra sol-jel metodu ile hazırlanan katkılandırılmış ve katkılandırılmamış TiO₂ çözeltileri ile kaplanmıştır. TiO₂ filmleri ince film ve AFM analizleri ile karakterize edilmişlerdir. TiO₂ filmleri yapışma, taber aşındırma, çizilme ve tuz püskürtme testleri ile fiziksel olarak test edilmişlerdir. TiO₂ filmlerinin fotokatalitik aktiviteleri ve % geçirgenlikleri tuz püskürtme testinden önce ve sonra ölçülmüştür. SiO₂ filminin % geçirgenlik üzerindeki etkisi incelenmiştir. Diğer karakterizasyon çalışmaları için TiO₂ sollarının jelleştirilmesi ile elde edilen TiO₂ tozları kullanılmıştır. TiO₂ çözeltilerinin raf ömürleri tespit edilmiş ve raf ömrünün fotokatalitik aktivite, % geçirgenlik ve ışık ile uyarılmış ıslanabilirliğe etkisi incelenmiştir.

Çözeltiler hazırlandıktan 60 gün sonra bile kullanıldıklarında hala düzgün kaplamalar elde etmek mümkün olmuştur. TiO₂ ince filmleri görünür bölge geçirgenliğini önemli ölçüde azaltmazken, UV geçirgenliğini ciddi şekilde bloke etmişlerdir. Fotokatalitik parçalanma çalışmaları; Ag katkısının fotokatalitik aktiviteyi hafifçe arttırdığını, Zn katkısının fotokatalitik aktiviteyi hafifçe azalttığını ve Cr katkısının fotokatalitik aktiviteyi çok ciddi şekilde azalttığını göstermiştir. Ag'nin optimum konsantrasyonunun % 1 olduğu bulunmuştur.

Haziran, 2013

Ceyda Zeynep, KOYUNCU

ABSTRACT

EFFECTS OF Cr, Zn, Ag DOPANTS ON PHOTOCATALYTIC PROPERTIES OF TiO₂

TiO₂ that is preferred for self cleaning applications due to its photocatalytic property can just be activated by UV light that composes a very small part of solar spectrum.

In this study it is aimed to investigate the effects of three different concentrations (0.5 %, 1 %, 1.5 %) of Ag, Zn and Cr dopants on photocatalytic activity of TiO₂ film formed on SLS glass.

To prevent Na⁺ diffusion, SLS glasses were first coated with SiO₂ solution then with doped and undoped TiO₂ solutions prepared by sol-gel method. TiO₂ films were characterized by thin film and AFM analysis. TiO₂ films were tested physically by adhesion, taber abrasion, scratch and salt spray test. Photocatalytic activity and transmittance % of TiO₂ films were measured before and after salt spray test. The effect of SiO₂ film on transmittance % of TiO₂ films was investigated. For further characterization studies, TiO₂ powders that were obtained by gelation of TiO₂ solutions were used. Shelf lives of TiO₂ solutions were determined and the effect of shelf life on photocatalytic activity, transmittance % and photoinduced wettability was investigated.

Fine coatings were obtained when solutions were used even at the 60th day of their preparation. TiO₂ thin films did not reduce visible region transmittance significantly while they blocked UV transmittance seriously. Photocatalytic degradation studies indicated that while Ag dopant promoted slightly, Zn dopant inhibited slightly and Cr dopant inhibited very seriously the photocatalytic activity of TiO₂ film. The optimum concentration of Ag was found to be 1 %.

June, 2013

Ceyda Zeynep, KOYUNCU

CLAIM FOR ORIGINALITY

EFFECTS OF Cr, Zn, Ag DOPANTS ON PHOTOCATALYTIC PROPERTIES OF TiO₂

This thesis records a comprehensive work carried out to investigate the effects of Ag, Zn, Cr dopants on photocatalytic properties of TiO₂. Whether three different concentrations (0.5 %, 1 %, 1.5 %) of these three dopants contribute to the photocatalytic activity of TiO₂ which can only be activated with a small part of solar spectrum or not is studied detailed taking different aspects of the subject into consideration.

My original contributions to the knowledge with this thesis can be listed as:

1. I prepared TiO₂ solutions which stayed stable for nearly 1 year and I showed that by using this solutions at the 60th day of their preparation it is still possible to produce fine coatings on glass.
2. I showed that films that are produced by using undoped, Ag doped and Zn doped TiO₂ solutions at the 60th day of their preparation still show photocatalytic activity.
3. I showed that films that are produced by using undoped, Ag doped and Zn doped TiO₂ solutions at the 60th day of their preparation still show photoinduced wettability.
4. I showed that films that are produced by using TiO₂ solutions do not decrease transmittance at visible region seriously.
5. I showed that films that are produced by using TiO₂ solutions behave like UV blockers and SiO₂ intermediate layer causes this behaviour to enhance.

I hereby declare that this thesis comprises only my original work. Acknowledgement has been made in the text to other information derived from the published work of others and references are given in the list of literature.

April, 2013 Prof. Dr. M. A. Neşet KADIRGAN Ceyda Zeynep, KOYUNCU

SYMBOLS

A	: Absorption
Ag	: Silver
°C	: Celcius
cP	: Centipoise
Cr	: Chromium
d	: Film thickness (nm)
f	: Area fraction of the projected wet area
K	: Kelvin
M	: Metal
n	: The valance of metal atom
OR	: Alkyl group
r	: Roughness factor
Ra	: Roughness (nm)
r_f	: Roughness factor of wetted area
SiO₂	: Tetraetoxysilane
TiO₂	: Titaniumdioxide
V	: Withdrawal speed (cm/min.)
Vo	: Oxygen vacancy
Zn	: Zinc
Θ_y	: Young's contact angle
Θ_w	: Wenzel's contact angle
γ_{SG}	: Solid-gas interfacial tension
γ_{SL}	: Solid-liquid interfacial tension
γ_{LG}	: Liquid-gas interfacial tension
Θ_{CB}	: Cassie-Baxter's contact angle

ABBREVIATIONS

AFM	: Atomic force microscope
CERAMERS	: Ceramic polymers
CVD	: Chemical vapor deposition
DTA-TG	: Differential thermal analysis-thermo gravimetry
Endo	: Endothermic
Exo	: Exothermic
FTIR	: Fourier transform infrared spectroscopy
HRTEM	: High-resolution transmission electron microscopy
MI	: Materials Institute
min.	: Minute
MRC	: Marmara Research Center
ORMOSILS	: Organically modified silicates
ORMOCERS	: Organically modified ceramics
POLYCERAM	: Polymeric ceramics
RB	: Rhodamine B
SEM	: Scanning electron microscope
SLS	: Soda-lime-silica
SAED	: Selected area diffraction
TEM	: Transmission electron microscopy
TMOS	: Tetrametoxysilane
TTIP	: Titanium tetra isopropoxide
TUBITAK	: The Scientific and Technological Research Council of Turkey
UV-VIS DRS	: Ultraviolet-visible diffuse reflection spectroscopy
XRD	: X-ray diffraction
XPS	: X-ray photoelectron spectroscopy

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1. INTRODUCTION

Recently TiO_2 mediated photocatalytic reactions are becoming more important and as a result of this, the number of theoretical studies and practical applications about this subject are increasing.

However TiO_2 has a serious disadvantage that it can just be excited by UV light that is a very small part of sunlight spectrum. Today, many methods are being studied to improve photocatalytic activity of TiO_2 .

This study aims to enhance photocatalytic activity of TiO_2 by doping Cr, Zn ve Ag through the sol-gel method. In this study metal ions are doped into the TiO_2 solution not into the powder form of the TiO_2 which has many disadvantages (The need for separation step, the problematic use in continuous flow systems and the particles agglomeration especially at high concentrations).

While as a primary objective effects of Cr, Zn ve Ag dopants and their amounts on photocatalytic activity of TiO_2 film is being investigated, various aspects of the subject are taken into consideration.

Properties (pH, viscosity, color, gelling time, shelf life) of TiO_2 solution before and after being doped with 0.5 %, 1 % and 1.5 % Cr, Zn and Ag are determined. After gelation, obtained powders of both undoped and doped TiO_2 were sintered at different temperatures and effects of sintering temperature, dopant type and dopant amount on phase transformation and crystallite size are examined. Other than XRD DTA-TG, FTIR, TEM and BET are used for characterization of doped and undoped TiO_2 .

SLS (soda-lime-silica) glasses are coated with prepared doped and undoped TiO_2 solutions by dip coating. The optimum sintering time and temperature are determined by the help of photocatalytic activity test. After that films that are obtained by sintering at chosen temperature for chosen time are characterized by AFM and thin film analysis, effects of dopant type and dopant amount on physical properties (contact angle, reflectance) of TiO_2 are investigated. Physical testing (adhesion, taber abrasion, scratch, salt spray test) of coated SLS glasses are done and results are evaluated according to dopant type and dopant amount. Also while testing taber abrasion and scratch hardness tin side and air side of SLS glass are taken into consideration.

1.1. Sol-gel Method

1.1.1. Fundamentals of sol-gel method

Interest in the sol-gel processing of inorganic ceramic and glass materials began as early as the mid-1900s with Ebelmanl and Graham's studies on silica gels. They observed that the SiO_2 in the form of a glass-like material, could be produced by hydrolysis of tetraethoxy silane (TEOS) under acidic conditions [1]. After that researches about sol-gel process had been continued however until Livage and his co-workers studied in 1981, the basic chemistry of sol-gel process had been little understood [2].

Sol-gel chemistry is based on two routes; gelation of the solution of colloidal powders (colloidal sol route) and hydrolysis and polycondensation of alkoxide precursors (alkoxide route) [1].

In colloidal route, metallic salt solutions (chlorides, nitrates, sulfates, etc.) and oxide or hydroxide sols are used as precursor [3]. Sol is a stable suspension of colloidal solid particles or polymers in a liquid and colloids are the suspensions in which the dispersed phase is so small (1-1000 nm) that gravitational forces are negligible and interactions are dominated by short-range forces such as Van der waals attraction and surface charges [4]. Colloidal route is much cheaper and easier than alkoxide route, but the reactions of colloidal route is more difficult to control [5].

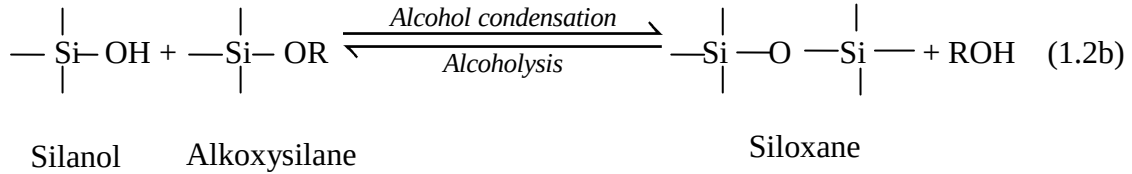
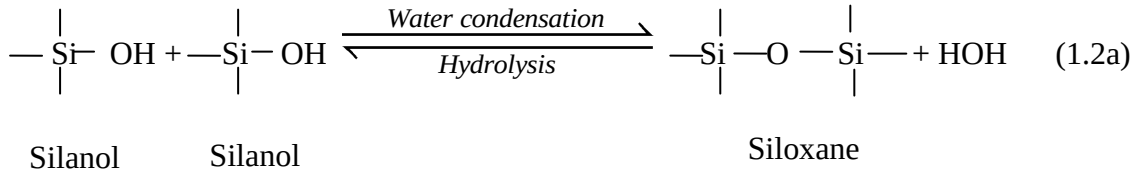
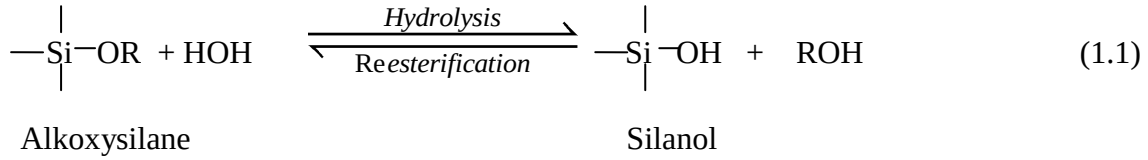
In alkoxide route, mostly metal alkoxides (Table 1.1) are used as precursors since they react readily with water. The most widely used metal alkoxides are the alkoxysilanes, such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) [6]. However, other alkoxides such as aluminates, titanates are also commonly used in the sol-gel process, often mixed with TEOS. The sol-gel process has three main reactions; hydrolysis, alcohol condensation and water condensation [7].

Table 1.1. General formula of metal alkoxides

M(OR)_n
M = Metal
OR = Alkyl group exp: CH_3 : methyl C_2H_5 : ethyl C_3H_7 : propyl
n = the valance of the metal atom

In hydrolysis reaction alkoxy silane precursor is hydrolyzed (1.1), through the addition of water, and alkoxide groups (OR) are replaced with hydroxyl groups (OH) producing silanol bond and by-product alcohol. Siloxane bonds with the by-products water or alcohol are produced by both water and alcohol condensation reactions (1.2a and 1.2b).

Hydrolysis is facilitated in the presence of this homogenizing agent, alcohol, since water and alkoxides are immiscible. It should be emphasized, however, that the addition of solvents and certain reaction conditions may promote esterification and depolymerization reactions according to the reverse of (1.1), (1.2a) and (1.2b) [9].



Hydrolysis and condensation reactions depend on many parameters and some of them are more important than the others. The main parameters that influence hydrolysis reaction can be listed as nature and concentration of catalyst (Table 1.2) and H₂O/Si molar ratio (R) [6,10].

Table 1.2. Gel times and solution pH for systems employing different catalysts

Catalyst	Concentration (mol of TEOS)	Initial pH of Solution	Gelation time (h)
HF	0,05	1,90	12
HCl	0,05	0,05	92
HNO ₃	0,05	0,05	100
H ₂ SO ₄	0,05	0,05	106
HOAc	0,05	3,70	72
NH ₄ OH	0,05	9,95	107
No catalyst	-	5,00	1000

Nature and Concentration of Catalyst

Although hydrolysis can occur without addition of an external catalyst, it is most rapid and complete when they are employed. Mineral acids (HCl) and ammonia are most generally used, however, other catalysts are acetic acid, KOH, amines, KF, and HF [4]. It has been observed that the rate and extent of the hydrolysis reaction is mostly influenced by the strength and concentration of the acid or base catalyst and it was also found that base catalyzed hydrolysis of silicon alkoxides proceeds much more slowly than acid catalyzed hydrolysis at an equivalent catalyst concentration [11].

In Table 1.2 the effects of various catalyst on the overall hydrolysis and condensation rates of TEOS and gelation times can be seen [12].

H₂O/Si molar ratio (R)

The most obvious effect of the increased value of R (H₂O/Si molar ratio) is the acceleration of the hydrolysis reaction which can also be seen from the equation 1.1. Additionally, higher values of R caused more complete hydrolysis of monomers before significant condensation occurs which also affects the relative rates of the alcohol or water producing condensation reactions [11].

The main parameters that influence condensation reaction can be listed as type of precursor, type of catalyst, type of solvent and pH.

Type of precursor

For a given metal atom or ion, large organic ligand or more complex organic ligand would result in a less reactive precursor. For example, $\text{Si}(\text{OC}_2\text{H}_5)_4$ is less reactive than $\text{Si}(\text{OCH}_3)_4$, and $\text{Ti}(\text{OPr})_4$ is less reactive than $\text{Ti}(\text{OEt})_4$ [13].

Type of catalyst

Like hydrolysis, condensation can proceed without catalyst too, however, it is helpful to use catalysts. It is observed that under more basic conditions, gel times are observed to increase [4,14].

Type of solvent

The polarity, dipolar moment, viscosity, protic/aprotic properties of the solvent are important in condensation reactions. Polar solvents stabilize polar gels by hydrogen bonding. Non-polar solvents are better for systems which are not completely hydrolyzed [4].

pH

In condensation below pH 2, the condensation rates are proportional to the $[\text{H}^+]$ concentration. Because the solubility of silica is quite low below pH 2, formation and aggregation of primary silica particles occur and the growth of the particles is stopped after their size exceed 2 nm in diameter. Between pH 2 and pH 6, condensation rates are proportional to $[\text{OH}^-]$ concentrations. The solubility of silica in this pH range is again low and particle growth stops when the particles reach 2-4 nm in diameter. Above pH 7, polymerization occurs the same as in the pH 2 to pH 6 range. However in this pH range, particle size, is therefore, mainly temperature dependent, in that higher temperatures produce larger particles. Additionally, in this pH range, the growth rate depends upon the particle size distribution [4].

By the commercialization of the sol-gel process in 1953 and by the first volume production (coated rear view mirrors for the automotive industry) of the process was done in 1959 [15] number of the studies in the field of sol-gel process began to increase.

Looking at the publications it can be especially observed that a remarkable increase took place at the end of the seventies [16] and today it is possible to speak about many commercial sol-gel products in many different fields such as biotechnology, electronics, material science,... [17]. The reason of this growing interest in sol-gel method is that it has many important advantages compared to conventional methods such as:

- By sol-gel method multi component compounds may be prepared with a controlled stoichiometry by mixing sols of different compounds.
- The sol-gel method prevents the problems with co-precipitation.
- The sol-gel method does not need expensive equipments.
- The sol-gel method enables mixing at an atomic level.
- The sol-gel method results in small particles, which are easily sinterable [18].

Although remarkable progress has been made so far in the sol-gel process, it has still some handicaps that should be considered such as:

- The very large shrinkage associated with the gelation process and the drying of gels,
- The presence of large concentrations of pores,
- The removal of undesirable residuals like hydroxyls and organics,
- The high cost of raw materials,
- The long processing times [19].

1.1.2. Applications of sol-gel method

Although interest in sol-gel method started with the powderless processing of glasses and ceramics, today sol-gel method is being used to prepare materials with a variety of shapes, such as porous structures, thin fibers, dense powders and films [7].

After obtaining the sol by condensation, the sol can be sprayed on the substrate or substrate can be dipped in the sol to form film. Sol can be shaped as fibers or powder respectively by drawing and drying. After the gelation step, gel will be obtained from the sol. If the gel is dried by evaporation, then the capillary forces will result in shrinkage, the gel network will collapse, and a xerogel is formed. If drying is performed under supercritical conditions, the network structure may be retained and a gel with

large pores may be formed. This is called an aerogel, the density will be very low ($< 0.005 \text{ g/cm}^3$) Powder will be obtained by grinding the xerogel and by sintering both aerogel and xerogel it is possible to synthesize dense ceramics (Figure 1.1).

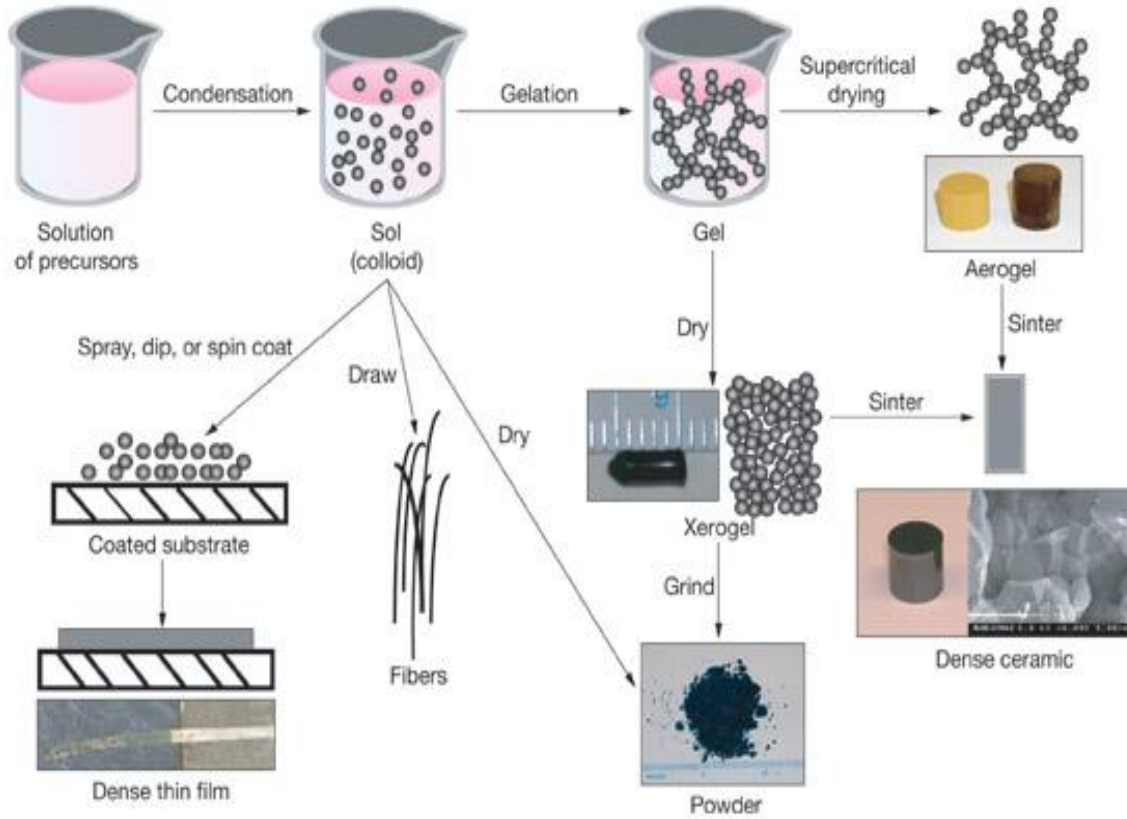


Figure 1.1. Various materials that can be synthesized by sol-gel method [20].

Some industrial applications of sol-gel method are listed below [15]:

Films and coatings

Films and coatings represent the earliest commercial application of sol-gel method and today they still have a big importance among the other applications since films deposited on substrates are the sol-gel products that can be produced in large quantities, the disadvantages of the sol-gel process can be minimized and the advantages of the sol-gel process can be attained easily with films [21]. The early applications for sol-gel films were in optical coatings. Since then many new applications of sol-gel films have been studied; optical coatings (antireflective coatings, colored coatings, optoelectronics, optical memory), electronic coatings (photo anodes, high temperature super conductors, conductive coatings), protective coatings (corrosion resistance, antibacterial (Figure

1.4.), scratch and wear resistance, laser damage resistance, moisture protection, self cleaning, hydrophobic coatings (Figure 1.3) and hydrophilic coatings (Figure 1.2)) [4].



Figure 1.2. Hydrophilic outside mirror (right) [22].



Figure 1.3. Water repellent glass [22, 23].

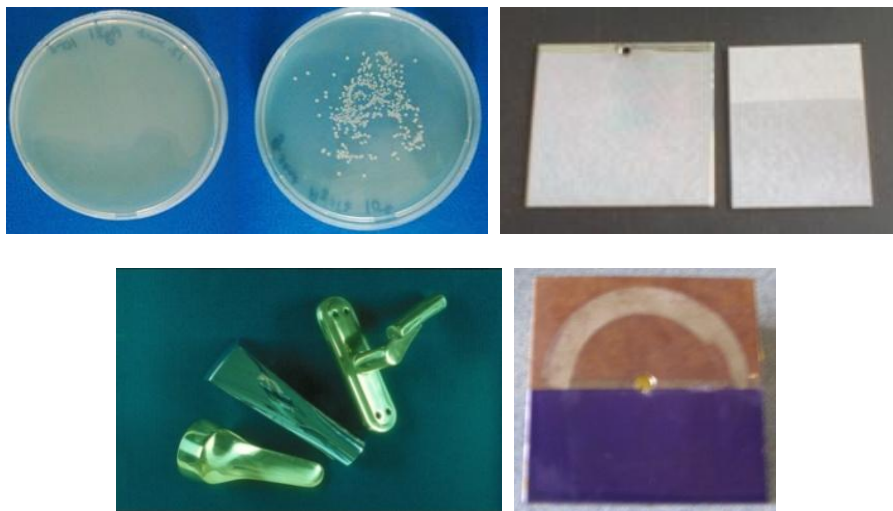


Figure 1.4. Samples of sol-gel film studies of TUBITAK MRC MI Top left to right: Antibacterial coating of glass, antibacterial coating of metal plates [24]. Bottom left to right: Corrosion resistance coatings, corrosion and abrasion resistance coatings

The range of substrates that can be coated is very wide (glasses, metals, plastics, textiles, ...) since not a very high temperature is needed to form the film. Substrates can be coated by spin coating, spray coating or dip coating (Figure 1.5). Each coating method has its own advantages. For example by dip coating an excellent homogeneity and uniformity can be obtained, in spin coating thickness control is a little easier than the other two methods, spray method is the most appropriate method for the substrates that do not have a rigid shape. Among these methods, dip coating method is the most preferred method in processing of commercial products since it is available to coat any size of substrates by this method.



Figure 1.5. From left to right: Dip coater, Spray gun, spin coater

Ceramics

Sol-gel process is important in the production of ceramic powder precursors which have molecular homogeneity, have the correct particle size distribution to aid densification and densify at temperatures below those required for conventional processing. Alumina can be given as an example of engineering ceramics that is produced by sol-gel method.

Porous gels and membranes

Porous gels (xerogels or aerogels) have high surface areas and small pore sizes and these properties are unattainable by conventional ceramic processing methods. Because of their unique properties porous gels and membranes are used in filtration, separation, catalysis, chromatography and thermal and acoustical insulation.

Fibres

Three ways can be listed to synthesize fibres by using sol gel method; conventional high temperature fiber formation from sol-gel derived preforms, drawing fibers directly from viscous sols at room temperature and unidirectional freezing of gels. Fibers produced by these methods tend to be microporous, contain relatively high quantities of organic residuals and many of them have noncircular cross sections. Because of these reasons these fibers are not appropriate for optical fiber applications. They are usually used in reinforcement, refractory textiles and high temperature superconductors.

Powders, grains and spheres

Beside the production of the powders that are the starting point of most polycrystalline ceramics, production of nanosized powders is today one of the most studied application of sol-gel process. These powders are used at many different areas such as electro-optics, magnetic devices, abrasives, catalysts, pigments, fillers. Uranyl spheres produced by sol-gel method are used as nuclear fuels. Compared to the conventional powders sol-gel powders have some advantages such as controlled size and shape, molecular scale homogeneity, lower processing temperatures.

Monoliths

Monoliths are the bulk gels whose smallest dimension ≥ 1 mm and processed without cracking. The main application area of monoliths is optic and the products can be listed as fiber optic lenses, near-net shape components, graded refractive index glasses.

Composite material

Composites materials provide unique combinations of properties that can not be achieved by one material alone. Since the processing temperatures are low in sol-gel method many different combinations can be produced such as; ORMOSILS (organically modified silicates), ORMOCERS (organically modified ceramics), CERAMERS (ceramic polymers), POLYCERAM (polymeric ceramics). They can be used in various applications; solar cells, UV protection layers, sensors, dental materials, electronics, optics, photonics, construction, ... [4].

1.1.3. Dip coating process

Films formed by a dip-coating process represent the oldest commercial application of sol-gel technology. The first patent based on this process was issued to Jenaer Glaswerk Schott & Gen. in 1939 for silica films [25]. The sol-gel dip-coating process is almost exclusively applied for the fabrication of transparent layer, primarily for the deposition of oxide films on float glass as a transparent substrate with a high degree of planarity and surface quality. Other substrates are possible, provided they can withstand the required curing temperature of about 500 °C. Film thickness up to 1 µm can be deposited.

Besides the dip-coating process, there are some other techniques such as lowering, spin coating, spraying. In lowering, instead of withdrawing the substrates from the solution the level of the tank solution can be lowered and the substrates to be coated remain stable. In spin coating, liquid film is spread out by spinning the substrate surface. This process is most suitable for the small discs or lenses. In spraying process, the substrate surfaces are sprayed with fine disperse solutions [26].

Among these processes dip coating process is the most widely used since it has many advantages compared to the other processes:

- High degree of uniformity,
- Ability to produce multi-layer coatings,
- Ability to coat both sides of the substrates,
- Substrates that have various shapes (sheets, tubes, rods, pipes,...) can be coated by dip coating process,
- Required investment does not increase by increasing the substrate size.

In dip-coating process, the substrate is dipped into the coating solution and uniformly withdrawn vertically from the coating bath at a constant speed. The liquid film runs off the substrate, adheres to the substrate surface and solidifies rapidly through the evaporation of solvent forming the layer. During the evaporation of the solvent water vapor diffuses from the atmosphere into the deposited layer and keeps the hydrolysis going. At the same time the polycondensation process continues until the sol-gel layer formed by calcination (Figure 1.6).

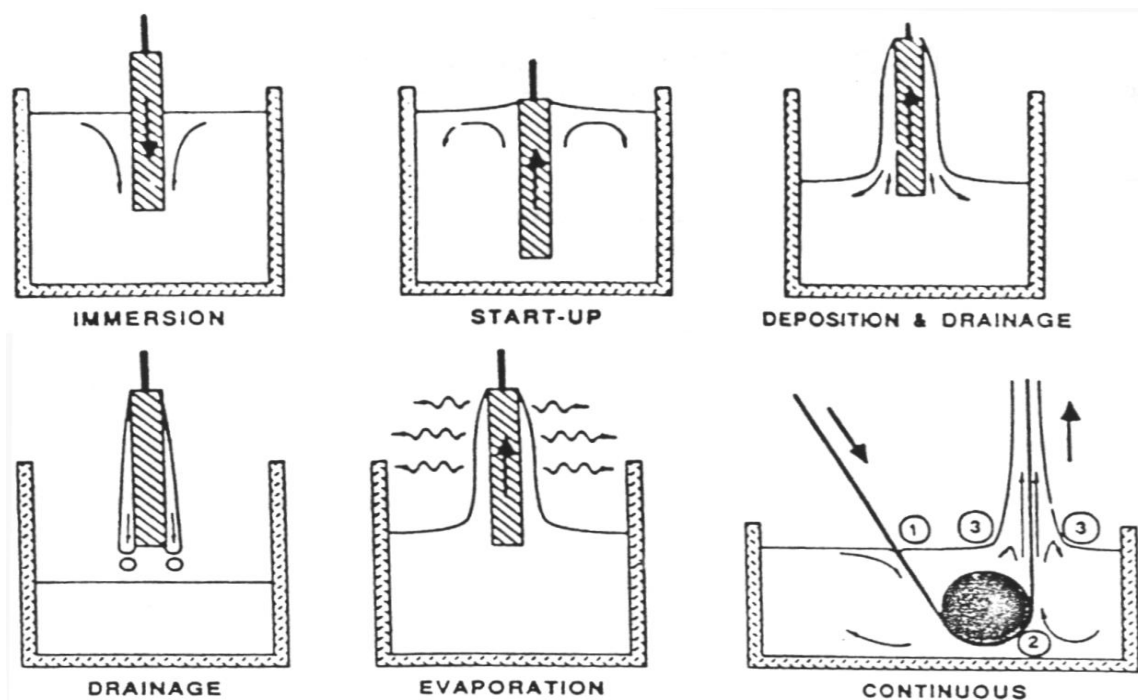


Figure 1.6. The steps of the dip coating process: immersion, start-up, deposition drainage, evaporation. The all five steps can be seen totally in continuous dip coating process [4].

The main parameters that affect the coating thickness are withdrawal speed, evaporation rate, viscosity and the concentration of the solution. The other parameters can be listed as surface tension of the solution, vapor pressure and relative humidity above the coating bath.

The coating thickness (d) increases by increasing the withdrawal speed (V). A simple relationship shows that the thickness (d) of the film is proportional to the withdrawal speed (V) to a power of $2/3$.

The film is thinned by evaporation as it is transported by the substrate that is withdrawn from the coating bath (Figure 1.7). Since it can be said that one of the important parameter that controls the thickness is the rate of evaporation. Because the evaporation rate is not constant, the film thickness decreases coming close to the substrate having a thickness profile of parabolic shape [27].

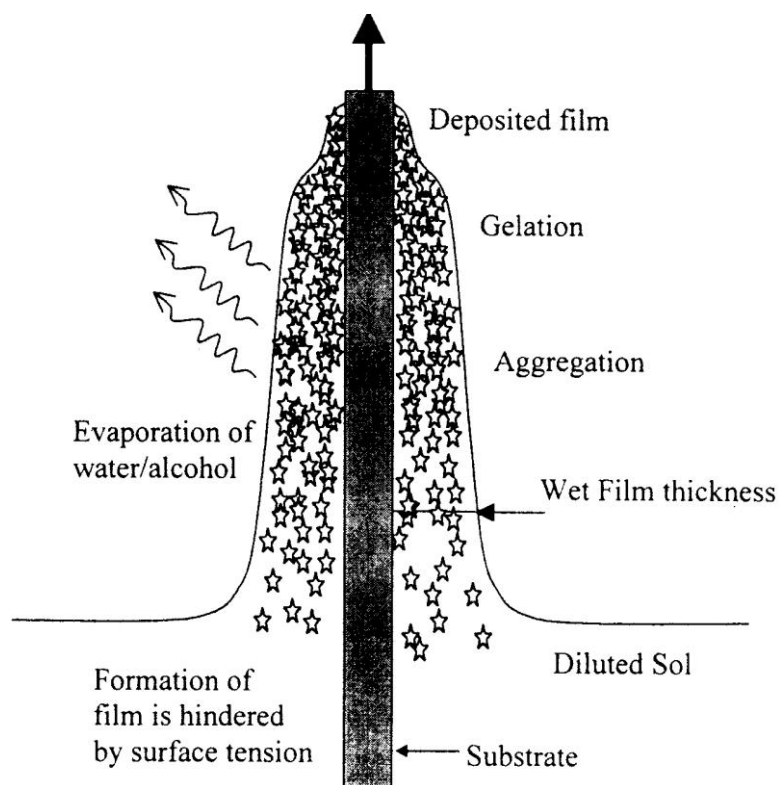


Figure 1.7. Film formation by evaporation [28].

1.2. Titanium Dioxide (TiO_2)

Titanium dioxide (TiO_2), also known as titania, belongs to the family of transition metal oxides. Titanium dioxide that is obtained from a variety of ores that contain ilmenite (FeTiO_3), rutile, anatase and leucosene ($\text{TiO}_2 \cdot x\text{FeO} \cdot y\text{H}_2\text{O}$) is produced by chloride or sulfate process [29].

1.2.1. Structural properties of TiO_2

TiO_2 exists mainly in three polymorphs which occur at atmospheric pressure; Anatase, rutile and brookite. Crystal structures and properties of these polymorphs can be seen in Figure 1.8 and Table 1.3 respectively. TiO_2 also has polymorphs that can be synthesized at high pressure; Srilankite type, cubic fluorite type, pyrite type, monoclinic B and cotunnite type. However from all phases of TiO_2 , only anatase and rutile play an important role in TiO_2 researches and applications [30, 31].

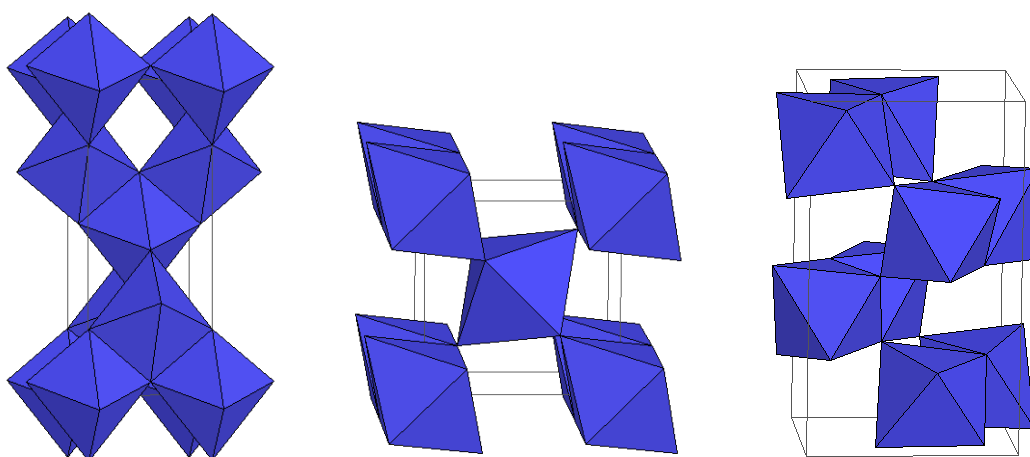


Figure 1.8. The crystal structure of Anatase, Rutile and Brookite [32]

Both anatase and rutile are photocatalytically active however anatase is considered to have higher photocatalytic activity which is thought to be related to its ability to adsorb water and hydroxyl groups [34-36].

However several studies have shown that a mixture of anatase and rutile phases has a better photocatalytic activity than that of anatase phase. The most known example of this theory is the product called Degussa P25, which is fine TiO_2 powder with a mass ratio of anatase to rutile nanocrystals being 4:1 [37-45].

Table 1.3. Properties of anatase, rutile and brookite [29, 33]

Property	Anatase	Rutile	Brookite
Crystal structure	Tetragonal	Tetragonal	Rhombohedral
Density (kg/m^3)	3830	4240	4170
Band gap (eV)	3.2	3.0	3.1
Solubility in water	Insoluble	Insoluble	Insoluble

It is believed that the difference between conduction band gaps of anatase (3.2 eV) and rutile (3.0 eV) phase is the reason of the better photocatalytic activity of the mixed phase since it is thought that this difference may produce irreversible electron transfer

from anatase to rutile and relative alignment of the anatase and rutile conduction band edges suppresses the recombination of photogenerated electrons and holes which is known to have an important role in increasing photocatalytic activity [45-48].

1.2.2. Application areas of TiO₂

In the beginning of the 20th century, industrial production started with titanium dioxide replacing toxic lead oxides as pigments for white paint [29]. Nowadays TiO₂ is still mostly used as white pigment in paint industry (51 % of total production) because of its high refractive index [31]. The consumption of TiO₂ as a pigment increased in the last few years in a number of minor end-use sectors such as textiles, food (it is approved in food-contact applications and as food coloring (E-171)), leather, pharmaceuticals (tablet coatings, toothpastes, and as a UV absorber in sunscreen cream with high sun protection factors and other cosmetic products) and various titanate pigments [29].

Other than these applications, due to its chemical stability, non-toxicity, low cost, and other advantageous properties TiO₂ is also used as a corrosion protective coating, as anti-reflection coating in silicon solar cells and in many thin-film optical devices, as gas sensor (due to the dependence of the electric conductivity on the ambient gas composition, as a biomaterial (as bone substituent and reinforcing mechanical supports) [29,31].

By the discovery of photocatalytic splitting of water on TiO₂ electrodes by Fujishima and Honda in 1972, photocatalysis has begun to be one of the important research and application areas of TiO₂ [49].

Today photocatalysis mechanism of TiO₂ is used in many application areas such as; self cleaning, photocatalytic sterilization, photocatalytic cancer treatment, air cleaning, water purification. A list of applications in these areas can be seen in Table 1.4 [29,50].

Table 1.4. Applications of photocatalysis

Self-cleaning	
Materials for residential and office buildings	Exterior tiles, kitchen and bathroom components, interior furnishings, plastic surfaces, aluminium siding, building stone and curtains, paper window blinds
Indoor and outdoor lamps and related systems	Translucent paper for indoor lamp covers, coatings on fluorescent lamps and highway tunnel lamp cover glass
Materials for roads	Tunnel wall, soundproofed wall, traffic signs and reflectors
Others	Tent material, cloth for hospital garments and uniforms and spray coatings for cars
Anti-fogging	
Materials for road	Road mirror
Materials for buildings	Bathroom mirror
Materials for stores	Refrigerated showcase
Materials for vehicles	Inside window, glass film, helmet visor
Material for optical instrument	Optical lens
Air cleaning	
Indoor air cleaners	Room air cleaner, photocatalyst-equipped air conditioners and interior air cleaner for factories
Outdoor air purifiers	Concrete for highways, roadways and footpaths, tunnel walls, soundproof walls and building walls
Water purification	
Drinking water	River water, ground water, lakes and water-storage tanks
Others	Fish feeding tanks, drainage water and industrial wastewater
Accelerated drying	
Materials for buildings	Toilet, window, bathroom
Self-sterilizing	
Hospital	Tiles to cover the floor and walls of operating rooms, silicone rubber for medical catheters and hospital garments and uniforms
Others	Public rest rooms, bathrooms and rat breeding rooms

Self cleaning applications

Interest in the self-cleaning effect of TiO_2 is increasing since it is a great alternative for the conventional cleaning procedures that need high consumption of energy, high maintenance cost and high usage of detergents [51].

Sunlight is necessary for TiO_2 coatings to gain self cleaning property. When a TiO_2 coated surface is exposed to UV light a photocatalytic reaction is occurred. By this reaction organic pollutants decompose into mineral acids that can be easily cleaned by water. After that when rain falls onto this TiO_2 coated surface by the help of the superhydrophilicity property that was gained by UV light, surface can be easily cleaned. An illustration of this mechanism can be seen in Figure 1.9 [52].

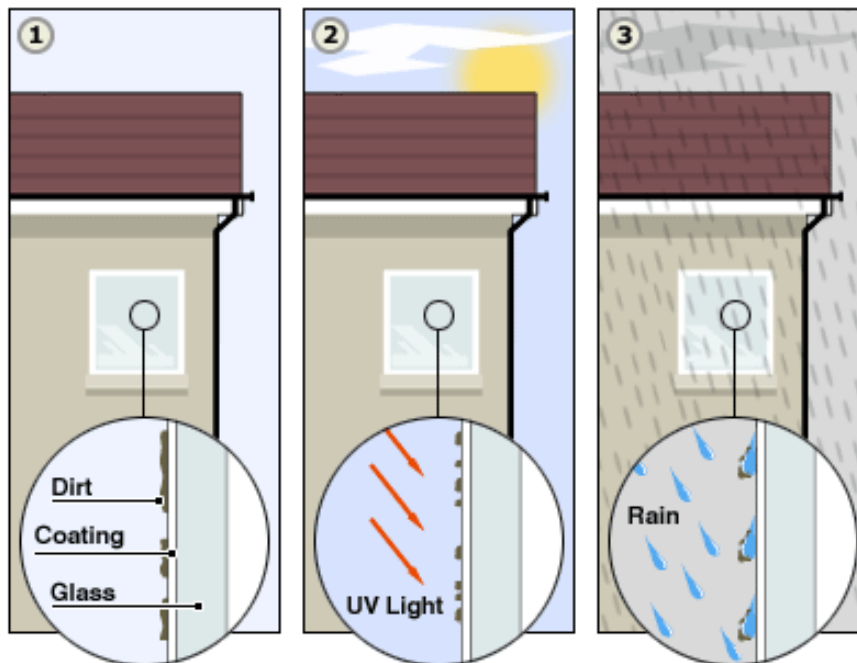


Figure 1.9. Illustration of self cleaning property

From self cleaning mechanism of TiO_2 surfaces it can be easily understood that TiO_2 surfaces should be exterior construction materials, since these materials could be exposed to abundant sunlight and natural rainfall [50].

It is possible to see such materials (tiles, glass, aluminium siding, plastic films, tent materials, cement, etc.) in the market since late 1990s [50]. Some real life self cleaning applications of TiO_2 can be seen in Figure 1.10.



Figure. 1.10. Applications of self-cleaning exterior building materials. Top left to right: MM Towers in Yokohama coated with self-cleaning tiles, Matsushita Denso building covered with self-cleaning glass. Bottom left to right: Self-cleaning roof of a train station in Motosumiyoshi [53] dives in Misericordia Church, Rome, Italy [54,55].

1.3. Effect of Glass Substrate On TiO_2 Film Properties

1.3.1. Effect of Na^+ diffusion on the structure of TiO_2

When a substrate is coated with a TiO_2 solution, a film is formed on the substrate and a heat treatment (sintering) is needed to make this TiO_2 film crystallize. As mentioned before it is believed that the anatase phase of TiO_2 is the one that shows the best photocatalytic activity and to have this phase TiO_2 films should be heated up to 500°C .

If a glass substrate is chosen for the coating, the crystalline structure of the TiO_2 film is strongly influenced by the composition of this glass substrate. If glass substrate does not contain sodium (Na) compounds, anatase formation and at higher temperatures rutile

formation can be observed. However if glass substrate contains a noticeable amount of Na compounds, Na^+ ions are diffused into the TiO_2 film during heat treatment and cause the formation of brookite and some other structures which are shown as Na_xTiO_2 [56]. Brookite formation is not wanted since it is known that brookite has no photocatalytic activity. Many studies have been done to prevent Na^+ diffusion.

Bach and Schroeder tried precoating glass substrate with SiO_2 to prevent Na^+ diffusion. They have studied 5 different SiO_2 thicknesses; 0, 6, 12, 18, 24 nm and have used two different alkoxides of Titanium; Titanium (IV) ethoxide and Titanium (IV) butoxide. They heated all films that they have prepared up to 600 °C by two different rates; 10°C/min. and 25°C/min. Structures of the films were examined by electron diffraction. They found that until the thickness of SiO_2 layer was 12 nm it is not possible to see just anatase phase, there were also Na_xTiO_2 and brookite. When the thickness of SiO_2 layer was 18 nm, it was possible to obtain anatase at both heating rates if Titanium (IV) butoxide was chosen as precursor. However if titanium (IV) ethoxide was chosen as precursor, while anatase was obtained at the slower heating rate, anatase and Na_xTiO_2 was produced at faster heating rate. They found that to obtain anatase phase at any condition, thickness of SiO_2 layer should be 24 nm [56].

Paz and Heller used the proton exchanged surface of soda lime glass to prevent the effect of sodium contamination. They boiled soda lime glass in sulphuric acid for 30 minutes to obtain a proton exchanged film on surface of soda lime glass (a hydrogen glass). They coated both soda-lime glass and hydrogen glass by spinning poly (titanyl acetlacetate) as TiO_2 precursor and found out that a sodium transport blocking layer was formed and highly photocatalytic film was obtained when hydrogen glass was used as substrate [57].

Hattori and his friends precoated soda-lime glass with a SiO_2 film containing fluorine ($\text{F}:\text{SiO}_2$) as a solution for Na^+ diffusion. They measured the diffusion amount of fluorine and sodium into the TiO_2 layer by using Rutherford Backscattering Spectroscopy (RBS). It was found that while 3 % atom of fluorine diffused into the TiO_2 layer from a 45 ± 5 nm thick $\text{F}:\text{SiO}_2$ layer, there was no Na^+ diffusion. It was also determined by the XRD results that fluorine containing SiO_2 underlayer had enhanced the crystallinity of anatase [58].

Watanabe and his friends investigated the effect of Na^+ diffusion on photocatalytic decomposition of gaseous acetaldehyde and the photoinduced wettability of TiO_2 films. They precoated soda-lime glass with a SiO_2 film to prevent thermal diffusion of sodium ion. Photocatalytic activity results evaluated by monitoring the change in concentration of gaseous acetaldehyde as a function of UV irradiation time showed that a 0.1 μm thick SiO_2 underlayer increased photoactivity of TiO_2 film by preventing sodium ion diffusion. However contact angle measurements showed that SiO_2 underlayer did not change photoinduced wettability of TiO_2 films too much [59].

Yu and Zhao prepared anatase TiO_2 films by sol-gel method on soda-lime glass, fused quartz and soda-lime glass precoated with a SiO_2 layer. They proved that the type of the substrate affects the photocatalytic activity by comparing photocatalytic rate constants of TiO_2 film on fused quartz glass and on soda-lime glass. Since photocatalytic rate constant of TiO_2 film on fused quartz glass was greater than photocatalytic rate constant of TiO_2 film on soda-lime glass, they had concluded that diffusion of sodium and calcium ions from soda lime glass into the TiO_2 film decreases the photocatalytic activity. By XPS studies and the photocatalytic decolorization of aqueous methyl orange solution they showed that instead of using fused quartz glass which is expensive and is not preferred as self cleaning window, soda-lime glass that is precoated with a 0.3 μm thick SiO_2 can be used to prevent Na^+ diffusion [60].

Yu, Yu and Cheng tried to prove that Na^+ diffusion occurs by calcination at high temperatures. They prepared Na-free TiO_2 films on soda-lime glass from a TiF_4 and boric acid solution. While putting one of the films at 500 $^\circ\text{C}$ for 2 hours for calcination they did not do calcination to the other film and compare photocatalytic activity of these films. As a result TiO_2 film prepared without calcination showed a higher photocatalytic activity than the TiO_2 film that was calcined, which showed that Na^+ is diffused into the TiO_2 film during calcination process [61].

Tomaszewski and his friends deposited TiO_2 films on soda-lime glass and soda-lime glass on which a 40 nm thick SiO_2 barrier coating e-beam evaporated, by dc magnetron sputtering. Reaction rate of photocatalytic breakdown of ethanol was measured before and after calcination. Reaction rate was similar for both soda lime glasses before calcination however after calcination, film deposited on soda lime glass with a SiO_2

barrier coating showed a higher photocatalytic activity compared to the one that deposited on soda-lime glass [62].

Yu and his friends investigated the effect of coating thickness and grain size on photocatalytic activity. Although they had increased the film thickness to prevent sodium ion diffusion they had seen that increasing the film thickness decreased the photocatalytic decolorization rate of aqueous methyl orange solution prominently [63].

1.3.2. Effect of tin bath on physical properties of TiO_2 film

The float process which enables glass sheet production with a uniform thickness and smooth surface was developed in the late 1950's by Alastair Pilkington [64].

In the float process (Figure 1.11) the raw materials (sand, limestone, soda ash, dolomite, iron oxide and salt cake) are mixed together and then charged into the furnace to be melted at 1580°C . The formed molten glass in a process of physical transformation is then fed to float/tin bath which consists of molten tin at 1100°C . The molten glass floats on top of the molten tin and it forms a ribbon of uniform thickness which is controlled by drawn off speed of solidifying glass. The glass is then transferred to annealing lehr to be cooled down. At this stage perfect flatness is provided by releasing internal stresses. Finally glass goes to cutting, quality control and storage area [65].

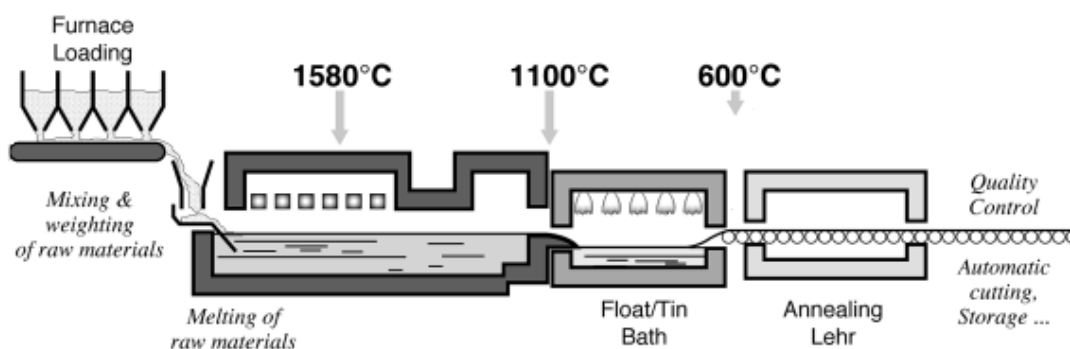


Figure 1.11. Schema of a float bath production line [66].

Molten tin is chosen as the liquid on which molten glass floats since molten tin is the only liquid on which molten glass can float without sinking (Density of tin (7.3 kg/m^3) is approximately 3 times greater than the density of glass (2.3 kg/m^3)), melting (232°C)

and boiling temperatures (2270 °C) of tin is appropriate to the temperature of molten glass (~600 °C to 1050 °C) in float bath, tin does not react chemically with glass and it can be easily found [67].

Because of the diffusion occurred in tin bath, on the one side of the glass that contacts with molten tin some amount of tin is found. Therefore float glasses are known as two sided; Tin side and air side.

Some studies have been done to find out the performance differences of these two sides when float glasses are coated. Kılıçoğlu, in her PhD Thesis coated float glass with a nanosized antibacterial TiO₂ solution and took into consideration the two sides of float glass while doing contact angle, thickness and reflectance measurements and it was found that there was no remarkable difference between two sides [67]. Kırtay, in his PhD Thesis compared the tin and air side of coated float glass according to their mechanical properties and he found out that tin side has lower mechanical strength compared to air side [68].

1.4. TiO₂ Photocatalysis

Discovery of photocatalytic splitting of water on TiO₂ electrodes by Fujishima in 1972 is accepted to be the first realization of strong oxidation and reduction power of photoexcited TiO₂ [69,70].

This strong oxidation and reduction power of TiO₂ at ambient temperature and pressure is one of the most important property that makes it the mostly preferred photocatalyst for environmental purification. The other properties of TiO₂ can be listed as: [50,54,71]

- It is anti-bacterial,
- It has self-cleaning property,
- It is non-toxic,
- It has superhydrophilicity ability,
- It is highly stable chemically,
- It is cheap and readily available,
- It is able to convert a wide spectrum of organic contaminants to water and CO₂,
- No chemical reactants must be used and no side reactions are produced.

1.4.1. Mechanism of TiO₂ photocatalysis

To make photocatalysis process start, first of all TiO₂ should be excited by a light with sufficient energy. Here sufficient means an energy that equals to or higher than the band-gap energy (E_{bg}) of the TiO₂ (3.2 eV) (Figure 1.12). By exposure to such energy, electrons would be excited from the valance band to the conduction band of TiO₂ and holes would be left in the valance band.



These photogenerated holes in the valance band which has strong oxidizing power diffuse to the surface and react with adsorbed water in order to produce hydroxyl radicals ($\bullet\text{OH}$) while the electrons in the conduction band react with molecular oxygen in the air to produce the superoxide radical anion ($\bullet\text{O}_2^-$).



By the holes and hydroxyl radicals which are very strong oxidizers organic pollutants degrade [71,72].

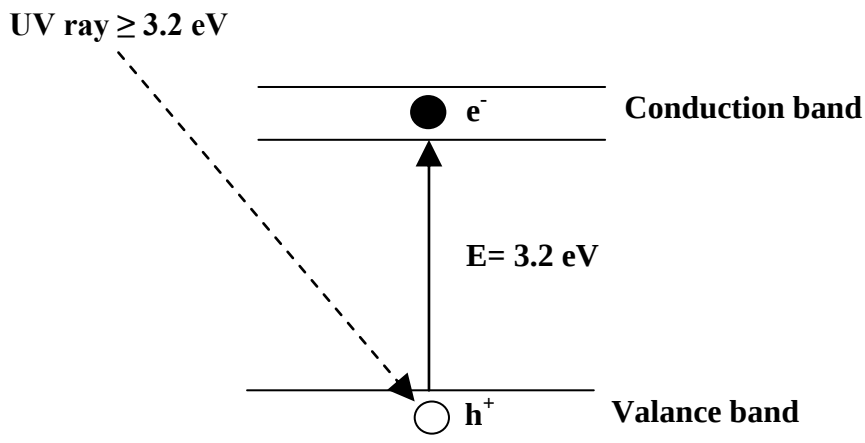


Figure 1.12. The process of TiO₂ photocatalysis

1.4.2. Enhancing the photocatalytic activity of TiO₂ by doping ions

Although TiO₂ seems to be a very convenient semiconductor for photocatalytic degradation of organic substances, it does not have the ability of working under visible light. What makes TiO₂ work under ultraviolet light is that energy of ultraviolet light (< 387 nm) exceeds band gap of anatase phase of TiO₂ (3.3 eV). The problem is that ultraviolet light has only a 3 %-5 % part at sunlight spectrum. Many methods (surface sensitization, metal coating, doping, composite semiconductors) have been studied to enhance photocatalytic activity of TiO₂ under UV light and under visible light ($\lambda > 400$ nm) which is the main part of solar spectrum [29,69,71].

In this study metal ion doping through sol-gel method is chosen to enhance photocatalytic activity of TiO₂. The reason that this method works can be explained by a new energy level produced in the band gap of TiO₂ which can be seen in Figure 1.13. By the production of this new level, electron can be excited from the valance band to the conduction band with energy equals $h\nu_2$ instead of $h\nu_1$. Besides, by metal ion doping electron-hole recombination is inhibited which also helps enhancing photocatalytic activity [69].

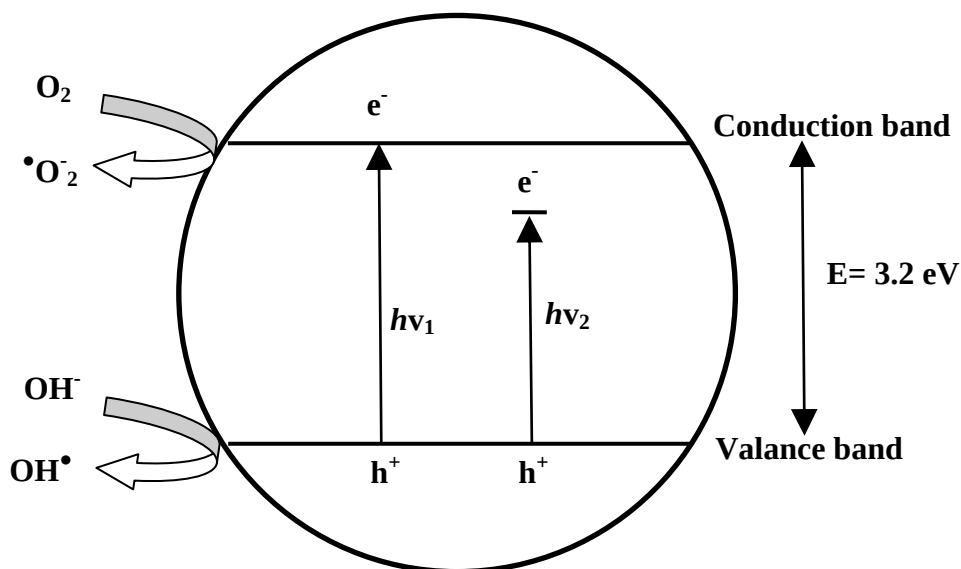


Figure 1.13. $h\nu_1$: pure TiO₂; $h\nu_2$: metal-doped TiO₂ [69].

Below a literature research can be found about some of the metals that were doped into the TiO₂ to enhance its photocatalytic activity:

Liu and his friends studied the effect of Zn^{2+} doping on the photocatalytic activity of TiO_2 . Zn^{2+} doped TiO_2 nanoparticles were prepared by two different methods; sol-gel method and solid phase reaction method. To prepare Zn^{2+} doped TiO_2 nanoparticles by sol-gel method tetrabutyl titanate and isopropanol were used. pH of the prepared solution was adjusted approximately 3 with HCl. Then to this solution, zinc nitrate was added dropwise by continuous stirring to obtain a translucent sol. In a few minutes gel and after drying this gel the dry gel formed. After the calcination process at 500 °C for 2 hours, Zn^{2+} doped TiO_2 nanoparticles were obtained. To prepare Zn^{2+} doped TiO_2 nanoparticles by solid phase reaction method, the powder of % 0.1, 0.3, 0.5, 0.8, 1.0, 1.5, 2.0 mol ZnO and the pure powder of TiO_2 were mixed and sieved through # 120 mesh. After the calcination process at 500 °C for 2 hours the powder was sieved again through # 120 mesh to prevent agglomeration and finally the Zn^{2+} doped TiO_2 nanoparticles were obtained. Zn^{2+} doped TiO_2 nanoparticles were characterized by XRD and TEM. The TEM results showed that powders prepared by solid phase reaction have smaller particle size. This also indicates that they have higher specific surface area and better photocatalytic activity. XRD results showed that method did not affect the crystal form of the TiO_2 , by both methods anatase structure was obtained. To measure the photocatalytic activity, hollow cylindrical photoreactor and Rhodamine B solution were used. It was observed that Zn^{2+} doping by sol-gel method has slightly increased the photocatalytic activity while Zn^{2+} doping by solid phase reaction has a great influence on photocatalytic activity [73].

Behnajady and his colleagues prepared silver doped TiO_2 by liquid impregnation and photodeposition. In liquid impregnation method, a TiO_2 suspension was obtained with TiO_2 and water then different amounts of AgNO_3 was added to this suspension to make Ag^+/TiO_2 mol concentration 0.5, 1.0, 1.5, 2.0 and 2.5. After stirring, the slurry was left for resting 24 hours and then dried and calcinated. In photodeposition method again a TiO_2 suspension was obtained with TiO_2 and water then the pH of the suspension was adjusted to 3 by adding perchloric acid. Afterwards different amounts of AgNO_3 were added to this suspension to make Ag^+/TiO_2 mol concentration 0.5, 1.0, 1.5, 2.0 and 2.5 then the mixtures were irradiated with UV light, dried and calcinated. SEM images of the powders showed that the distribution of the silver ions was not uniform and the shape of the silver ions were not regular. Decolorization of a textile dye, Acid Red 88

was observed to determine the photocatalytic activity. First of all, it was observed that doping TiO_2 increased its photocatalytic activity. Results showed that silver doped TiO_2 by photodeposition method was more efficient than the silver doped TiO_2 by liquid impregnation method. Optimum silver content was 2 % in liquid impregnation method and was 0.5 % in photodeposition method [74].

Seery and his co-workers studied silver doping to TiO_2 by sol-gel method to enhance its visible light photocatalytic activity by promoting anatase to rutile transformation. The clear transparent sol was prepared with titanium isopropoxide, acetic acid and water. 1, 2, 3 and 5 % mol of AgNO_3 was added to this solution and then some of this sol was preirradiated before drying and calcination to reduce Ag^+ and some of them were dried in oven without pre-irradiation and silver ion was formed during calcination. From the XRD results it could be seen that when calcinated at 600 °C, both pre-irradiated and not- preirradiated powders consisted of anatase phase. While no silver peaks were detected in the powders calcinated at 600 °C, metallic silver peaks were obvious in the powders calcinated at 700 °C. This results indicated that at 600 °C silver particles were distributed homogenously in TiO_2 matrix however at 700 °C agglomeration began. XRD results also showed that Ag addition reduced the particle size. Photocatalytic activities of the powders were measured by examining the decomposition of Rhodamine G6. Suspension made by synthesized powders and RG6 solution were irradiated by solar test chamber simulating the Dublin summer sunlight at noon and behind a sunny window. Looking at the absorption spectra of the samples recorded at increasing time intervals it is obvious that silver doping enhanced the photocatalytic activity of both pre-irradiated and non-irradiated TiO_2 powders. By addition Ag, degradation rate of Rhodamine G6 increased from 0.06 to 0.24 min^{-1} at pre-irradiated samples and from 0.06 to 0.34 min^{-1} at nonpre-irradiated powders when irradiated by solar test chamber simulating the Dublin summer sunlight at noon. When the solutions of R6G in the presence of titania and silver doped titania placed behind a sunny window degradation rate became 1.95×10^{-2} and $1.3 \times 10^{-2} \text{ min}^{-1}$ for undoped and doped samples respectively [75].

Chao and his friends investigated the effect of Ag doping on TiO_2 anatase to rutile phase transformation. They studied five different Ag concentrations (2, 4, 6, 8, 10 mol %) and they used AgNO_3 as the silver source. They added AgNO_3 and nitric acid to the

TiO₂ sol which was prepared with tetrabutyl orthotitanate, acetylacetone and ethyl alcohol. The sol was stirred until getting a clear and transparent sol. After the calcination of the TiO₂ xerogel, at different temperatures, which was obtained by drying the sol at 100 °C for several days, TiO₂ powders were prepared. According to XRD results, anatase phase started to appear at the calcination temperature of 400 °C. For the TiO₂ powders which were not doped with Ag, rutile phase did not appear until the calcination temperature is 750 °C and still some amount of anatase remained when the calcination temperature was 800 °C. It was seen that when TiO₂ powders doped with Ag anatase to rutile transformation started at lower temperatures. It was also obvious that increasing the Ag concentration decreased the rutile phase appearance temperature; for the concentrations of 4, 8, 10 % Ag dopants, rutile phase appearance temperatures were 700 °C, 650 °C, 600 °C respectively. Rutile nucleation and grain growth in Ag doped TiO₂ powders were enhanced since anatase grain sizes decreased and the specific surface areas increased in the presence of Ag dopant. This idea was also supported by HRTEM and SEM images [76].

Chen, Yao and Wang studied the effects of eight transition metal ion dopants (Ni²⁺, Cr⁵⁺, Fe³⁺, V⁵⁺, Co²⁺, Cu²⁺, Zn²⁺, Mn²⁺) on photocatalytic activity and structural properties of TiO₂. Both doped and undoped TiO₂ nanoparticles were prepared by sol-gel method. Titanium butoxide was used as precursor, triethanolamine as controlling agent and ethanol as solvent. Ion suspensions of the dopants (ZnSO₄·7H₂O, Fe₂(SO₄)₃·xH₂O, CuSO₄·5H₂O, Co(NO₃)₂·6H₂O, NiSO₄·6H₂O, CrCl₃·6H₂O, NH₄VO₃, and MnSO₄·H₂O) were added to the sol obtained by sol-gel method. Three different amounts of TiO₂ (0.3, 0.18, 0.06), three different calcination temperatures (580 °C, 520 °C, 460 °C), three different drying time and different doping concentrations ranging from 0.00002 % to 0.2 % were studied. The crystal phase and size of both doped and undoped TiO₂ powders were studied by XRD and the photocatalytic activity of both doped and undoped TiO₂ powders were measured by the decolorization rate of methyl orange. The study showed that Ni²⁺ doping moved the absorption edge to visible light region. When the Ni²⁺ concentration was 0.002 % the highest photocatalytic activity was measured. The diameter of anatase phase reduced from 25.47 nm to 18-20 nm when TiO₂ was doped with V⁵⁺ and Fe³⁺. The optimum concentration rate was 0.00002 % for V⁵⁺ and 0.002 % for Fe³⁺ to reach the highest photocatalytic activity and for both

dopants it was observed that photoreactivity of TiO_2 decreased when the dopant concentration was 0.2 %. Mn^{2+} doped TiO_2 showed highest photocatalytic activity when its concentration was 0.00002 % and similar to V^{5+} and Fe^{3+} , higher concentrations (0.2 %) of Mn^{2+} reduced the photoreactivity. Co^{2+} and Cr^{3+} doping increased the fraction of anatase phase compared to undoped TiO_2 . While the optimum concentration of Co^{2+} dopant was found to be 0.00002 %, Cr^{3+} dopant did not enhance photocatalytic activity at that concentration and both Cr^{3+} and Co^{2+} dopants showed lower photocatalytic activity when their concentrations were ≥ 0.002 %. Both Cu^{2+} and Zn^{2+} dopants achieved highest photocatalytic activity at the ion concentration of 0.002 % and reduced photoreactivity when the ion concentration was too high (0.2 %) and too low (0.00002 %) [77].

Li and his friends were studied the effect of doping TiO_2 with alkaline-earth metal ions (Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}) on its photocatalytic activity. They prepared doped TiO_2 powders by sol-gel method and doped TiO_2 powders by impregnation and coprecipitation methods. $\text{Ti}(\text{OBu})_4$, ethanol, water and HNO_3 were used to obtain a transparent sol and TiO_2 powder was obtained after aging, drying and calcination. To prepare doped TiO_2 by coprecipitation method an aqueous MCl_2 ($\text{M} = \text{Be}, \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$) solution was used instead of the water that was used in sol-gel method and to prepare doped TiO_2 by impregnation method undoped TiO_2 powder was added into a given concentration of MCl_2 ($\text{M} = \text{Be}, \text{Mg}, \text{Cr}, \text{Sr}, \text{Ba}$) solution. The XRD results of pure TiO_2 and the alkaline-earth metal ion doped TiO_2 prepared by impregnation method showed that only the anatase phase was found in the undoped TiO_2 and in doped TiO_2 indicating that doping with alkaline-earth metal ions did not influence the crystal patterns of the TiO_2 particle. Photocatalytic activities were evaluated by the photocatalytic production of hydrogen. According to evaluated results it was found that when the radius of the doping ion (Be^{2+} , Mg^{2+} , Ca^{2+}) was smaller than or similar to that of Ti^{4+} , the doping effect was obvious; while when the radius of the doping ion (Sr^{2+} , Ba^{2+}) was much larger than that of Ti^{4+} , the effect of doping was smaller. It was also found that impregnation method was more efficient than coprecipitation method since the samples prepared by the coprecipitation method had fewer alkaline-earth metal ions on the TiO_2 surface than by impregnation method. The optimum molar contents of dopant ions, doped by impregnation method, Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} were 1.25,

1.25, 2.25, 2.25 and 2.25 %, respectively and the optimum calcination temperature and time were 400 °C and 1 hour respectively [78].

Kim, Hwang and Choi synthesized platinum ion doped TiO₂ by sol-gel method and its visible light photocatalytic reactivity was investigated by oxidative and reductive degradation of chlorinated organic compounds. Colloidal suspension of undoped TiO₂ was prepared with the Titanium isopropoxide precursor, absolute ethanol and nitric acid after evaporation at 50 °C and calcination at the temperatures from 373 K to 873 K. To prepare Pt doped TiO₂ the same procedure was followed, only chloroplatinic acid was added to the above suspension. The XRD analysis of Pt doped TiO₂ samples calcined at various temperatures showed that the anatase phase was dominant up to 673 K, above which the phase transformation to rutile started and nearly finished at 873 K. From the X-ray peak width particle sizes were estimated 7-8 nm up to 673 K and increased to 18.3 nm and 26.8 nm (for anatase) and 31.1 nm and 33.7 nm (for rutile) at 773 and 873 K, respectively. The band gap of doped TiO₂ was lower than that of undoped TiO₂ by about 0.2 eV according to X-ray absorption spectroscopy results. Under UV irradiation Pt doped TiO₂ showed higher photocatalytic activity than undoped TiO₂. It was found that the visible light activity of Pt doped TiO₂ was strongly affected by the calcination temperature and the concentration of Pt ion dopant, which were optimal at 673 K and 0.5 atom %, respectively. Pt doped TiO₂ was able to degrade dichloroacetate, 4-chlorophenol and trichloroacetate under visible light with the same photoreactivity showed under UV light, however it could not degrade substrates such as tetramethylammonium and trichloroethylene, which are degraded under UV irradiation [79].

Shah and his friends synthesized TiO₂, doped with transition metal ions (Pd²⁺, Pt⁴⁺, Nd³⁺ and Fe³⁺) by metallorganic chemical vapor deposition process. The effects of dopants (~1 %) on photocatalytic reactivity were studied by the degradation of 2-chlorophenol under an ultraviolet light source. The results showed that doping TiO₂ with transition metal ions enhanced photocatalytic activity. Nd was the most effective dopant; The 90 % destruction time of 2-chlorophenol was reduced from 60 minutes to 25 minutes by Nd doping to TiO₂. It was observed that size difference between the host ionic radii and the dopant's ionic radii is very important. Dopants that had larger ionic radii were (for example Nd dopant compared to Fe dopant) more effective than the

dopants that had smaller ionic radii. According to X-ray diffraction and transmission electron microscope both Nd^+ (0.6, 1, 1.5 %) doped and undoped TiO_2 consisted of anatase phase with a particle size of 20-23 nm. Nd^+ doping reduced the particle size slightly. It can be seen from the ultraviolet visible light absorption measurements that Nd^+ doping reduced the band gap. Maximum band gap reduction (0.55 eV) was obtained when the concentration of Nd dopant was 1.5 % [80].

Sonawane and Dongare prepared Au/ TiO_2 films on soda-lime glass substrates by dip coating method. Photocatalytic activity of the films were studied by decomposition of phenol under sunlight. To obtain Au doped TiO_2 sol, the gold colloidal solution that was prepared by reduction of HAuCl_4 with NaBH_4 was added dropwise to the TiO_2 sol that was prepared by sol-gel method with titanium isopropoxide precursor. The substrates that were going to be coated were cleaned with mixture of H_2SO_4 and H_2O_2 (3:1) followed by 2–3 times wash with double distilled water and stored in desiccators. These glasses were dipped in Au doped TiO_2 sol for 2-3 minutes and then pulled out at approximate pulling rate of 1 mm/s. The coated glasses that were first dried at room temperature finally dried in oven at 100 °C for 2 hours. It was observed from the UV-vis absorption spectra that while undoped TiO_2 shows absorption in the UV region at around 360 nm 1 % Au doped film shows the absorption edge at around 450 nm and this is telling that Au doping was shifted the absorption wavelength of TiO_2 to the visible region. According to XRD results in undoped TiO_2 anatase phase occurred at 400–600 °C while it occurred at 200–275 °C in Au doped TiO_2 . Anatase to rutile phase transformation started at 350–500 °C in Au doped TiO_2 . However, in the undoped TiO_2 peroxide this anatase to rutile transformation took place at 600–900 °C temperature. TEM images indicated that average particle size of Au particles in films was within 15-20 nm range. Photocatalytic activity measurements indicated that for complete decomposition of phenol (95 %) undoped TiO_2 film required 9 h, 1% Au/ TiO_2 required 4 hours and 2 % Au/ TiO_2 required 3.5 hours respectively which showed that reaction rate was enhanced by Au doping [81].

Behpou, Ghoreishi, Razavi studied the photocatalytic properties of silver doped TiO_2 by degradation of methyl orange. TiO_2 nanoparticles without Ag were prepared by anodization technique. Ti sheets were used as cathode and anode electrodes and sulfuric acid as electrolyte solution. After the electrochemical process TiO_2 sheet was calcinated

at 500 °C. Ag was doped by immersing the TiO₂ sheet in AgNO₃ solution for several times then after drying the surface by hot air the sheet was calcinated at 500 °C. SEM images showed that surface structure and the particle size of Ag doped TiO₂ particles are identical with undoped TiO₂. Photodegradation of MO dye under UV light source was investigated to measure the photocatalytic activity of synthesized particles. The results showed that Ag ion doping increased the rate and efficiency of decomposition of MO. The efficiency increased by increasing the immersion number of Ti sheet to AgNO₃ solution. 30 times immersion gave the most effective result. However immersion more than 30 times decreased the photocatalytic activity. 56 cm was measured to be the best distance to radiation source. When the distance between the radiation source and TiO₂ nanoparticles was less than 52 cm or more than 66 cm photocatalytic reactivity decreased [82].

Iketani and his friends prepared vanadium (V⁴⁺) doped TiO₂ (V_xTi_{1-x}O₂) films on pyrex glass substrates by sol-gel method to show that V⁴⁺ dopant enhances the visible light photocatalytic activity of TiO₂. Solution of Vanadium oxyacetylacetonate (VO(acac)₂), water, nitric acid, and tetrahydrofuran (THF) was added into the titanium isopropoxide that was dissolved in (THF). Films were synthesized by spin-coating the sol on pyrex glass substrates. After coating, the substrates were pre-heated at 100 °C for 1 hour and calcinated at 500 °C for 1 hour. XRD results showed that all V⁴⁺ (x = 0, 0.01, 0.05, 0.075 and 0.1 %) doped TiO₂ films consisted of TiO₂ anatase phase, and no V-derived peaks were detected. XPS measurements indicated that vanadium was uniformly distributed in the film. Photocatalytic activity under UV and visible light irradiation was measured by decomposition of methylene blue and gaseous acetaldehyde. Results showed that the absorption spectrum of the (V_xTi_{1-x}O₂) film shifted to longer wavelengths when x increased and this proves that (V_xTi_{1-x}O₂) film was also active under visible light irradiation which was also supported by decomposition of methylene blue. However it was also a fact that the photocatalytic activity of the film in the visible light region was still low compared to the activity in the UV region [83].

Pan and Wu prepared Cr and N doped titanium dioxide using sol-gel method and ammonia treatment. Different amounts of Chromium Chloride (Cr/Ti molar ratios of 0, 0.32, 1.0, 2.5, 4.1 and 8.8 %) were dissolved in ethanol and then mixed with titanium

butoxide. The mixed solution was slowly drop-by-drop added in a 0.1 M HCl solution. After the hydrolysis completed, the sol was dried at 110 °C and dried gel was then calcined at 400 °C for 30 minutes. Pure TiO₂ was prepared using the same above procedure without mixing chromium chloride. After calcination, the powders were thermally treated in pure ammonia atmosphere at 400, 450, 500, 550 and 600 °C for 180 minutes and N doped TiO₂ powders were obtained. Finally, following the preparation method of Cr/TiO₂, nitrogen modified Cr/TiO₂ was treated in pure ammonia atmosphere at desired temperature to obtain both chromium and nitrogen-doped TiO₂. The visible-light photocatalytic activity was evaluated by the de-colorization of methylene blue and degradation of isopropyl alcohol in a visible light reactor. From the XRD results it was found that the particle size of Cr doped TiO₂ powders ranged from 6.5 nm to 11.8 nm, and decreased with increasing chromium concentration and the particle size of N doped TiO₂ ranged from 6.8 nm to 20 nm, increased with increasing treated temperature. Isolated narrow bands formed in the band gap of Chromium doped TiO₂ and this reduced the photon energy required to excite the electrons, similar to chromium the substitution of nitrogen atom into TiO₂ lattice was proved to enhance the band-gap narrowing and visible-light photocatalytic activity. However the Cr and N co-doped TiO₂ showed less photoactivity than either Cr or N-doped TiO₂ due to the extra imperfection of TiO₂ lattice during preparation [84].

Cao and his firends prepared Ag doped TiO₂ nanoparticles by sol-gel method and photocatalytic activity was investigated by degradation of acetamiprid. Titanium isopropoxide was slowly added to ethanol and then the pH of the solution was adjusted with nitric acid. Finally, AgNO₃ was added to this solution as the source of Ag dopant (Ag: Ti molar ratios of 0.02, 0.04, 0.06, 0.08 and 0.12). After the formation of gel, it was dried at 60-70 °C for 8 hours and calcinated at 500 °C for 2 hours. XRD and BET results showed that Ag dopant accelerated anatase to rutile transformation and at relatively low Ag concentrations (2–6 %), anatase grain sizes decreased and specific surface areas of the TiO₂ powders increased. The results taken from UV visible absorbance detector showed that the presence of Ag doping to TiO₂ increased the photocatalytic activity of TiO₂. The photocatalytic degradation velocity constant (k) increased rapidly when the Ag content increased from 0.02 to 0.06, and then decreased

slowly as the Ag content increased from 0.06 to 0.12. The optimum mole percentage of Ag was found to be between 4 % and 8 % [85].

Wang and his friends studied the photocatalytic activity of TiO₂ clusters on which Ag nanoparticles were deposited via a two-step route, which included a ⁶⁰Co γ -ray irradiation method after acidic peptization of amorphous TiO₂. Photodegradation of methylene blue was observed to measure the photocatalytic activity. According to TEM images the synthesized composite consisted of TiO₂ particles with about 5 nm and Ag particles with less than 2 nm in diameter and it was highly dispersed in aqueous solution and thermodynamically stable. Photodegradation of methylene blue experiments showed that although the nanocomposites with different Ag loadings before activation exhibited poorer photocatalytic activity compared to pure TiO₂, they enhance photocatalytic activity of TiO₂ after being calcinated in flowing N₂ gas [86].

Tomas and his co-workers studied optical and morphological properties and photocatalytic activity of silver doped TiO₂ films. TiO₂ sols were prepared with titanium isopropoxide, acetic acid and isopropanol. AgNO₃ solution was added to this sol to make Ag concentration in the final sol 1 % and 3 %. Before being coated, glass substrates were cleaned by a standard chemical cleaning process based on deionized water and hydrogen peroxide solution then the substrates were withdrawn from the titanium sol at a constant velocity of 15.1 cm/min. After coating the glasses by dip coating method, coated glasses were dried at 100 °C for 1 hour and calcinated at 500 °C. Photocatalytic activity and SEM results showed that without calcination Ag⁺ ions were not able to enter the TiO₂ matrix and form a stable material. However after calcination at 500 °C Ag⁺ dopant enhanced photocatalytic activity since larger specific surface area were obtained by high temperature treatment [87].

Choi and his friends measured the photoreactivities of 21 metal ion (Fe³⁺, Mo⁵⁺, Ru³⁺, Os³⁺, Re⁵⁺, V⁴⁺, Rh³⁺, Co³⁺, Al³⁺, Mn³⁺, Ni²⁺, Zr⁴⁺, Zn²⁺, Ta⁵⁺, Sb⁵⁺, Nb⁵⁺, Sn⁴⁺, Li¹⁺, Ga³⁺, V³⁺, V⁵⁺) doped TiO₂ colloids in terms of both the conduction band electron reduction of an electron acceptor (CCl₄ dechlorination) and the valence band hole oxidation of an electron donor (CHCl₃ degradation). TiO₂ colloids were synthesized by sol-gel method by using titanium tetraisopropoxide, ethanol, water and nitric acid. To obtain powder samples, the colloidal solution was evaporated at 35 °C and dried under

vacuum. Doped TiO₂ was prepared according to the above procedure in the presence of metal salts at the doping level from 0.1 to 3.0 %. The results of the study showed that doping with Fe³⁺, Mo⁵⁺, Ru³⁺, Os³⁺, Re⁵⁺, V⁴⁺, and Rh³⁺ at 0.1-0.5 % significantly increased the photoreactivity for both oxidation and reduction while Co³⁺ and P⁺ doping decreased the photoreactivity. In general, photoreactivities were shown to increase with the relative concentration of trapped charge carriers. The photoreactivity of doped TiO₂ appeared to be a complex function of the dopant concentration, the energy level of dopants within the TiO₂ lattice, their d electronic configuration, the distribution of dopants, the electron donor concentration, and the light intensity [88].

Wetchakun and his friends synthesized V, Fe and Cu ion doped TiO₂ by modified sol-gel method using titanium isopropoxide as the precursor of TiO₂ and ammonium metavanadate, iron nitrate and copper nitrate as the precursors of metal ion dopants. Salt of the metal dopants were added to the solution made of titanium isopropoxide, ethanol water and ammonia at desired amounts (% metal/Ti ratio: 0.1, 0.5, 1.0, 2.0, 5.0 and 10.0). These solutions were loaded into a pouch type cellophane. After the completion of the dialysis process, the suspensions first centrifuged then washed and dried and the powders are finally calcined. Photocatalytic activities were studied by the mineralizing of sucrose, phenol, oxalic acid, formic acid, methanol, malonic acid under UVA, solar spectrum and visible light irradiation. It was found that under visible light Fe doped TiO₂ could mineralize only oxalic acid. The optimum doping amount was found to be 2 %. Under UVA irradiation the overall activity of the all photocatalysts decreased in the following order: Undoped TiO₂ > Cu doped TiO₂ > Fe doped TiO₂ > V doped TiO₂ and with the BET results it was proved that photocatalytic activity increased by the increasing of surface area. Under solar spectrum irradiation it was found that undoped TiO₂ had better photocatalytic activity than any of doped TiO₂. XRD results showed that the doped TiO₂ consisted of anatase and rutile phase however the dominant phase was anatase. It was observed that doping did not affect the anatase to rutile transformation. The crystalline size of the doped TiO₂ was found to be 10-20 nm by TEM [89].

Zhou and his friends prepared vanadium doped TiO₂ by sol-gel method. Titanium butoxide was used as precursor and NH₄VO₃ was used as the vanadium source. pH of the solution was adjusted with HNO₃. The obtained sols were aged and dried at 80 °C and calcined at 150 °C, 300 °C, 450 °C and 600 °C for 5 hours. The photocatalytic

activity of the vanadium doped TiO_2 powders was investigated under a fluorescent lamp by methyl orange degradation. Characterization of the powders showed that the doped vanadium presented mainly in the form of V^{5+} , and vanadium doping could prevent crystal growth and enhance the phase transformation from anatase to rutile. Since vanadium doping shifted the absorption wavelength from 380 nm to about 650 nm the photocatalytic of the V doped TiO_2 was higher than that of undoped TiO_2 . The optimum V doping amount and calcination temperature was found to be Ti: V = 40: 1 and 300 °C respectively [90].

Paola and his friends prepared transition metal (Co, Cr, Cu, Fe, Mo, V and W) doped TiO_2 by wet impregnation method. By reacting an aqueous solution of TiCl_3 with ammonia titanium hydroxide was precipitated. To remove the Cl^- ions, white precipitate was washed and after dried at 373 K for 24 hours and finally calcinated at 773 K for 24 hours. Later the obtained TiO_2 was impregnated with aqueous solutions of transition metal ions in order to make dopant content 0.3, 1.0, 2.0 and 5.0 % moles. The same drying and calcination procedure was applied to doped TiO_2 . Two different photocatalytic reactions (oxidation of ethanoic acid and photodegradation of 4-nitrophenol) under irradiation with light of wavelength $\lambda > 300$ nm were observed to find out the photocatalytic activities. Studies showed that there was an enhancement in the photocatalytic activity of TiO_2 only when it was doped with copper and tungsten. Cu doped TiO_2 powders showed to be more photoactive for the ethanoic acid oxidation while the W doped TiO_2 powders were more efficient for 4-nitrophenol degradation [91].

Zhou and his friends prepared Zn^{2+} and Eu^{3+} co-doped TiO_2 catalysts by modified sol-gel method. The photocatalytic activity of samples was evaluated by the photodegradation of methyl orange under natural light irradiation. TiO_2 sol was prepared by adding dropwise the solution of tetrabutyltitanate precursor and anhydrous alcohol to the solution of anhydrous alcohol and glacial acetic acid. Then the appropriate amount of zinc nitrate and europium nitrate was added to this sol. After continuously stirring for 0.5 hour, a transparent gel was formed and after the transparent gel was dried at 80-100 °C and calcined at 500 °C for 2 hours codoped TiO_2 powders were obtained. Pure TiO_2 , Zn^{2+} doped TiO_2 and Eu^{3+} doped TiO_2 powders were synthesized by the same procedure described above. XRD and TEM analysis of the

powders showed that all of Zn^{2+} and Eu^{3+} co-doped TiO_2 samples mainly consisted of anatase phase, the co-doping could retard the grain growth of TiO_2 and decreased the aggregation of TiO_2 nanoparticles. Ultraviolet-visible diffuse reflection spectroscopy (UV-vis DRS) showed that Zn^{2+} and Eu^{3+} co-doping increased the visible-light absorption ability of TiO_2 catalysts. According to photocatalytic degradation of methyl orange, optimal doping amounts for Zn^{2+} and Eu^{3+} were 1.0 % and 1.5 % respectively, and doping TiO_2 with both Zn^{2+} and Eu^{3+} dopant showed a synergistic effect, which significantly increased the photocatalytic activity of TiO_2 [92].

Klokeks and Raftery synthesized vanadium-doped TiO_2 photocatalyst whose visible light activity was studied by oxidation of ethanol. All catalysts were supported on transparent porous Vycor 7930 borosilicate glass (PVG). The TiO_2 /PVG catalyst was prepared on a vacuum rack via chemical vapor deposition (CVD) of TiCl_4 . The V/SiO_2 catalyst was prepared by immersing the PVG support overnight in a small test tube containing ammonium metavanadate solution. Water was then removed by slowly heating the PVG in solution to dryness. The catalyst was further dried under vacuum at 140 °C for 2 hours then calcined under dry O_2 at 500 °C for 10 hours. Four different catalysts were prepared: a TiO_2 monolayer catalyst supported on PVG, a vanadium oxide (V^{5+}) submonolayer catalyst supported on PVG, and two mixed oxide catalysts. The oxidation of ethanol over this catalysts showed that the vanadium oxide (V^{5+}) submonolayer catalyst enhanced the photocatalytic activity compared to TiO_2 monolayer catalyst under visible light irradiation. Under UV/visible conditions, the photoactivity of the mixed oxide catalyst was comparable to the TiO_2 /PVG catalyst [93].

Sakthivel and Kisch studied daylight photocatalysis of 4-chlorophenol and remazol red by Carbon-Modified Titanium Dioxide. To synthesize Carbon-Modified Titanium Dioxide powder a solution of tetrabutylammonium hydroxide was added dropwise to 0.25 ml TiCl_4 at 0 °C until a pH value of 5.5 was reached. After aging the suspension for 24 hours at room temperature, the precipitate was collected by filtration and dried at 70 °C. The residue was crushed into a fine powder and calcined at 400 °C for 0.25 and 1 hour, and at 550 °C for 4 hours. While some of the carbon-modified titanium dioxide mineralized 4-chlorophenol and the azo dye remazol red the unmodified TiO_2 was almost inactive under daylight. While the samples that were calcinated at 400 °C

complete mineralization after 210 minutes (sample calcinated for 0.25 hour) and 180 minutes (sample calcinated for 1 hour), unmodified TiO_2 and the C doped TiO_2 that was calcinated at 550 °C did not show any photocatalytic activity under visible light. XRD results showed that all of the doped samples were in anatase phase except the one calcinated at 550 °C for 4 hours. Some rutile traces were found in this sample. Diffuse reflectance spectra showed that the visible light absorption was related to the carbon content. It was stronger for the sample calcinated at 400 °C for 0.25 hour than the sample calcinated at 400 °C for 1 hour and completely absent in the sample calcinated at 550 °C for 4 hours [94].

2. MATERIAL AND METHOD

2.1. Materials

2.1.1. Chemicals used to prepare TiO₂ solutions

Ti(OC₃H₇)₄, Si(OC₂H₅)₄, AgNO₃, Cr(NO₃)₃·9H₂O, Zn(CH₃COO)₂·2H₂O, C₃H₇OH were purchased from Merck. SLS window glasses were provided from Şişecam A.Ş. Properties of the chemicals and the SLS glass and the chemical composition of the SLS glass are given in Table 2.1, 2.2 and 2.3 respectively.

It should be noted that throughout this thesis study except adhesion, scratch and taber abrasion tests, microscope lamels made of SLS glass that were purchased from ISOLAB were used instead of window glasses and both microscope lamels and window glasses were named as SLS glass.

Table 2.1. Properties of chemicals used to prepare TiO₂ solutions

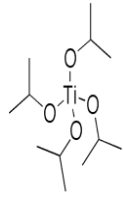
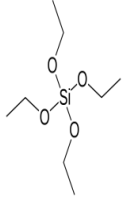
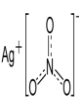
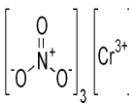
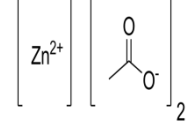
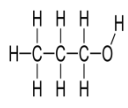
	Ti(OC ₃ H ₇) ₄	Si(OC ₂ H ₅) ₄	AgNO ₃	Cr(NO ₃) ₃ ·9H ₂ O	Zn(CH ₃ COO) ₂ ·2H ₂ O	C ₃ H ₇ OH
IUPAC name	titanium isopropoxide	tetraethoxy-silane	silver nitrate	chromium nitrate nonahydrate	zinc acetate dihydrate	Propan-1-ol
Molecular weight (gr/mol)	284.26	208.33	169.87	400.21	219.50	60.10
Chemical structure						
Appearance	Colorless liquid	Colorless liquid	White solid	Blue-violet crystals	White solid	Colorless liquid
Density (g/cm ³)	0.937	0.940	4.350	1.850	1.735	0.803

Table 2.2. Properties of the SLS glass

Thickness	Day Light (EN 410)		Sun Energy (EN 410)			
	Permeability	Reflection	Reflection	Absorption	Direct Permeability	Total Permeability
3 mm	90 %	8 %	8 %	8 %	84 %	0.86 %

Table 2.3. Chemical composition of the SLS glass (%)

SiO ₂	73	Al ₂ O	0.15	CaO	9	TiO ₂	0.02
Na ₂ O	14	K ₂ O	0.03	MgO	4	Fe ₂ O ₃	0.1

2.1.2. Chemical used to determine photocatalytic activity

Rhodamine B, a chemical compound that is often used as a tracer dye was used to determine photocatalytic activity of TiO₂ films. It was purchased from Merck. Properties of Rhodamine B can be seen in Table 2.4.

Table 2.4. Properties of Rhodamine B

	C ₂₈ H ₃₁ ClN ₂ O ₃
IUPAC name	[9-(2-carboxyphenyl)-6-diethylamino-3-xanthenylidene]-diethylammonium chloride
Molecular weight (gr/mol)	479.02
Chemical structure	
Appearance	red to violet powder

2.2. Method

2.2.1. Preparation of the solutions

To prepare pure TiO_2 solution $\text{Ti}(\text{OC}_3\text{H}_7)_4$ (titanium isopropoxide) was used as alkoxide precursor, $\text{C}_3\text{H}_7\text{OH}$ (propanol) was used as solvent and HNO_3 (nitric acid) and water were used as catalyst.

The solution was prepared at room temperature in a glass beaker by using a magnetic stirrer. 0.5 %, 1.0 % and 1.5 % Ag, Zn, Cr doped TiO_2 solutions were prepared as described in Figure 2.1. Composition range of pure TiO_2 solution can be seen in Table 2.5.

After 7 days aging which was found experimentally to be the best duration for the coating process, these prepared TiO_2 solutions were diluted 1 to 1 with propanol and used for coating process. These solutions are named in Section 3.6 as the TiO_2 solutions that were used at the 0th day of preparation.

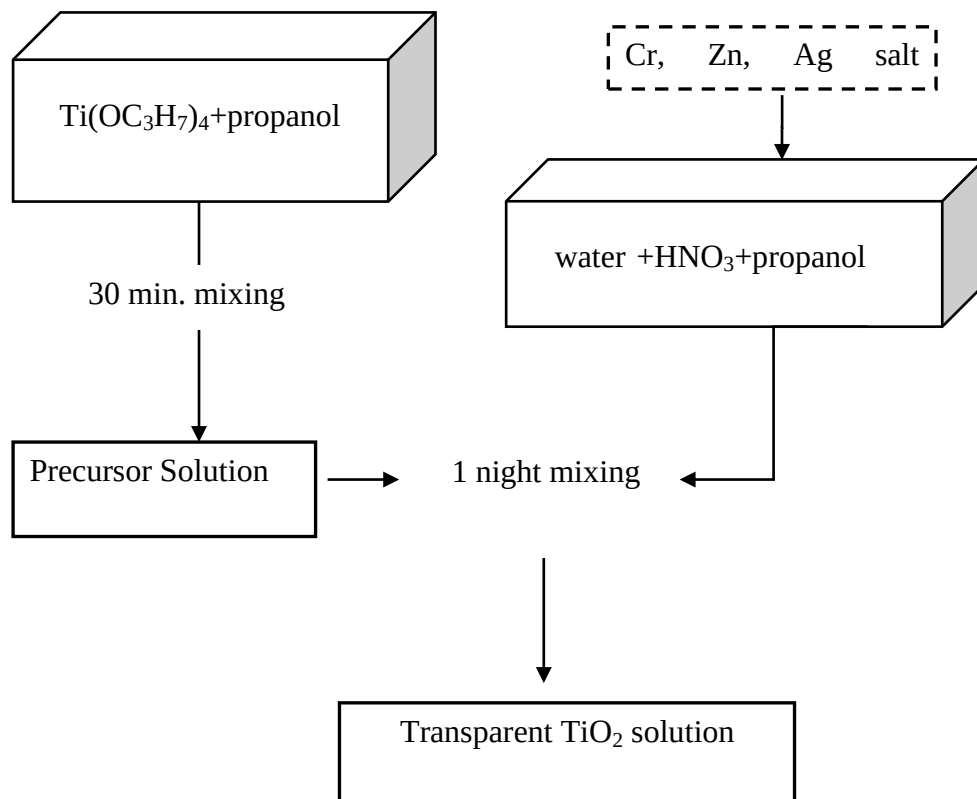


Figure 2.1. Preparation route of TiO_2 solutions

Table 2.5. Composition range of pure TiO₂ solution

Chemical name	Weight Amount	Chemical name	Weight Amount
Ti(OC ₃ H ₇) ₄	45-75	HNO ₃	3-15
C ₃ H ₇ OH	840-870	H ₂ O	7.5-10.5

2.2.2. Determination the properties of TiO₂ solutions**2.2.2.1. pH**

pH value of each TiO₂ solution was measured by 744 Methrom type pH meter. All pH values can be seen in Table 2.6.

Table 2.6. pH values

Solution name	pH
Undoped TiO ₂ solution	1.67
0.5 % Ag doped TiO ₂ solution	1.35
1 % Ag doped TiO ₂ solution	1.32
1.5 % Ag doped TiO ₂ solution	1.54
0.5 % Zn doped TiO ₂ solution	1.48
1 % Zn doped TiO ₂ solution	1.48
1.5 % Zn doped TiO ₂ solution	1.45
0.5 % Cr doped TiO ₂ solution	1.58
1 % Cr doped TiO ₂ solution	1.43
1.5 % Cr doped TiO ₂ solution	1.40

2.2.2.2. Viscosity

Viscosity of each TiO₂ solution was measured 51 cP by Brookfield KU-2 type viscosimeter.

2.2.2.3. Color of the solutions

Effect of the dopants on the color of the TiO_2 solution was observed by eye. Figure 2.2 shows that while Ag and Zn doping do not change the color of undoped TiO_2 solution, Cr doping turns the color to green.

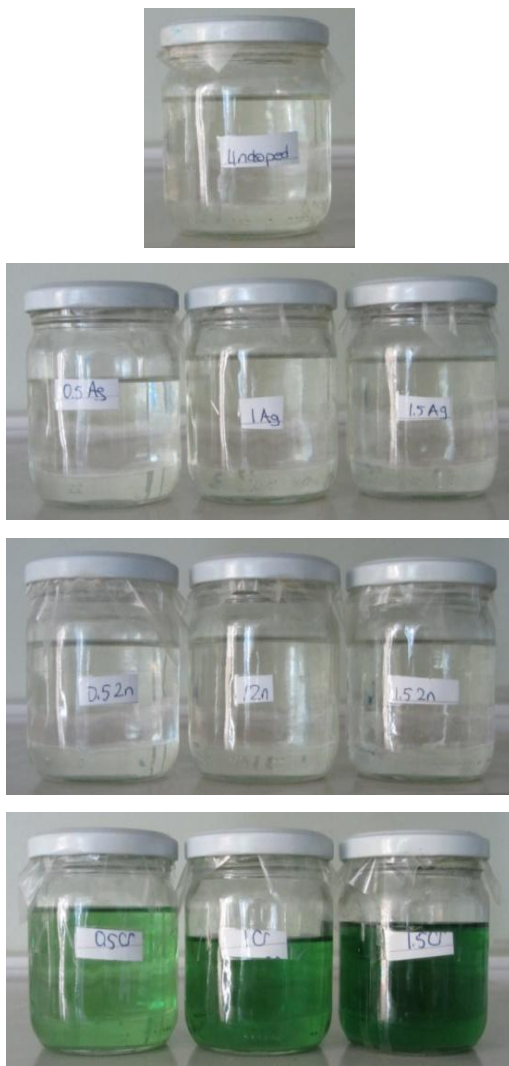


Figure 2.2. Color of the solutions (Up to bottom; undoped TiO_2 solution, Ag doped TiO_2 solutions, Zn doped TiO_2 solutions, Cr doped TiO_2 solutions)

2.2.2.4. Gelling times

After preparing 900 ml from each TiO_2 solution, solutions were poured in a borcam tray and placed in the oven at 33 °C to determine gelling times. Gelling time of each solution was determined approximately 1 hour 45 minutes. It should be noted that if stored in a sealed jar, all TiO_2 solutions stayed without gelation nearly for 1 year.

2.2.2.5. Shelf life

900 ml prepared solution of each TiO_2 solution was stored for 2 months. Viscosity and particle size of the solutions were measured and the color of the solutions was observed. SLS glasses were coated with these solutions and transmittance % and photocatalytic activities of TiO_2 films were measured.

2.2.3. Characterization of the TiO_2 powders

2.2.3.1. DTA-TG analysis

Thermal analysis of undoped TiO_2 powder was done by ExStar 6300 TG/DTA thermal analysis equipment (Figure 2.3).



Figure 2.3. ExStar 6300 TG/DTA thermal analysis equipment

2.2.3.2. Fourier transform infrared spectroscopy (FTIR) analysis

Organic species formed throughout the production of undoped TiO_2 powder were determined by Perkin Elmer Spectrum BX Fourier transform infrared spectrometer (Figure 2.4).

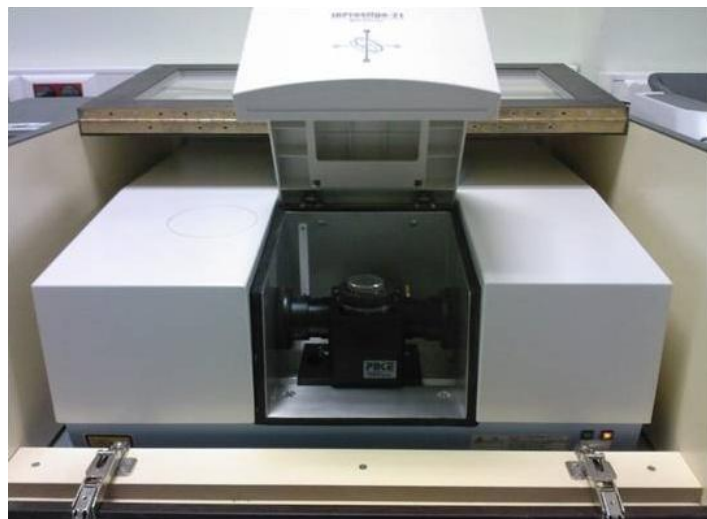


Figure 2.4. Fourier transform infrared spectroscopy

2.2.3.3. XRD analysis

XRD-6000 was used to determine the phases of undoped TiO_2 powder and doped TiO_2 powders (Figure 2.5).



Figure 2.5. Shimadzu XRD-6000

2.2.3.4. TEM analysis

JEOL 100C transmission electron microscopy was used to do microstructural characterization of undoped TiO_2 powder and doped TiO_2 powders (Figure 2.6).



Figure 2.6. JEOL 100C transmission electron microscopy

2.2.3.5. BET analysis

A Nova 4000E model surface area analyzer was used to measure the surface areas of undoped TiO_2 powder and doped TiO_2 powders (Figure 2.7).



Figure 2.7. Nova 4000E Surface area analyzer

2.2.4. Preparation the SLS glasses for coating

SLS glasses were cut as 10 cm x 10 cm and afterwards they were washed. Washing process was done by WV-120/90 FinnSonic washing machine (Figure 2.8) at Şişecam Glass Research Center. This machine consists of 5 departmentants which are heated at 60 °C. In the first department there is NaOH solution whose concentration changes between 3 % and 10 %. After being kept in the first tank for 10 minutes, glasses were

put in the 2. department which includes distilled water and then in the 3. department which includes H_3PO_4 solution whose concentration changes between 2 % and 4 %. After staying 10 minutes in the 3. Department, glasses were put in 4. and 5. departments which include distilled water for the final rinsing process. At the end of the washing process, glasses were dried in FinnSonic CRD-90 machine at 100°C for 10 minutes.



Figure 2.8. WV-120/90 FinnSonic washing machine

2.2.5. Determination the air side and tin side of the SLS window glasses

Lamag UV-C lamp was used to determine the tin and the air side of SLS glasses. When the tin side is put under the lamp, the tin will fluorescence and produce a milky white image (Figure 2.9). If the air side is put under the lamp the lack of tin results in no fluorescence (Figure 2.10).

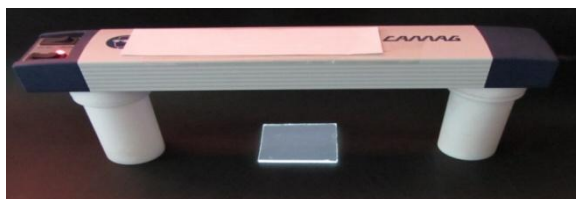


Figure 2.9. Tin side of SLS glass determined under UV C light

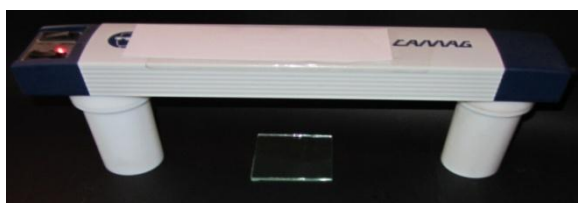


Figure 2.10. Air side of SLS glass determined under UV C light

2.2.6. Coating the SLS glasses with SiO₂ to prevent Na⁺ diffusion

Before starting the whole coating process, a preliminary study was done to find out the effect of the Na⁺ ion on structure and photocatalytic activity of undoped (pure) TiO₂. This preliminary study also was necessary to find out whether a SiO₂ film that is formed between glass and TiO₂ film can be a solution for Na⁺ diffusion or not.

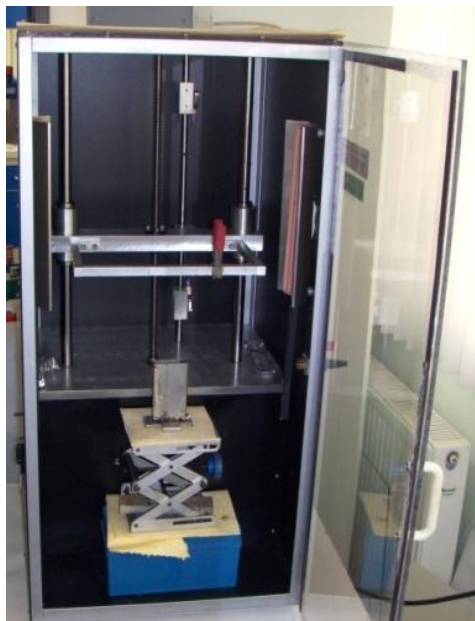


Figure 2.11. Dip coating equipment Chemat Technology INC. Model 201

However it should be noted that the pH of the TiO₂ solution that was prepared for this preliminary study was approximately 4-4.5 which was different from the pH of TiO₂ solution mentioned in Section 2.2.1. As given in Section 2.2.2.1, pH of the TiO₂ solution that was used for doping studies was 1.67 which provided enough time for usage of the solutions due to its longer shelf life.

In this preliminary study, two sets of coatings were done by dip coating equipment (Figure 2.11) to find out the effect of the Na⁺ ion; One set of SLS glasses was coated as single layer (coating directly with TiO₂ solution) the other set was coated as double layer (first coating with SiO₂ solution then coating with TiO₂ solution).

SiO₂ solution that was used at double layer coatings, was obtained by the hydrolysis of TEOS (Tetraethoxysilane). SLS glasses were coated with this SiO₂ solution with a

withdrawal rate of 2 cm/min. The coated SLS glasses were dried in the oven at 100 °C for 1 hour. Then SLS glasses were cooled to the room temperature and they were coated with TiO₂ solution with a withdrawal rate of 12 cm/min. After the coating process, SLS glasses were dried in the oven at 100 °C for 1 hour and later they were sintered in the muffle oven at chosen sintering temperatures (300 °C, 350 °C, 400 °C, 450 °C, 500 °C, 550 °C, 600 °C) for 2 hours. SLS glasses that were coated as single layer were directly coated with TiO₂ solution with a withdrawal rate of 12 cm/min and after being dried in the oven at 100 °C for 1 hour they were sintered in the muffle oven at the chosen sintering temperatures (300 °C, 350 °C, 400 °C, 450 °C, 500 °C, 550 °C, 600 °C) for 2 hours.

Film analysis was done for both single layer and double layer coated SLS glasses by PANalytical XPert PRO diffractometer.

To measure the photocatalytic activity of the coated SLS glasses, first of all SLS glasses were put in the test container which has 6 compartments and 60 ml 2 ppm Rhodamine B solution was poured in each compartment. Test container was put in Suntest CPS+ (Light source = Xenon Lamp, Filter type = UV Filter, Black standart temperature = 35 °C, Irradiation rate = 765 W/m²) and UV irradiated. Afterwards absorbance values of Rhodamine B solutions were measured by UV-VIS spectrophotometer.

It was observed that the SLS glasses that were sintered at 600 °C were bended since SLS glasses are not durable to high temperature. Photocatalytic activity of these SLS glasses were measured anyway and characterization of these SLS glasses were done from more uniform parts.

Table 2.7. Film analysis of single layer coatings

Sintering Temperature	Phases	Sintering Temperature	Phases
300 °C	Amorphous	500 °C	Anatase, brookite and amorphous
350 °C	Amorphous	550 °C	Anatase, brookite and amorphous
400 °C	Amorphous	600 °C	Brookite and amorphous
450 °C	Amorphous		

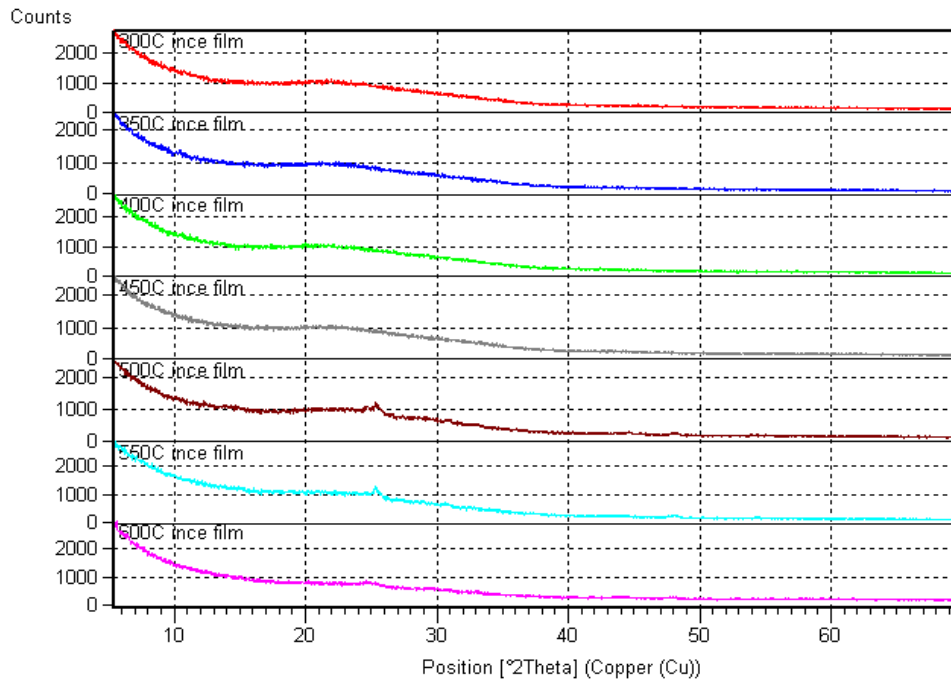


Figure 2.12. Film analysis of single layer coatings

From the results of film analysis, it can be seen obviously that there are significant differences between single layer coatings and double layer coatings. Looking at the Table 2.7 and Figure 2.12 it can be seen that when SLS glasses were coated only with TiO_2 solution (single layer), at sintering temperatures of 300 °C, 350 °C, 400 °C ve 450 °C no phase formation occurred, there was only amorphous structure. At sintering temperatures 500 °C and 550 °C film consisted of anatase and brookite phases and amorphous structure, at 600 °C film consisted of brookite phase and amorphous structure.

Table 2.8. Film analysis of double layer coatings

Sintering Temperature	Phases	Sintering Temperature	Phases
300 °C	Amorphous	500 °C	Anatase
350 °C	Anatase	550 °C	Anatase
400 °C	Anatase	600 °C	Anatase
450 °C	Anatase		

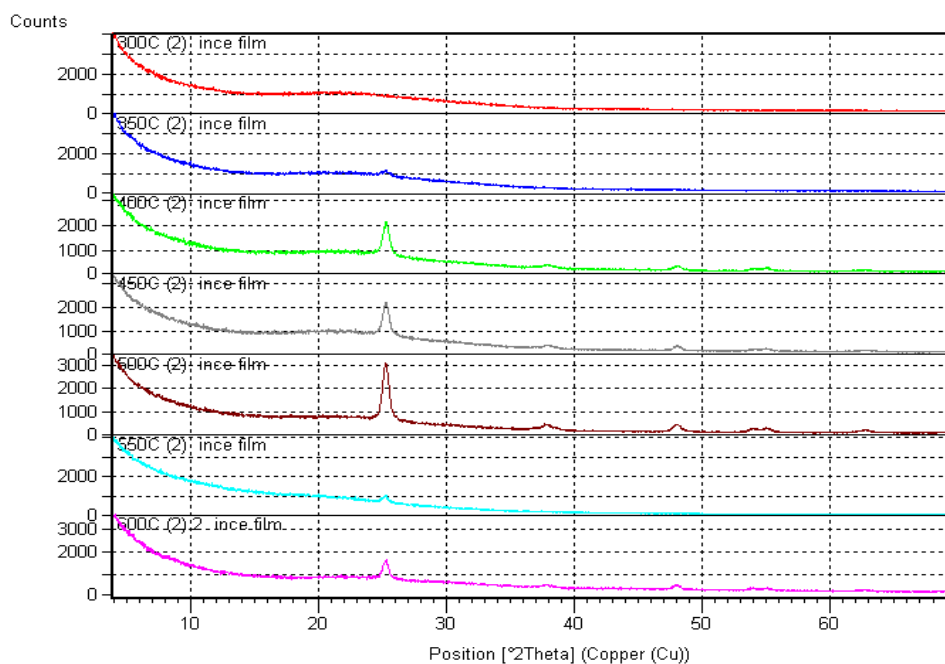


Figure 2.13. Film analysis of double layer coatings

Looking at the Table 2.8 and Figure 2.13 it can be seen that when SLS glasses were coated with SiO_2 before coated with TiO_2 solution (double layer) at all sintering temperatures except 300 °C films consisted of only anatase phase. When the sintering temperature was 300 °C no phase formation occurred, there was only amorphous structure. Brookite phase that was seen at single layer films when the sintering temperatures were 500 °C, 550 °C and 600 °C, was not seen at double layer films. Besides, it was significant that when the coatings were single layer, anatase phase turned to brookite phase by increasing the sintering temperature. As mentioned before while anatase and rutile phases have photocatalytic property, brookite phase has known to be no photocatalytic property. It is thought that at single layer coatings when the sintering temperature increases, Na^+ ion that exists in the SLS glass diffuses to coating and make anatase phase turn into brookite phase. It is possible to prove this idea by the help of photocatalytic activity results.

Photocatalytic activity results can be seen in Table 2.9. Evaluation can be also done by the graphics that were drawn by using these results (Figure 2.14, Figure 2.15, Figure 2.16). It can be seen from the Figure 2.14 that when the sintering temperature was 300

°C unlike the expected result absorbance value increased by increasing of the radiation time. Estimated reason for this is that the negative effect of the Na⁺ ion diffusion from SLS glass to TiO₂ film increased when the radiation time increased. Similar results can be seen for the other sintering temperatures except 550 °C. Generally it can be said that when SLS glasses were coated only with TiO₂ solution (single layer) it was not possible to find a correlation between the sintering temperatures and absorbance values.

Table 2.9. Results of Photocatalytic Activity

		Absorbance (A)					Wavelength (nm)
		After 6 hrs.	After 7 hrs.	After 8 hrs.	After 9 hrs.	After 10 hrs.	
Rhodamine B		0.443					554
Tested Rhodamine B		0.465	0.470	0.503	0.527	0.580	550
Tested uncoated SLS glass		0.489	0.512	0.536	0.599	0.717	550
300 °C	Single layer	0.201	0.217	0.228	0.231	0.267	540
	Double layer	0.225	0.220	0.231	0.247	0.237	543
350 °C	Single layer	0.240	0.234	0.239	0.230	0.215	543
	Double layer	0.123	0.120	0.120	0.108	0.078	543
400 °C	Single layer	0.338	0.339	0.334	0.350	0.398	546
	Double layer	0.131	0.088	0.067	0.046	0.006	540
450 °C	Single layer	0.307	0.299	0.299	0.314	0.337	545
	Double layer	0.096	0.072	0.045	0.030	0.007	541
500 °C	Single layer	0.446	0.440	0.454	0.490	0.537	550
	Double layer	0.065	0.036	0.017	0.002	0	550
550 °C	Single layer	0.294	0.267	0.247	0.221	0.202	550
	Double layer	0.053	0.037	0.014	0	0	550
600 °C	Single layer	0.340	0.343	0.341	0.322	0.335	550
	Double layer	0.119	0.093	0.071	0.052	0.030	550

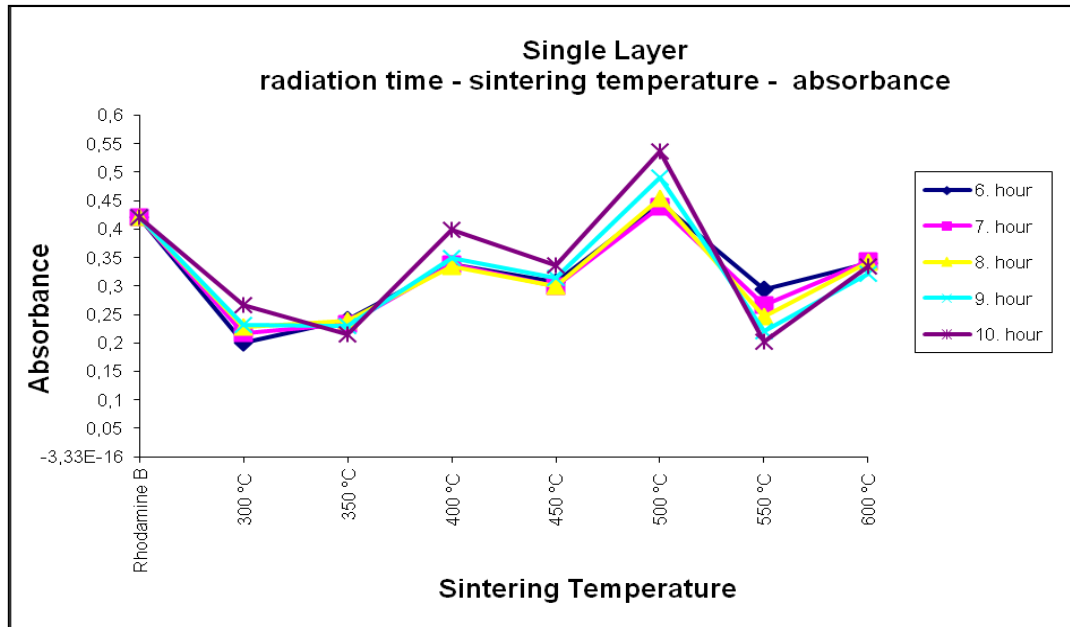


Figure 2.14. Radiation time-sintering time-absorbance relation for single layer coatings

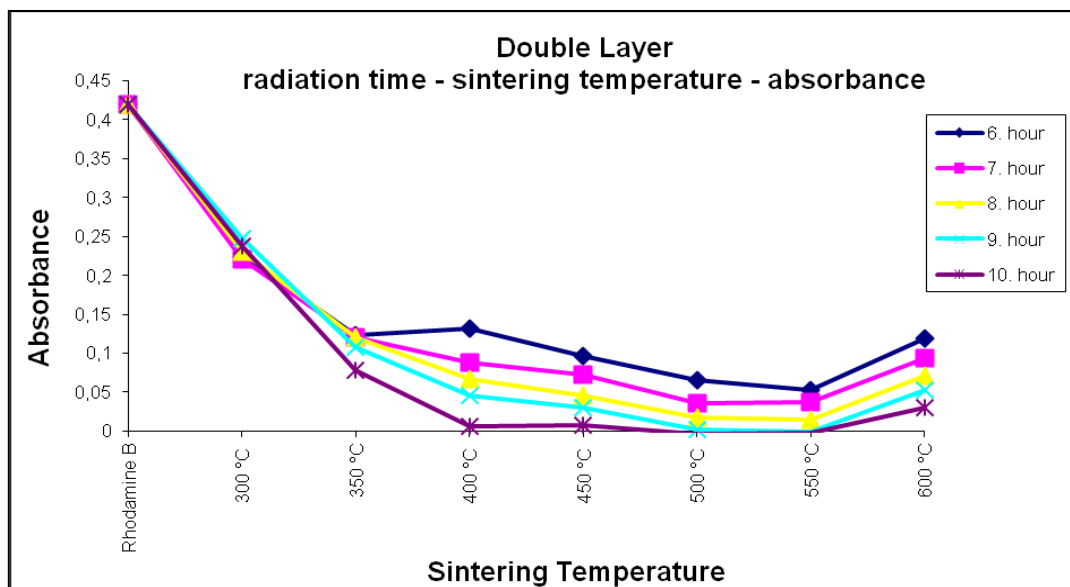


Figure 2.15. Radiation time-sintering time-absorbance relation for double layer coatings

It can be seen from the Figure 2.15 that when the SLS glasses were coated with SiO_2 solution before TiO_2 solution (double layer), absorbance value decreased by the increasing of sintering temperature and radiation time. However this was not valid at

600 °C and most probably the reason for that was as mentioned before SLS glasses that were sintered at 600 °C were not uniform.

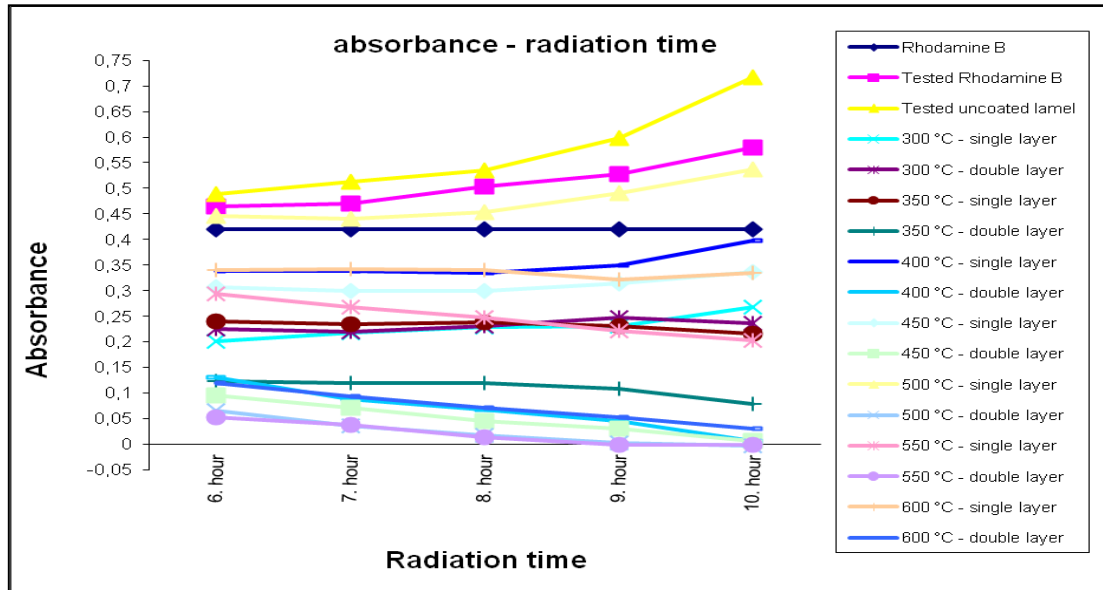


Figure 2.16. Radiation time- absorbance relation for single and double layer coatings

Figure 2.16 shows all irradiated samples together. When straight dark blue line that belongs to Rhodamine B is taken as a reference, it is obvious that except the absorbance value of single layer coated sample sintered at 500 °C, absorbance values of all single and double layer coated samples are smaller than the absorbance value of Rhodamine B. Above the straight dark blue line that belongs to Rhodamine B there are two more curves which belong to tested Rhodamine B and tested uncoated SLS glass. It is possible to make two groups from the curves below the straight dark blue line; the upper group belongs to single layer coatings that were sintered at 300 °C, 350 °C, 400 °C, 450 °C, 550 °C and 600 °C. The most significant thing about this group is that the curves are nearly linear which shows that when SLS glasses are coated only with TiO₂ solution (single layer), irradiation time has no effect on photocatalytic activity. This proves that with a single layer coating it is not possible to get succesful results since it is not possible to prevent Na⁺ diffusion. The only curve that belongs to double layer coating in this upper group is the absorbance curve of the SLS glass that was sintered at 300 °C and as mentioned while discussing the results of thin film analysis, this sintering temperature is not enough for crystallization of TiO₂. The lower group consists of the curves that belong to double layer coatings and the slope of these curves decreases by

the increasing of irradiation time and this shows us that a SiO₂ layer is needed to prevent Na⁺ ion diffusion.

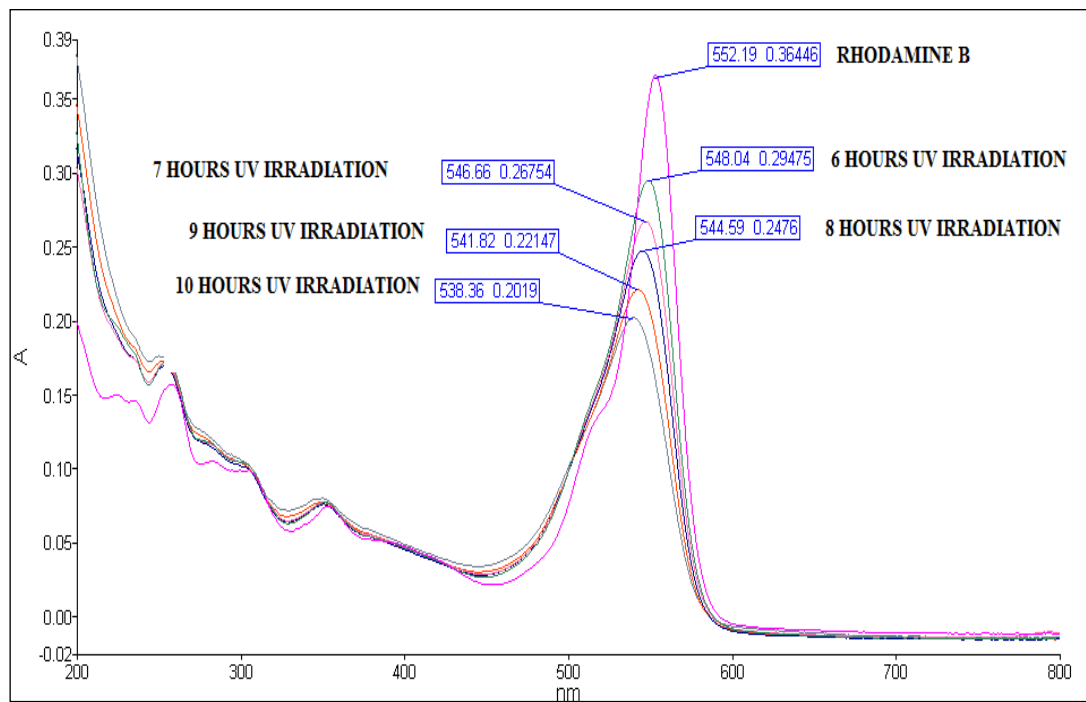


Figure 2.17. Absorbance graphic of single layer coatings sintered at 550 °C

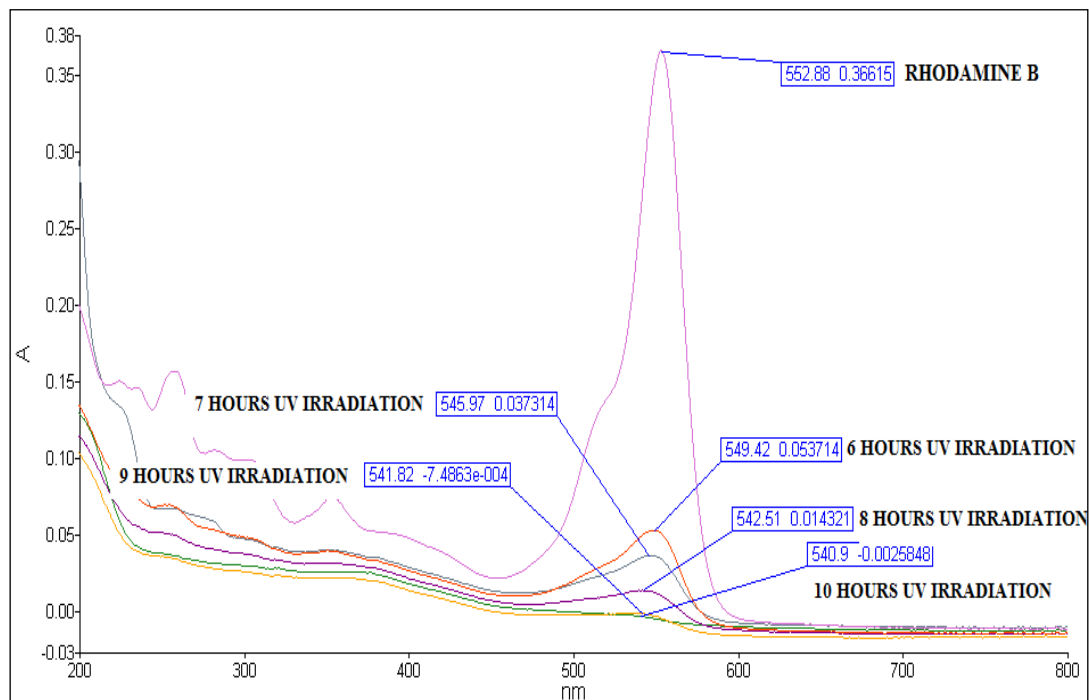


Figure 2.18. Absorbance graphic of double layer coatings sintered at 550 °C

When we compare the absorbance graphic taken from UV-VIS Spectrophotometer that belongs to single layer coating sintered at 550 °C (Figure 2.17) with the absorbance graphic that belongs to double layer coating sintered at 550 °C (Figure 2.18) it is possible to see difference between the single layer and double layer coatings clearly. From the graphics it can be seen that when SLS glasses are coated only with TiO₂, (single layer) absorbance value decreases a little by increasing the irradiation time, however when SLS glasses are coated SiO₂ before coated with TiO₂ (double layer) absorbance value decreases to 0 by increasing the irradiation time.

Results of this preliminary study showed that each SLS glass must be coated with SiO₂ solution before being coated with TiO₂ solutions to prevent Na⁺ diffusion.

It should be noted that taking the results of this preliminary study into consideration throughout this thesis study for all evaluations except transmittance % measurements, SLS glasses that had an intermediate SiO₂ layer were used. Only at transmittance % measurements, to find out the effect of SiO₂ layer on transmittance, SLS glasses both with SiO₂ intermediate layer and without SiO₂ intermediate layer were used and only at transmittance % measurement studies SiO₂ intermediate layer was notated as “SiO₂”.

2.2.7. Coating SLS glasses with TiO₂ solutions

After being coated with SiO₂ solution and dried, SLS glasses were coated with TiO₂ solutions by dip coating equipment branded Chemat Technology INC. Withdrawal rate of the dip coating equipment changes from 0 cm/min. to 30.7 cm/min. To choose the best withdrawal rate a preliminary study was done. SLS glasses were coated at different withdrawal rates (2 cm/min., 12 cm/min., 15 cm/min., 18 cm/min., 21 cm/min., 24 cm/min., 30.7 cm/min.).

Coated SLS glasses were dried in the oven at 100 °C for 1 hour. After drying, some crackings were observed on the surface of the SLS glass that was coated with a withdrawal rate of 30.7 cm/min. For this reason this glass was not sintered. The other coated glasses were sintered in Nabertherm Muffle oven at 400 °C for 1 hour. After the sintering process, while the surfaces of the SLS glasses that were coated with a withdrawal rate of 2 cm/min and 15 cm/min were uniform, some crackings were observed on the surfaces of the glasses that were coated with withdrawal rates of 18 cm/min, 21 cm/min and 24 cm/min. These crackings that were observed on the surfaces

of the SLS glasses, pointed out that these withdrawal rates (18 cm/min, 21 cm/min and 24 cm/min, 30.7 cm/min) were not suitable for the coating. Withdrawal rates between 2 cm/min and 15 cm/min were seen to be the more appropriate ones.

For this thesis study it was decided to use 15 cm/min withdrawal rate as it is the highest withdrawal rate that does not cause any problems (nonuniform surface or surface with cracks). Looking at the literature also it can be seen that the the most preferred withdrawal rates for this kind of coatings are 12 cm/min [81, 95-99] and the withdrawal rates between 2 cm/min and 12 cm/min [100-105]. It is discussed detailed in Section 3.4.1 why 15 cm/min was chosen instead of 12 cm/min as withdrawal rate in this thesis study.

2.2.8. Drying process

SLS glasses that were coated with SiO₂ solution were dried in Heraus T 6060 oven at 100 °C for 1 hour then they were coated with TiO₂ solutions and again dried in Heraus T 6060 oven at 100 °C for 1 hour.

2.2.9. Sintering process

After being dried, coated SLS glasses were sintered in Nabertherm muffle oven (Figure 2.19) at 400 °C for 1 hour. It is discussed detailed in Section 3.4.1 why 400 °C was chosen for the sintering temperature. Besides, powders that were obtained after the gelation of the solutions were sintered in Nabertherm muffle oven at different temperatures (300 °C, 400 °C, 500 °C, 600 °C, 700 °C, 800 °C) for 1 hour for XRD studies.



Figure 2.19. Nabertherm muffle oven

2.2.10. Characterization of the TiO₂ films

2.2.10.1. Panalytical Xpert Pro analysis

Panalytical Xpert Pro diffractometer was used to determine phases of undoped and doped TiO₂ films (Figure 2.20).



Figure 2.20. Panalytical Xpert Pro diffractometer

2.2.10.2. AFM analysis

Qusant Q-Scope atomic force microscope was used to determine topography and to measure the roughness of undoped TiO₂ film and doped TiO₂ films (Figure 2.21).



Figure 2.21. Qusant Q-Scope atomic force microscope

2.2.11. Determining the physical properties of TiO₂ film

2.2.11.1. Contact angle measurement

Krüss DSA 100 model contact angle measurement equipment was used to determine the contact angles of undoped and doped TiO₂ films (Figure 2.22).



Figure 2.22. Krüss DSA 100 model contact angle measurement equipment

2.2.11.2. Transmittance measurement

Perkin Elmer Lambda 750S UV-VIS Spectrophotometer was used to measure transmittance % of undoped TiO₂ film and doped TiO₂ films.

2.2.12. Determining the photocatalytic activities of TiO₂ films

2 ppm Rhodamine B solution was used to determine photocatalytic activities of TiO₂ films. To prepare 2 ppm Rhodamine B solution accurately, first of all 50 ppm Rhodamine B (12,5 mg Rhodamine B/ 250 ml distilled water) stock solution was prepared. Later this solution was diluted to have (125 ml 50 ppm Rhodamine B solution/250 ml distilled water) 25 ppm Rhodamine B solution. Finally by diluting this solution, 2 ppm Rhodamine B solution (20 ml 25 ppm Rhodamine B solution/250 ml distilled water) was prepared. Coated glasses were placed in the test container, which has 6 compartments, as seen in Figure 2.23 and 60 ml 2 ppm Rhodamine B was poured into each of them. Test container was put in Suntest CPS+ (Figure 2.24) (Light source =

Xenon Lamp, Filter type = UV Filter, Black standard temperature = 35 °C, Irradiation rate = 765 W/m²) for UV radiation. Coated glasses were irradiated for 20 hours and Rhodamine B samples were taken throughout the photocatalytic activity tests. Afterwards absorbance values of these Rhodamine B solution samples were measured by UV-VIS spectrophotometer (Figure 2.25).



Figure 2.23. Test container



Figure 2.24. Atlas Suntest CPS

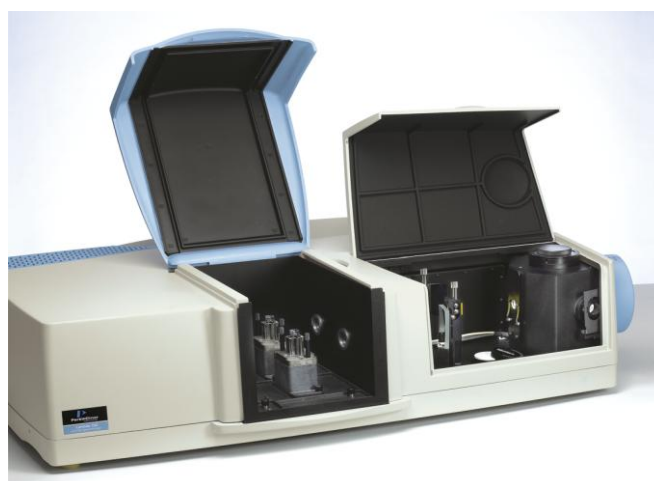


Figure 2.25. UV-VIS spectrophotometer (Perkin Elmer Lambda 750 S)

2.2.13. Physical testing of TiO₂ films

2.2.13.1. Adhesion test

Adhesion test was done to measure whether the TiO₂ films were adhered properly to the SLS glass or not. Erichsen multiple blade with 1 mm spacing was used for the test (Figure 2.26).



Figure 2.26. Multiple blade for adhesion test

2.2.13.2. Taber abrasion test

Taber abrasion resistances of the TiO₂ films were measured by Erichsen Taber Abrader 5131 (Figure 2.27). CS-10F was chosen as abrader wheel and number of cycles was chosen as 50.



Figure 2.27. Taber abrader

2.2.13.3. Scratch test

Erichsen Universal scratch tester 413 (Figure 2.28) was used to measure the scratch hardness of TiO_2 films. Load range was chosen 1 N to 10 N and tip according to Van-laar was chosen as testing tip.

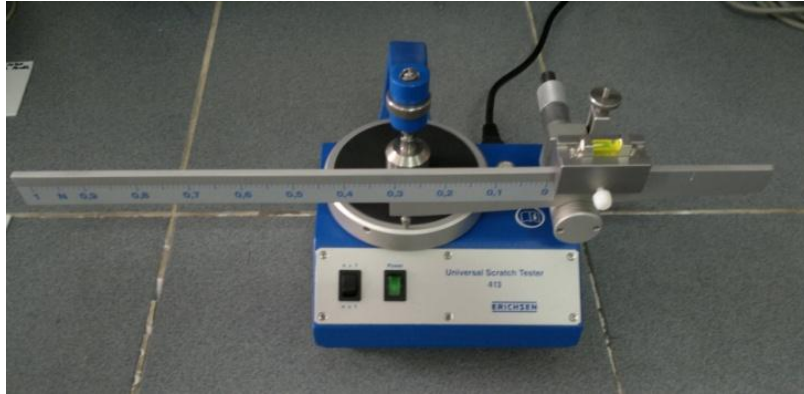


Figure 2.28. Erichsen Universal scratch tester 413

2.2.13.4. Neutral salt spray test

Neutral salt spray test was done according to EN 1096-2 (January 2001) (for 21 days at $35 \pm 1,5$ °C, NaCl concentration is $50 \text{ g/l} \pm 5 \text{ g/l}$) in Erichsen salt spray test cabinet (Figure 2.29) which is suitable to EN ISO 9227:2006.



Figure 2.29. Erichsen salt spray test cabinet

3. RESULTS AND DISCUSSION

3.1. Characterization Of TiO_2 Powders

3.1.1. Determination of the gelling temperature of TiO_2 solutions

After preparing undoped TiO_2 solution, TiO_2 gel (Figure 3.1) was obtained by drying this solution and from the thermal analysis of TiO_2 powder that was obtained from TiO_2 gel, phase transformation temperatures of TiO_2 powder were tried to be determined to choose a sintering temperature range.



Figure 3.1. TiO_2 gel

First of all the TiO_2 solution, whose R value was 2, was split into two equal parts. One part was dried at 33 °C and the other part was dried at 50 °C. It was observed that from the solution that was put at 50 °C a more yellowish powder was obtained.



Figure 3.2. TiO_2 powders obtained by drying TiO_2 solutions (R=2) at 33 °C and 50 °C

Before doing thermal analysis these two powder samples were put in the oven at 100 °C for 1 hour to remove their moisture. It was observed that while the color of the powder that was obtained at 33 °C was yellow, the color of the powder that was obtained at 50 °C was white (Figure 3.3).



Figure 3.3. TiO₂ powders after moisture removal at 100 °C

Figure 3.4 and Figure 3.5 show thermal analysis of both powder samples. It was measured that total mass % loss was almost same for both powder samples which continued until 550 °C.

It is believed that the first weight loss which is the biggest in quantity for both samples was due to the removal of adsorbed water. The first sharp exothermic peak that can be seen at both graphs approximately at the same temperature, nearly at about 160 °C can be attributed to the oxidation of some organic residues. It is not very easy to explain the following three exothermic peaks at about 250 °C, 420 °C and 557 °C. They can be showing both burning of organic substances and phase transformation of TiO₂. In literature there are different studies and different opinions about thermal analysis of TiO₂ [102, 106-112].

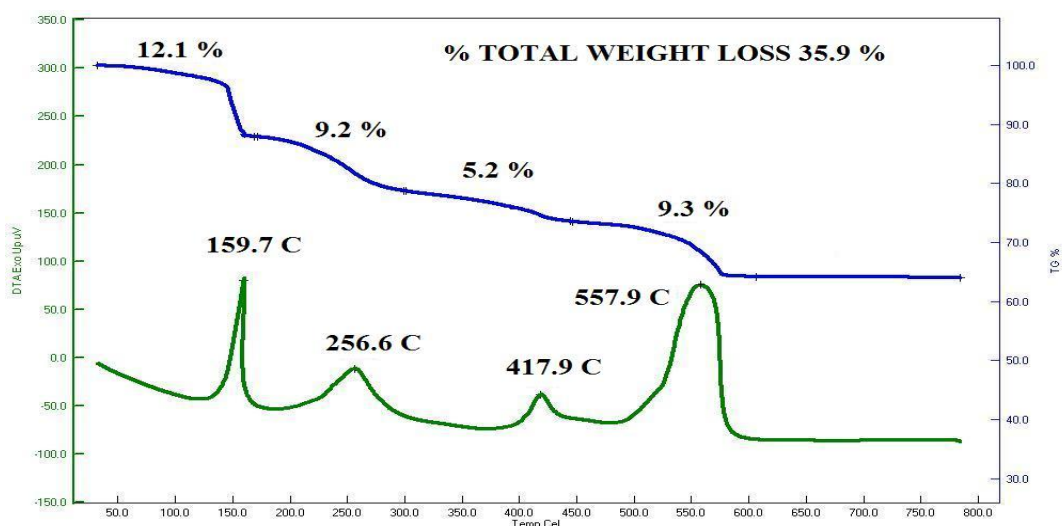


Figure 3.4. DTA-TG graph of TiO₂ powder (R=2, drying temperature=33 °C, moisture removal at 100 °C)

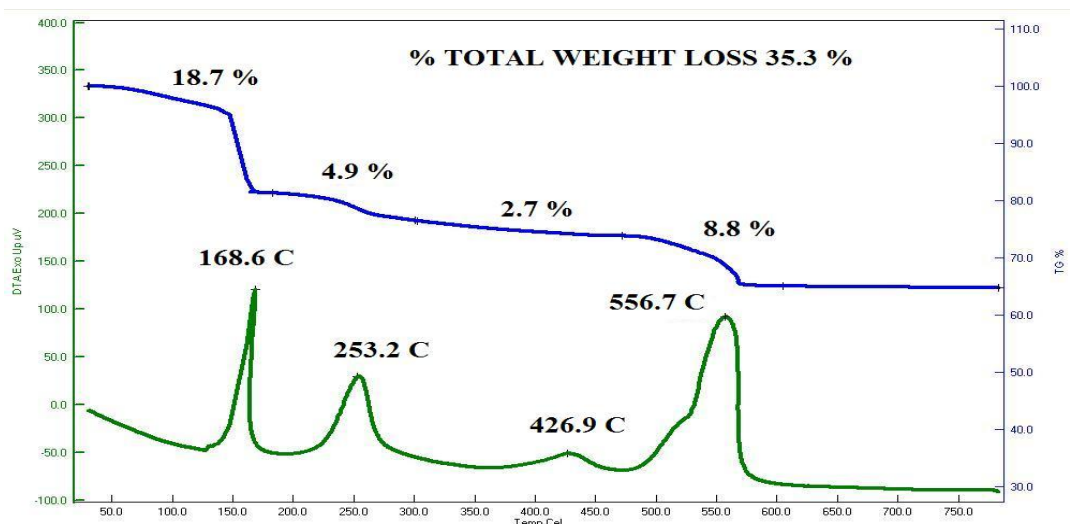


Figure 3.5. DTA-TG graph of TiO₂ powder (R=2, drying temperature=50 °C, moisture removal at 100 °C)

To find out an explanation for the peaks at 250 °C, 420 °C and 557 °C two more different studies were done. In one of them a solution of TiO₂, whose R value was 2, was prepared as in the previous study however this time amount of the solvent in the solution decreased 50 % ($\frac{1}{2}$ propanol). In the other one, a solution of TiO₂ whose R value was 4 was prepared. Both of the solutions were splitted into two equal parts. One part of each was dried at 33 °C and the other part was dried at 50 °C to obtain TiO₂ gel. It was observed that when R value was 2, a more whitish powder was obtained compared to the powder obtained from the solution whose R value was 4 (Figure 3.6).



Figure 3.6. TiO₂ powders obtained by drying TiO₂ solutions (R=2, $\frac{1}{2}$ propanol, R=4) at 50 °C

Before doing thermal analysis, these four powder samples were put in the oven at 100 °C for 1 hour to remove their moisture. It was observed that while the colors of the

powders that were obtained at 33 °C were yellowish, the colors of the powder samples that were obtained at 50 °C were whitish (Figure 3.7).

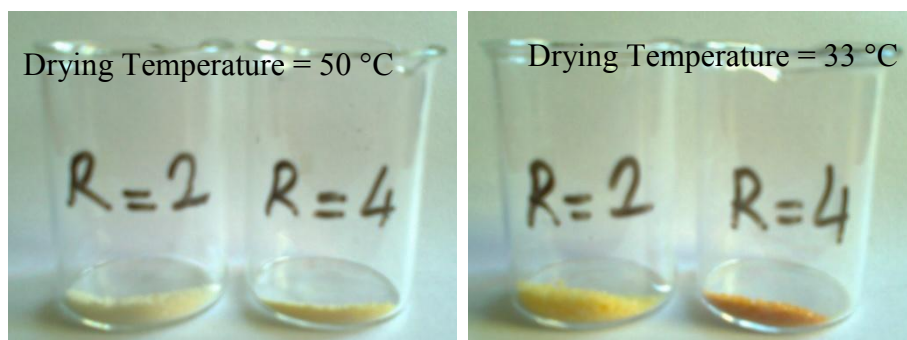


Figure 3.7. TiO₂ powders after moisture removal at 100 °C

Looking at the DTA-TG graph of each powder, the first remarkable thing is that while the graphs of the powders that were obtained from the solution that had a R value of 2 and from the solution that had also a R value of 2 however had 50 % less solvent (Figure 3.8, Figure 3.9) are nearly the same, the graphs of the powders that were obtained from the solution that had a R value of 4 (Figure 3.10, Figure 3.11) are totally different.

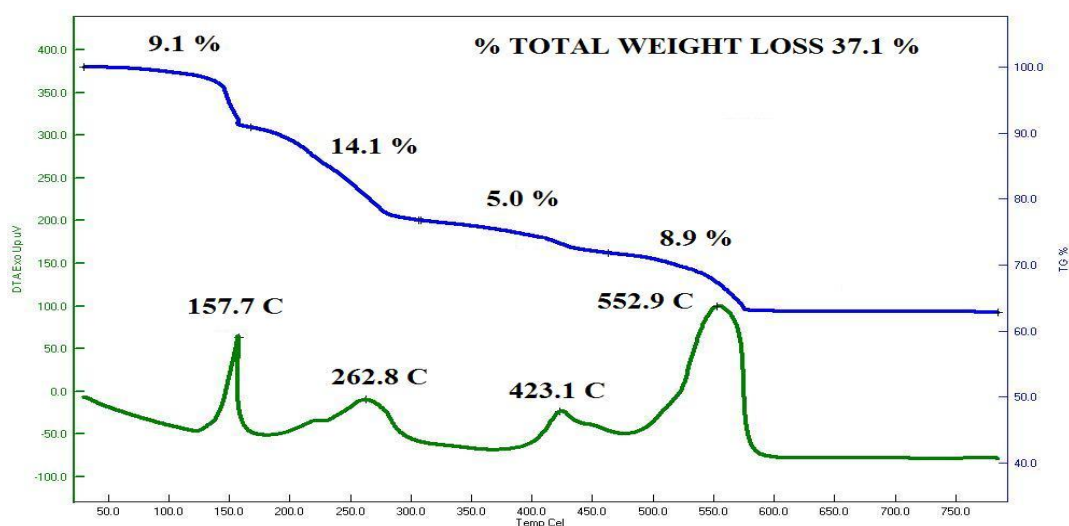


Figure 3.8. DTA-TG graph of TiO₂ powder (R=2, 1/2 propanol, drying temperature=33 °C and moisture removal at 100 °C)

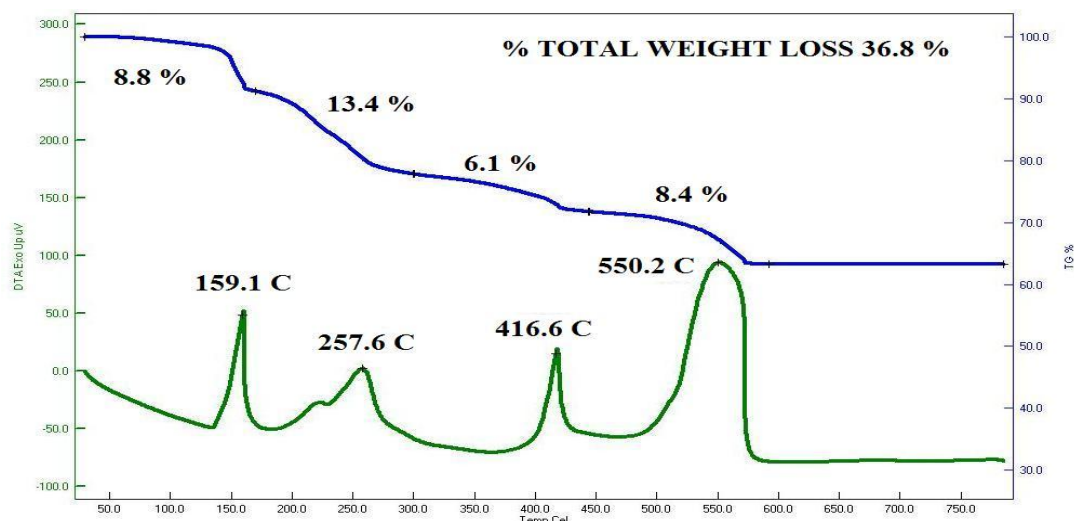


Figure 3.9. DTA-TG graph of TiO₂ powder (R=2, 1/2 propanol, drying temperature=50 °C and moisture removal at 100 °C)

The total mass loss of the powders ends at approximately 150 °C when R value of solution is 4. Since there is a marginal weight loss (1.8 % for TiO₂ powder (R=4, drying temperature=50 °C and moisture removal at 100 °C) and 4.5 % for TiO₂ powder (R=4, drying temperature=50 °C and moisture removal at 100 °C) it is now more appropriate to say that the peaks at the temperatures 250 °C and 430 °C can be anatase transformation of amorphous TiO₂ and rutile transformation of anatase TiO₂ respectively. These low transformation temperatures can be due to acidic environment [113]. As given in Section 2.2.2.1, pH of TiO₂ solution was measured as 1.67. Acidic environment is known to increase hydrolysis rate while decreasing condensation rate and this can be the reason of earlier formation of anatase structure. On the other hand in literature it is usually believed that anatase transformation of amorphous TiO₂ occurs at about 400 °C-500 °C [72, 74] while anatase to rutile transformation occurs at a temperature range of 700 °C-900 °C [102]. However it was proved that there can be some exceptional cases; if the crystallite size of TiO₂ is smaller, anatase to rutile transformation temperature can decrease approximately 200 °C and can become 480 °C [111]. It is also reported that when the environment is acidic crystallite size of TiO₂ is smaller [113]. There are also some studies that not able to explain the peaks at 400 °C-450 °C yet [102, 106] or claimed that the peak at 400 °C-450 °C can represent both

combustion of organics and crystallization of TiO_2 if there is a negligible weight loss [109].

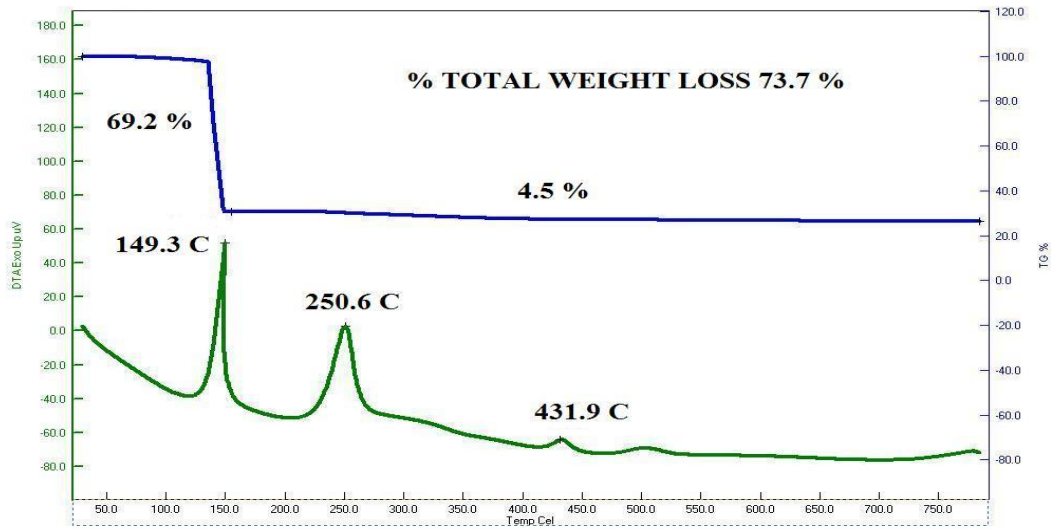


Figure 3.10. DTA-TG graph of TiO_2 powder (R=4, drying temperature=33 °C, moisture removal at 100 °C)

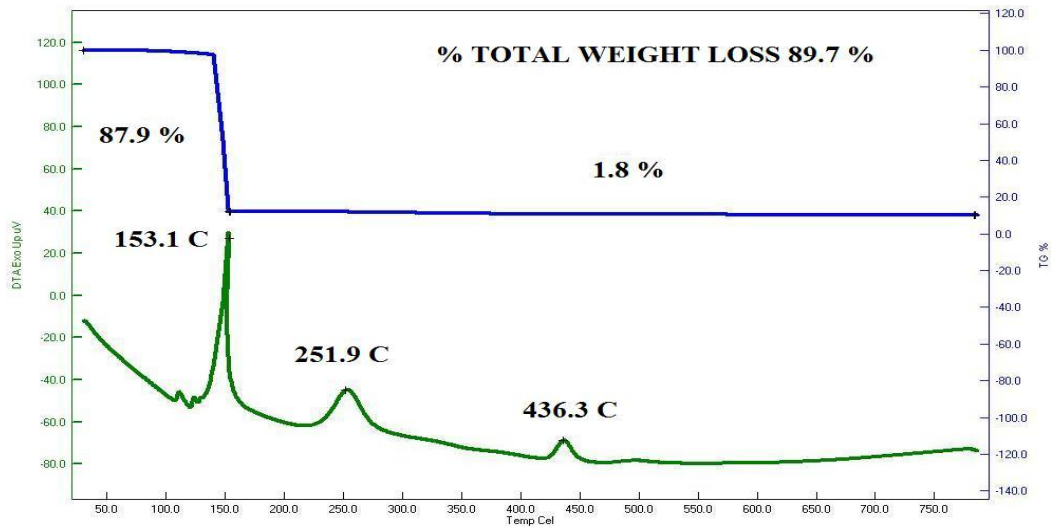
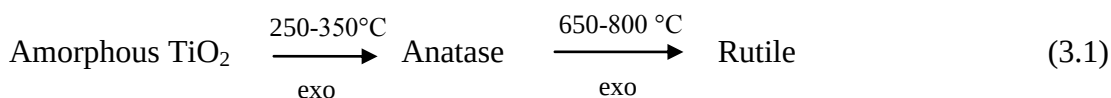
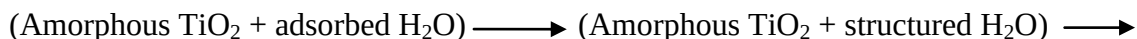


Figure 3.11. DTA-TG graph of TiO_2 powder (R=4, drying temperature=50 °C, moisture removal at 100 °C)

It is also possible to find a study which is totally different from the others by arguing that phase transformation of TiO_2 occurs as [112] :



3.1.2. FTIR of TiO₂ powders

To find out how the hydrolysis and condensation reactions occur, four different TiO₂ solutions were prepared with R values of 1, 2, 3 and 4. After the preparation, solutions were put in an oven at 33 °C to obtain TiO₂ powders. After that the powders were put in an oven at 100 °C for 1 hour for moisture removal.

As seen in the Figure 3.12 there is a slight difference between the colors of the powders that were obtained from the solutions that have different R values.

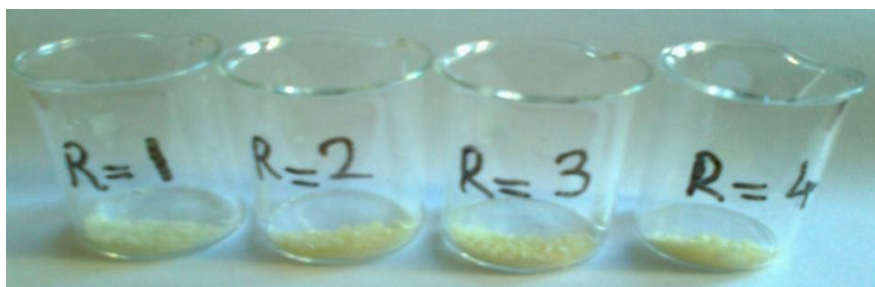


Figure 3.12. TiO₂ powders obtained by drying TiO₂ solutions (R=1, 2, 3, 4) at 33 °C

While the color of the powder that was obtained from the solution whose R value was 1, is white by increasing the R value of the solutions the color of the powders become more yellowish.

The difference between the colors becomes more obvious after the moisture removal process. From the Figure 3.13 it can be seen that by increasing the R value of the solutions the color of the powders becomes darker. While the color of the powder that was obtained from the solution whose R value was 1 is cream, the color of the powders that were obtained from the solutions whose R value were 2, 3, 4 are orange, brick red and brown respectively.

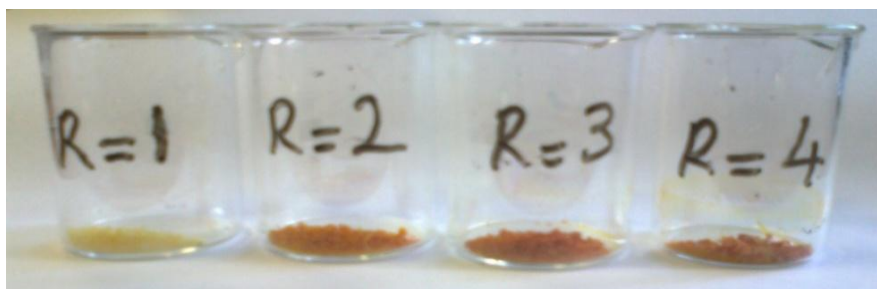
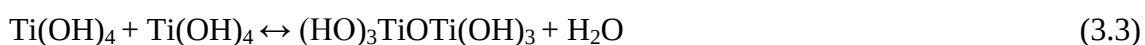
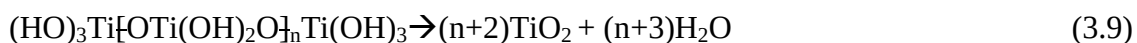


Figure 3.13. TiO₂ powders after moisture removal at 100 °C

The color of the powders that is becoming darker by increasing R value can be thought as a sign of hydrolysis degree. When R value is 4 although it is known that “complete hydrolysis to TiO₂ with cleavage of all the alkoxy groups is difficult to achieve” [114] it is assumed that all the propoxy groups are hydrolyzed.



However when R value is 1 only one of the four propoxy groups can be hydrolyzed and the others remain bonded to Ti. When the R value increases the free groups that can change the color of the powder when heated also increase.



It is also possible to see how the rates of the hydrolysis and condensation reactions change by changing the R value by looking at the FTIR results of the powders that were obtained by drying TiO₂ solutions (R=1, 2, 3, 4) at 33 °C, after moisture removal at 100 °C (Figure 3.14, Figure 3.15, Figure 3.16, Figure 3.17).

Looking at Figure 3.14, Figure 3.15, Figure 3.16 and Figure 3.17, it can be seen that the peaks in the 2970-2940 cm^{-1} range, in the 1454-1466 cm^{-1} range, in the 1111-1006 cm^{-1} range and two peaks at around 1555 cm^{-1} and 1380 cm^{-1} are nearly the same for all powders that were obtained from solutions that have different R values.

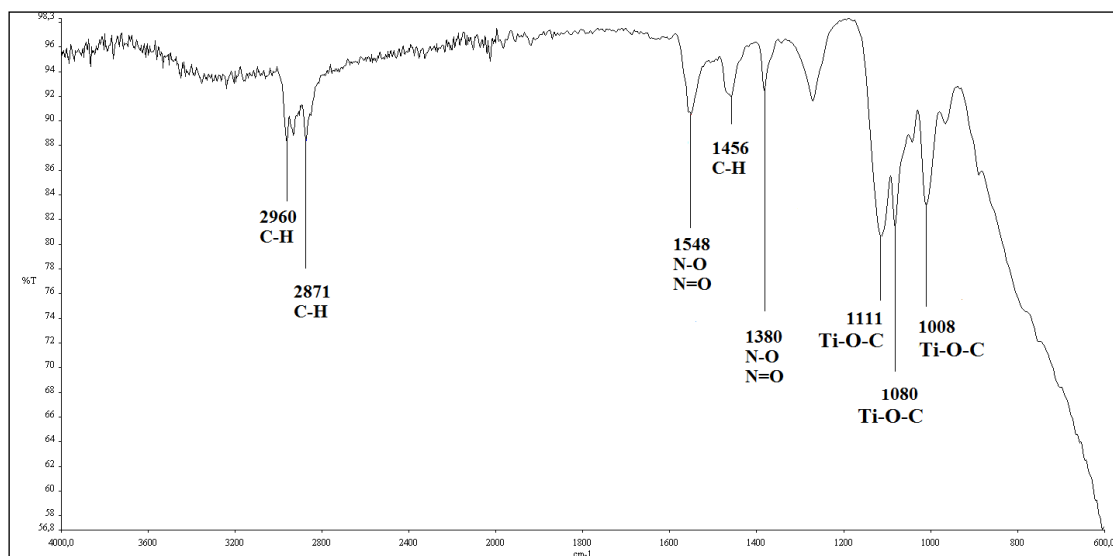


Figure 3.14. FTIR of TiO₂ powder, obtained by drying TiO₂ solutions (R=1) at 33 °C, after moisture removal at 100 °C

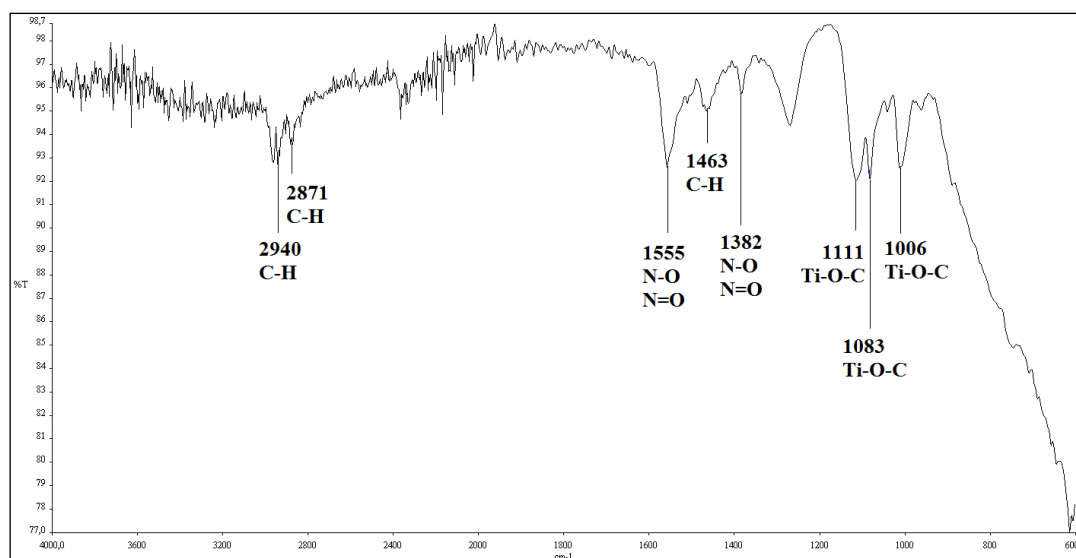


Figure 3.15. FTIR of TiO₂ powder, obtained by drying TiO₂ solutions (R=2) at 33 °C, after moisture removal at 100 °C

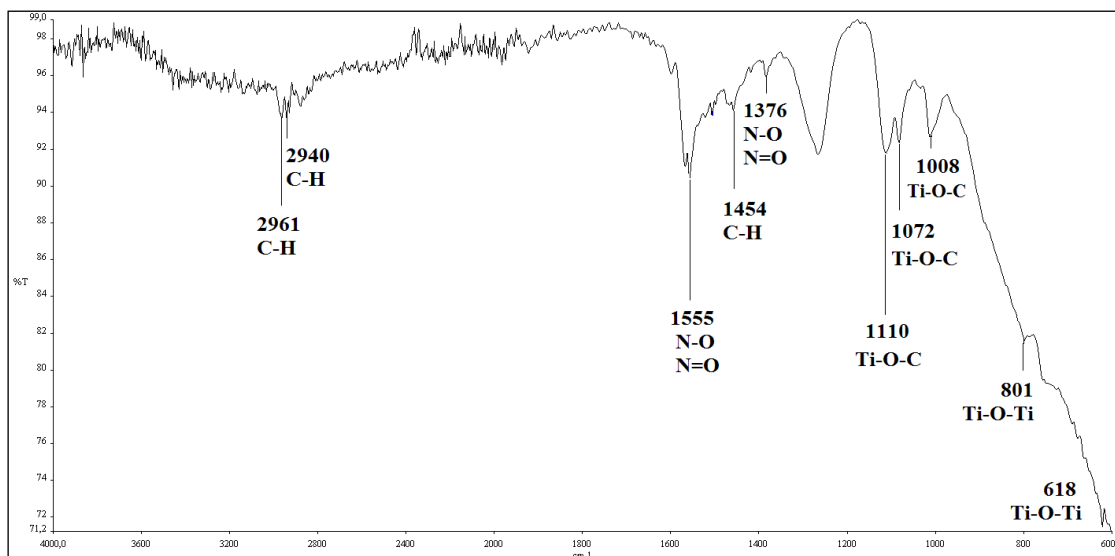


Figure 3.16. FTIR of TiO₂ powder, obtained by drying TiO₂ solutions (R=3) at 33 °C, after moisture removal at 100 °C

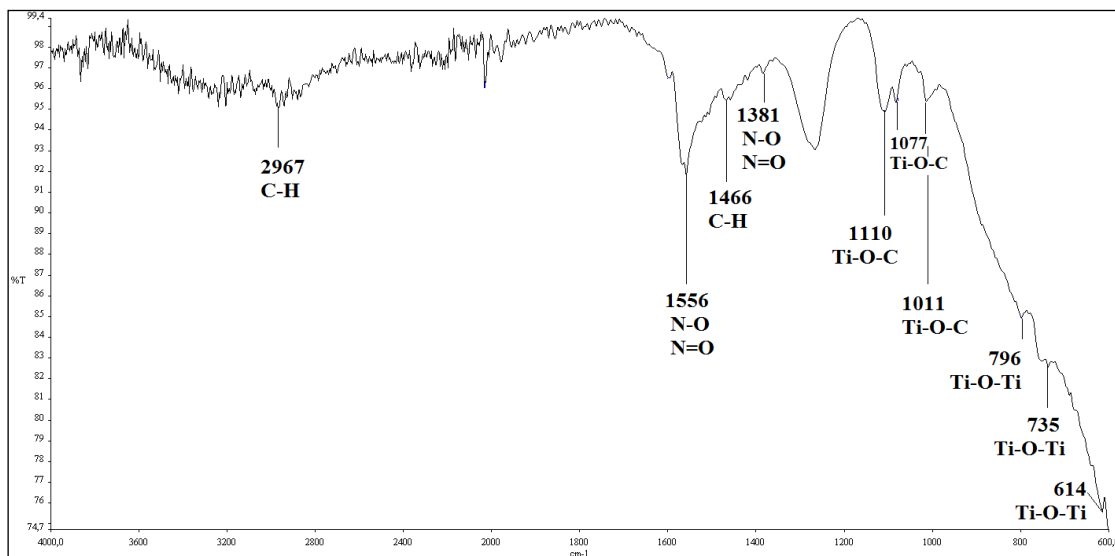


Figure 3.17. FTIR of TiO₂ powder, obtained by drying TiO₂ solutions (R=4) at 33 °C, after moisture removal at 100 °C

The peaks in the 2970-2940 cm⁻¹ range correspond to aliphatic C-H stretching vibrations and the peaks in the 1454-1466 cm⁻¹ range correspond to aliphatic C-H bending vibrations of CH₂ and CH₃ groups. These are probably due to residual organic C-H bands of residual propoxy groups [115-118].

The peaks in the $1111\text{--}1006\text{ cm}^{-1}$ range are due to the stretching vibration of O-C-C bonds of isopropoxide groups directly bonded to titanium isopropoxide. In other words these peaks show unhydrolyzed alkoxy groups [97, 117-120].

The peaks in the $800\text{--}600\text{ cm}^{-1}$ range are assigned to Ti-O and Ti-O-Ti groups, these are the characteristic vibrational modes of TiO_2 [90, 119, 121].

Two peaks at around 1555 cm^{-1} and 1380 cm^{-1} correspond to N-O and N=O bonds of HNO_3 [90].

Looking at Figure 3.18, it can be seen that when R value increases strength of the peaks in the $2970\text{--}2940\text{ cm}^{-1}$ and $1454\text{--}1466\text{ cm}^{-1}$ range decreases which means number of residual propoxy groups decreases faster by increasing R value. It is very obvious that also the strength of the peaks in the $1111\text{--}1006\text{ cm}^{-1}$ range decreases by increasing R value which means number of the unhydrolyzed alkoxy groups decreases when R value increases and the same result can also be seen by comparing Equations (3.2)-(3.4) and Equations (3.5)-(3.9). Peaks in the $800\text{--}600\text{ cm}^{-1}$ range can be seen only when the R value is 3 and 4. It is an evidence that Ti-O-Ti bond occurs faster in other words reaction rate is faster when R value is bigger.

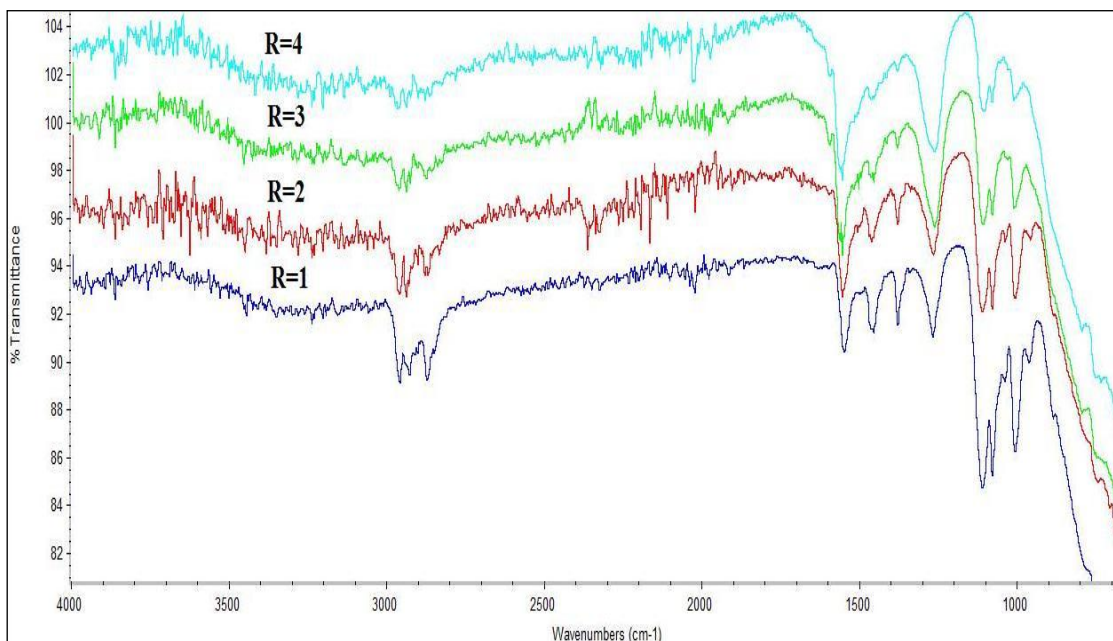


Figure 3.18. FTIR of TiO_2 powders, obtained by drying TiO_2 solutions (R=1, 2, 3, 4) at $33\text{ }^\circ\text{C}$, after moisture removal at $100\text{ }^\circ\text{C}$

3.1.3. XRD results of TiO₂ powders

900 ml of undoped TiO₂, 0.5 % Ag doped TiO₂, 1 % Ag doped TiO₂, 1.5 % Ag doped TiO₂, 0.5 % Zn doped TiO₂, 1 % Zn doped TiO₂, 1.5 % Zn doped TiO₂, 0.5 % Cr doped TiO₂, 1 % Cr doped TiO₂, 1.5 % Cr doped TiO₂ solutions were prepared. R value was chosen as 4 taking the results of study that were explained in Section 3.1.2 into consideration. After preparation of the solutions they were poured in an appropriate Borcam tray and put in the oven at 33 °C. First gelation occurred and then powders were obtained. As an example of how TiO₂ powders were prepared, pictures were taken during preparation of the 1 % Cr doped TiO₂ solution, gelation of 1 % Cr doped TiO₂ solution and drying of the 1 % Cr doped TiO₂. They can be seen at Figure 3.19, Figure 3.20 and Figure 3.21 respectively.



Figure 3.19. Preparation of 1 % Cr doped TiO₂ solution



Figure 3.20. Gel of 1 % Cr doped TiO_2 obtained in oven at 33 °C



Figure 3.21. Powder of 1 % Cr doped TiO_2 obtained in oven at 33 °C

The obtained powders of undoped TiO_2 and 0.5 % Ag, 1 % Ag, 1.5 % Ag, 0.5 % Zn, 1 % Zn, 1.5 % Zn, 0.5 % Cr, 1 % Cr and 1.5 % Cr doped TiO_2 were then sintered in muffle oven for 1 hour at eight different sintering temperatures; 300 °C, 400 °C, 500 °C, 550 °C, 600 °C, 650 °C, 700 °C, 800 °C.

The aim of this study is to find out how the sintering temperature, Ag, Zn and Cr dopants and the different amount of these three dopants affect phase transformation and crystallite size of TiO_2 .

3.1.3.1. Effect of sintering temperature on phase transformation

From Figure 3.22 it can be seen that although there are differences between the amounts % of synthesized TiO_2 powders depending on dopants and amount of dopants, it is clear that for each TiO_2 powder amount % of anatase phase decreases by increasing sintering temperature.

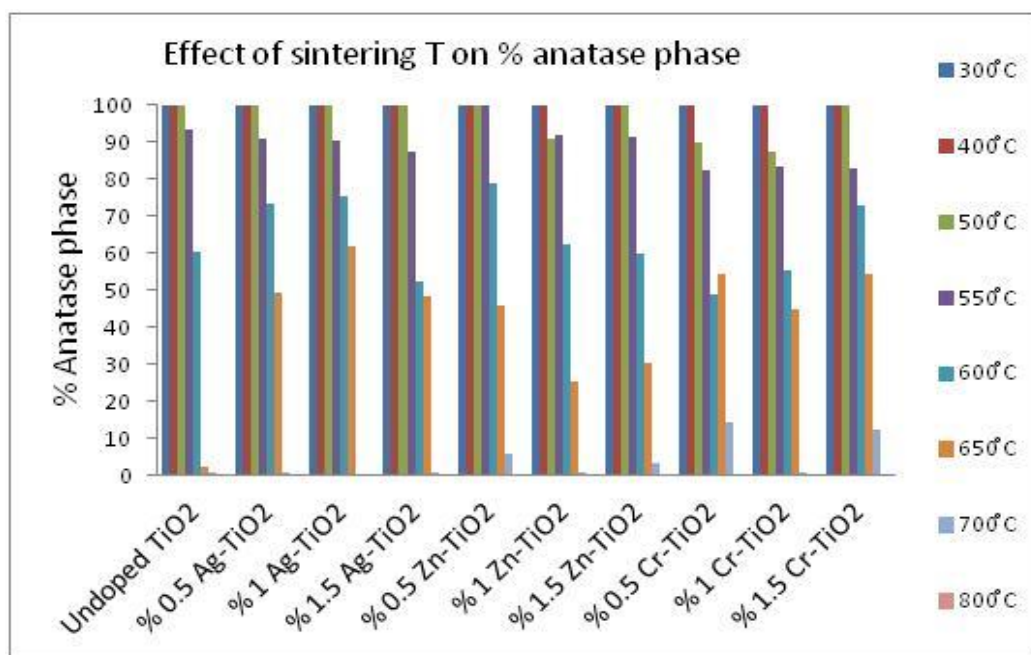


Figure 3.22. Effect of sintering temperature on anatase phase %

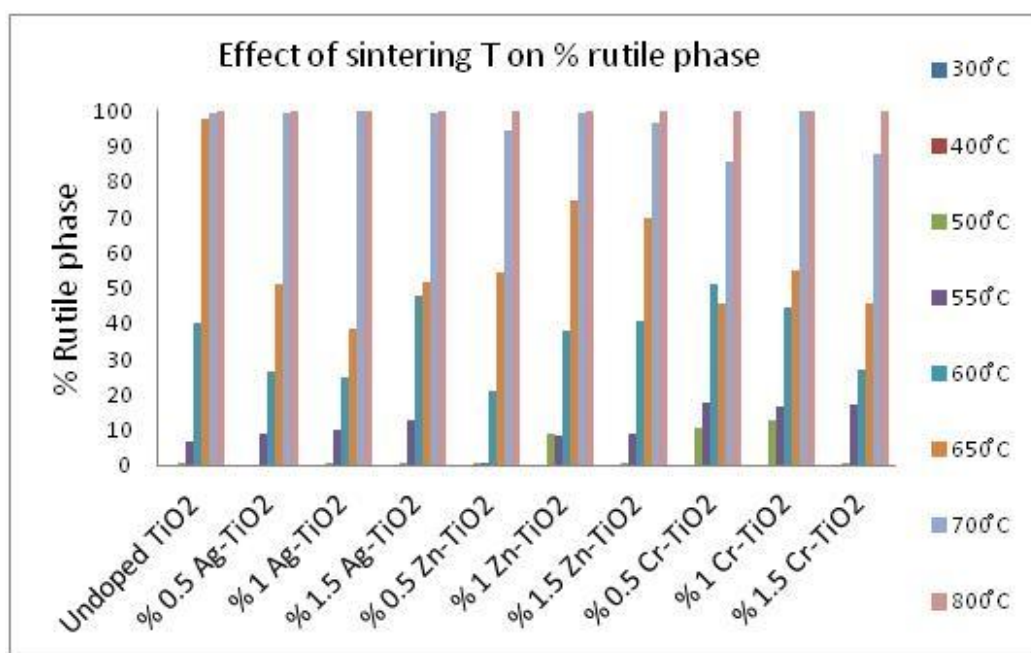


Figure 3.23. Effect of sintering temperature on rutile phase %

Similar to Figure 3.22 looking at Figure 3.23, it is obvious that for each TiO_2 powder amount % of rutile phase increases by increasing sintering temperature although there

are differences between the amounts % of rutile phase of synthesized TiO_2 powders depending on dopants and amount of dopants.

From Figure 3.22 and 3.23 it is also possible to find out at which sintering temperature phase transformation of TiO_2 occurs which was also discussed in previous section by the help of DTA-TG analysis. It can be seen from Figure 3.22 and from Figure 3.23 that undoped TiO_2 consists of only anatase phase when sintering temperature is 300°C , phase transformation of anatase into rutile starts when sintering temperature reaches to 500°C and finally TiO_2 consists of only rutile phase when sintering temperature is 800°C . These XRD results support the DTA-TG results given in previous section and these results are in good agreement with the literature [111, 112] mentioned in previous section which reported that in some cases anatase formation and anatase to rutile phase transformation can occur at lower temperatures than usually expected.

3.1.3.2. Effect of sintering temperature on crystallite size

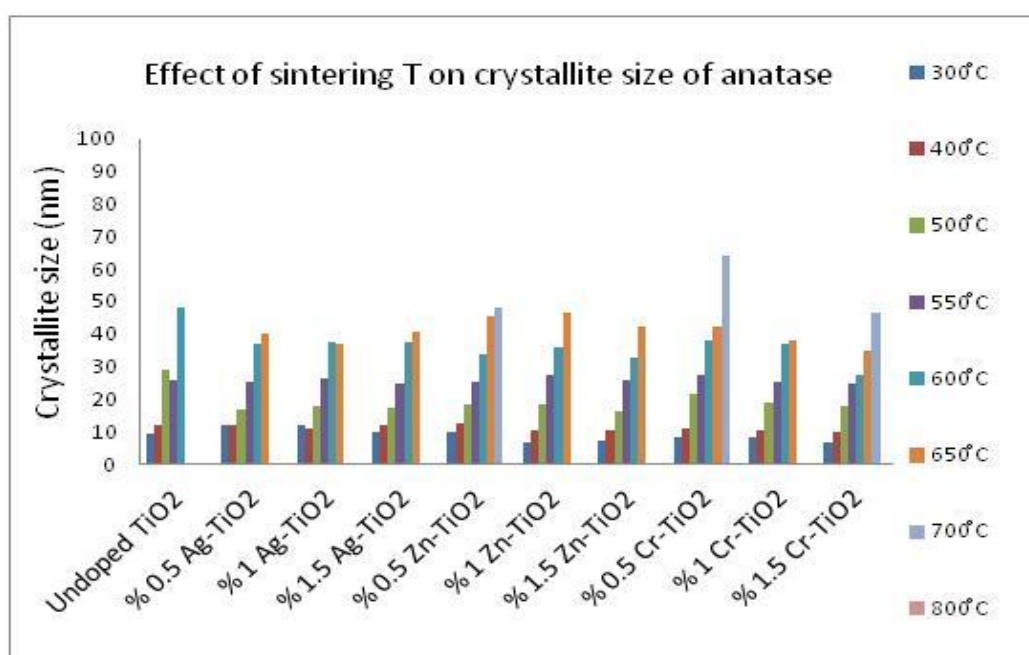


Figure 3.24. Effect of sintering temperature on crystallite size of anatase

From Figure 3.24 and Figure 3.25 it can be seen that for both doped and undoped TiO_2 , crystallite sizes of anatase phase and rutile phase increase by increasing sintering temperature.

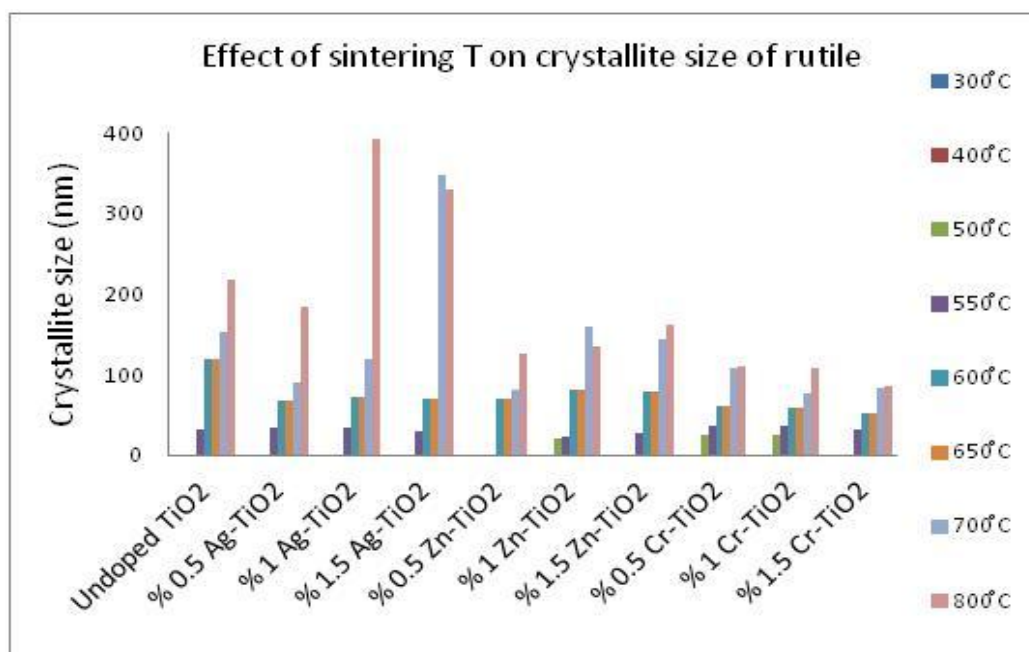


Figure 3.25. Effect of sintering temperature on crystallite size of rutile

3.1.3.3. Effect of dopant amounts on phase transformation

Table 3.1 shows effect of Ag % amount on phase transformation of TiO₂. For both doped and undoped TiO₂ powders phase transformation does not start until the sintering temperature is 500 °C. At 500 °C, rutile phase appears however not with a considerable amount. Looking at the amount of rutile phase of undoped, 0.5 %, 1 % and 1.5 % Ag doped TiO₂ at 550 °C, it can be said that all Ag dopants promote anatase to rutile phase transformation slightly and promotion rate increases by increasing dopant amount. When sintering temperature is increased to 600 °C, while 0.5 % and 1 % Ag doping cause inhibition, 1.5 % Ag doping causes promotion at anatase to rutile phase transformation. At 650 °C it can be seen that all Ag dopants cause a serious inhibition at anatase to rutile phase transformation. At 700 °C, it seems there is not an important difference between undoped TiO₂ powder and Ag doped TiO₂ powders. At 800 °C anatase to rutile transformation is completed for all TiO₂ powders.

Table 3.1. Effect of Ag % amount on phase transformation

	TiO ₂		0.5 % Ag-TiO ₂		1 % Ag-TiO ₂		1.5 % Ag-TiO ₂	
	A ¹ (%)	R ² (%)	A(%)	R(%)	A(%)	R(%)	A(%)	R(%)
300 °C	100	0	100	0	100	0	100	0
400 °C	100	0	100	0	100	0	100	0
500 °C	99.8	0.2	100	0	99.9	0.1	99.9	0.1
550 °C	93.3	6.7	91	9	90.3	9.7	87.3	12.7
600 °C	60.1	39.9	73.5	26.5	75.5	24.5	52.1	47.9
650 °C	2.4	97.6	49.1	50.9	61.8	38.2	48.2	51.8
700 °C	0.7	99.3	0.6	99.4	0	100	0.6	99.4
800 °C	0	100	0	100	0	100	0	100

¹Anatase, ²Rutile

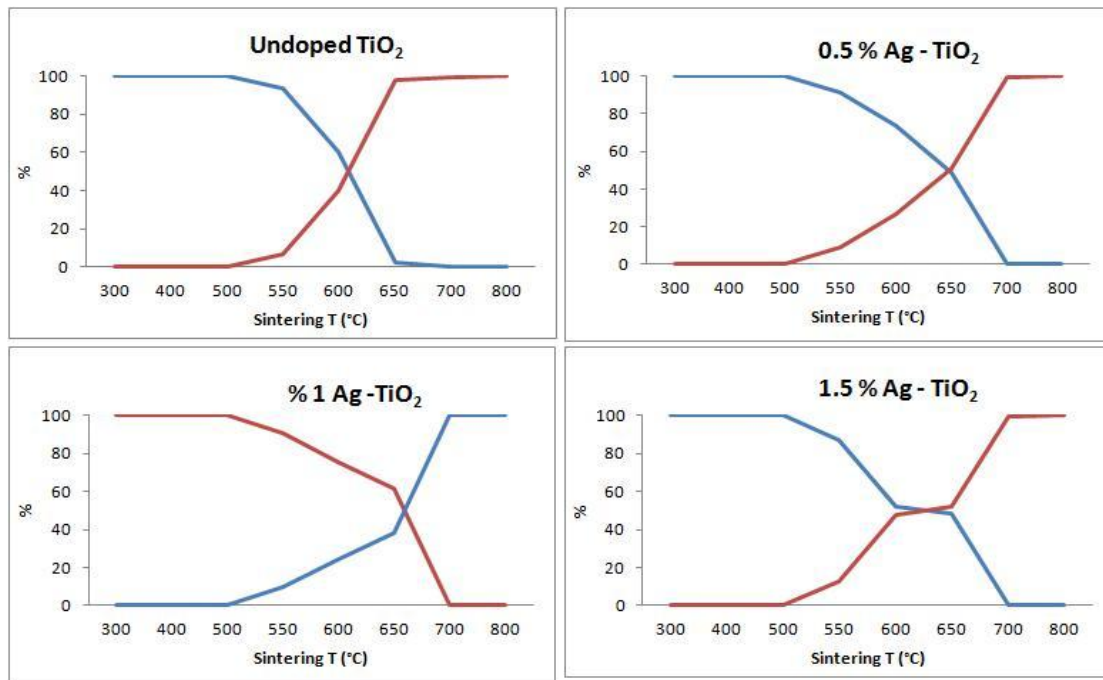


Figure 3.26. Effect of Ag % amount on phase transformation (blue line: anatase, red line: rutile)

Figure 3.26 also shows effect of Ag % amount on phase transformation of TiO₂. Looking at the phase % transformation graphics of undoped and 0.5 %, 1 % and 1.5 % Ag doped TiO₂ powders, it is obvious that until the sintering temperature reaches above 500 °C, all powders have nearly 100 % anatase phase and nearly all anatase phase transforms into rutile phase when sintering temperature reaches 700 °C. Doping TiO₂ with Ag seems to have an effect on phase transformation only at the sintering temperatures between 500 °C and 700 °C.

It is believed that anatase to rutile phase transformation is affected by grain size of anatase, surface area of TiO₂ powder and the concentration of oxygen vacancies on the surface of anatase grains. Anatase to rutile phase transformation is thought to occur at lower temperatures when anatase grain size decreases, surface area of TiO₂ powder and the concentration of oxygen vacancies on the surface of anatase grains increase [76].

Looking at the reason why it is so, it can be said that when specific surface area increases also the density of surface defects of anatase grains increases and surface defects are thought to be the nucleation sites of rutile phase [76]. It is a well known fact that Ag⁺ ion can not enter into the anatase phase since its ionic radius (ca. 129 pm) is much larger than the ionic radius of Ti⁴⁺ (ca. 74.5 pm) [76, 85]. This causes Ag dopant to distribute at the surface of TiO₂ which increases the density of surface defects and so the rutile nucleation. Although it is usually reported that Ag doping promotes anatase to rutile phase transformation, in other words lowers the sintering temperature that anatase to rutile phase transformation occurs [76, 85] it is also possible to find studies showing that Ag dopant causes anatase to rutile phase transformation to occur at higher temperatures [75]. This difference can be due to differences at preparation methods.

What happened in this study, different behaviours of Ag dopant at different sintering temperatures, has not been reported in the literature yet since sintering temperatures between 500 °C and 700 °C have not been studied so detailed before.

Table 3.2 shows effect of Zn % amount on phase transformation of TiO₂. Until the sintering temperature reaches to 500 °C, rutile phase does not appear for undoped and Zn doped TiO₂ powders. When sintering temperature is 500 °C, rutile phase starts to appear. At this sintering temperature although 0.5 % Zn and 1.5 % Zn doping seems not to alter phase transformation, doping TiO₂ with 1 % Zn promotes rutile phase

transformation which can be seen clearly from Figure 3.27. At 550 °C, Zn dopant seems to promote rutile phase transformation above the concentration 0.5 %. At this temperature 0.5 % Zn doping to TiO₂ inhibits rutile phase transformation. While 1.5 % Zn slightly promotes and 1 % Zn slightly inhibits, 0.5 % Zn doping inhibits more seriously anatase to rutile phase transformation. When sintering temperature reaches to 650 °C all concentrations of Zn inhibit anatase to rutile phase transformation apparently; while percentage of rutile phase is 97.6 % for undoped TiO₂, it is 54.4 %, 74.6 % and 69.8 % for 0.5 %, 1 % and 1.5 % Zn doped TiO₂ respectively. At 800 °C, undoped TiO₂ consists of only a little amount of anatase phase similar to 1 % Zn doped TiO₂ however 0.5 % Zn doped TiO₂ and 1.5 % Zn doped TiO₂ still have 5.7 % and 3.4 % anatase phase respectively. At 800 °C, Zn dopant has no effect on phase transformation and all TiO₂ powders both doped and undoped return to rutile phase completely.

Table 3.2. Effect of Zn % amount on phase transformation

	TiO ₂		0.5 % Zn-TiO ₂		1 % Zn-TiO ₂		1.5 % Zn-TiO ₂	
	A ¹ (%)	R ² (%)	A(%)	R(%)	A(%)	R(%)	A(%)	R(%)
300 °C	100	0	100	0	100	0	100	0
400 °C	100	0	100	0	100	0	100	0
500 °C	99.8	0.2	99.8	0.2	90.9	9.1	99.8	0.2
550 °C	93.3	6.7	99.8	0.2	91.9	8.1	91.3	8.7
600 °C	60.1	39.9	79	21	62.3	37.7	59.6	40.4
650 °C	2.4	97.6	45.6	54.4	25.4	74.6	30.2	69.8
700 °C	0.7	99.3	5.7	94.3	0.7	99.3	3.4	96.6
800 °C	0	100	0	100	0	100	0	100

¹Anatase, ²Rutile

Looking at Figure 3.27 it is possible to see all effects of Zn dopant that was mentioned in the above paragraph more clearly. It is obvious that intensity of the effect of Zn dopant on phase transformation not only depends on concentration of dopant but also

depends on sintering temperature. At the sintering temperatures 600 °C and 650 °C effect of Zn dopant is more obvious compared to other sintering temperatures.

While Dorion and his friends in their review paper reported Zn as a dopant that was experimentally observed to promote the anatase to rutile transformation [33]. Pawar and Chen reported separately that Zn doping inhibited anatase to rutile phase transformation [77,122]. The differences may be due to their preparation method, concentration of dopant and type of salt that they used as Zn source. In Dorion's paper ZnO, in Pawar's paper $\text{Zn}(\text{NO}_3)_2$ and in Jianhua's paper $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was reported to be used as Zn source, solubility of these different sources might have affected the anatase to rutile phase transformation. On the other hand it is known that ionic radius of Zn^{2+} (ca. 88 pm) is bigger than ionic radius of Ti^{4+} (ca. 74.5 pm), this causes Zn^{2+} to appear in the interstitial position in the lattice [77] and due to this information similar thing that was mentioned before for Ag^+ can be expected also for Zn^{2+} that appearance in the interstitial position in the lattice increases the rutile nucleation sites on TiO_2 surface. The mechanism needs to be further understood.

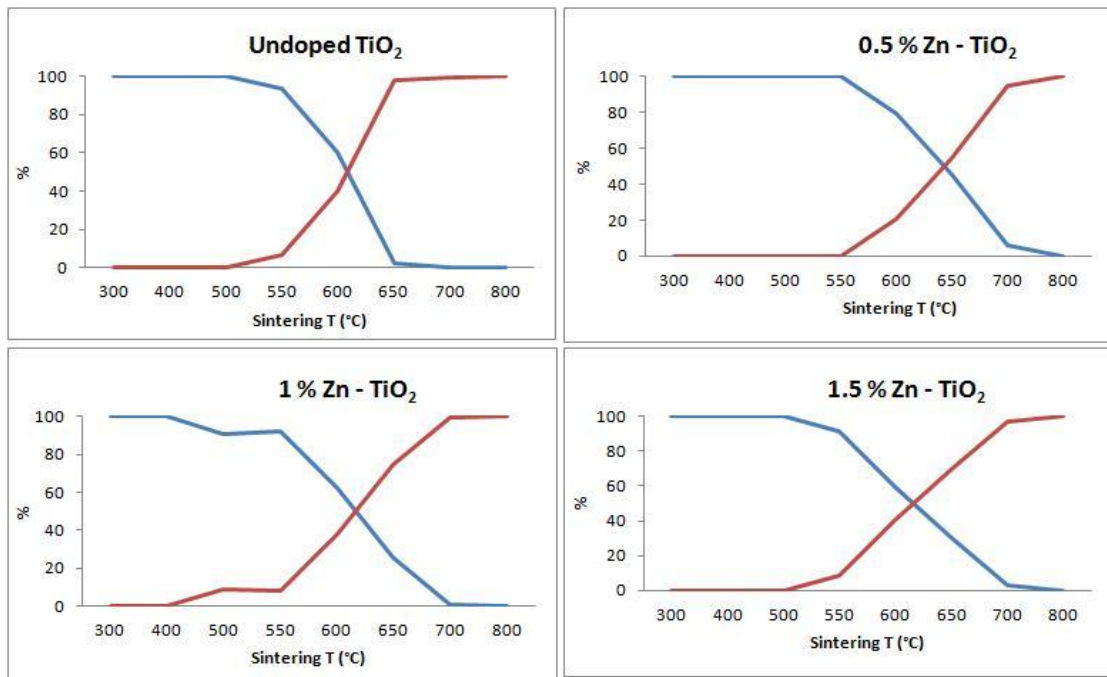


Figure 3.27. Effect of Zn % amount on phase transformation (blue line: anatase, red line: rutile)

Table 3.3 shows effect of Cr % amount on phase transformation of TiO₂. Rutile phase transformation does not start until the sintering temperature reaches to 500 °C for all doped and undoped TiO₂ powders. At 500 °C, Cr dopant promotes anatase to rutile phase transformation nearly at the same rate when its concentration is 0.5 % and 1 %. Besides, at this temperature 1.5 % Cr dopant has no significant effect on phase transformation. When sintering temperature is 550 °C, promotion effect of Cr dopant becomes more obvious; while 6.7 % of undoped TiO₂ turns to rutile phase, this percentage is 17.8 %, 16.5 %, 17.2 % for 0.5 %, 1 % and 1.5 % Cr doped TiO₂ respectively. At 600 °C, while 0.5 % and 1 % Cr doping still promotes rutile phase transformation, 1.5 % Cr doping seems to inhibit rutile phase transformation. At 650 °C, while nearly all the anatase seems to transform to rutile phase for undoped TiO₂, approximately 50 % of anatase seems to transform to rutile phase for 0.5 %, 1 % and 1.5 % Cr doped TiO₂. At this sintering temperature Cr dopant inhibits strongly the rutile phase transformation. 1 % Cr doped TiO₂ catches the same rutile phase transformation rate with undoped TiO₂ while 0.5 % and 1.5 % Cr doped TiO₂ powders still have an inhibiting effect on rutile phase transformation. All four powders consist of only rutile phase when sintering temperature reaches finally to 800 °C.

Table 3.3. Effect of Cr % amount on phase transformation

	TiO ₂		0.5 % Cr-TiO ₂		1 % Cr-TiO ₂		1.5 % Cr-TiO ₂	
	A ¹ (%)	R ² (%)	A(%)	R(%)	A(%)	R(%)	A(%)	R(%)
300 °C	100	0	100	0	100	0	100	0
400 °C	100	0	100	0	100	0	100	0
500 °C	99.8	0.2	89.6	10.4	87.3	12.7	99.9	0.1
550 °C	93.3	6.7	82.2	17.8	83.5	16.5	82.8	17.2
600 °C	60.1	39.9	49	51	55.4	44.6	72.8	27.2
650 °C	2.4	97.6	54.2	45.8	44.9	55.1	54.3	45.7
700 °C	0.7	99.3	14.4	85.6	0.6	99.4	12.2	87.8
800 °C	0	100	0	100	0	100	0	100

¹Anatase, ²Rutile

Briefly; with some little differences between the different concentrations of Cr dopant, generally it is possible to say that until the sintering temperature reaches to 650 °C, doping TiO₂ with Cr seems to promote anatase to rutile phase transformation however at 650 °C completely an opposite effect is observed which is possible to be seen also from the Figure 3.28.

There are different ideas about the effect of Cr dopant on anatase to rutile phase transformation. While some studies showed that Cr doping promoted anatase to rutile phase transformation [122-124] others reported that it inhibited anatase to rutile phase transformation [77, 125]. The reason for the inhibition effect of Cr³⁺ is thought to be the entrance of Cr³⁺ ion into the TiO₂ lattice due to its ionic radius (ca. 75.5 pm) which is similar to ionic radius of Ti⁴⁺ (ca. 74.5 pm) [125].

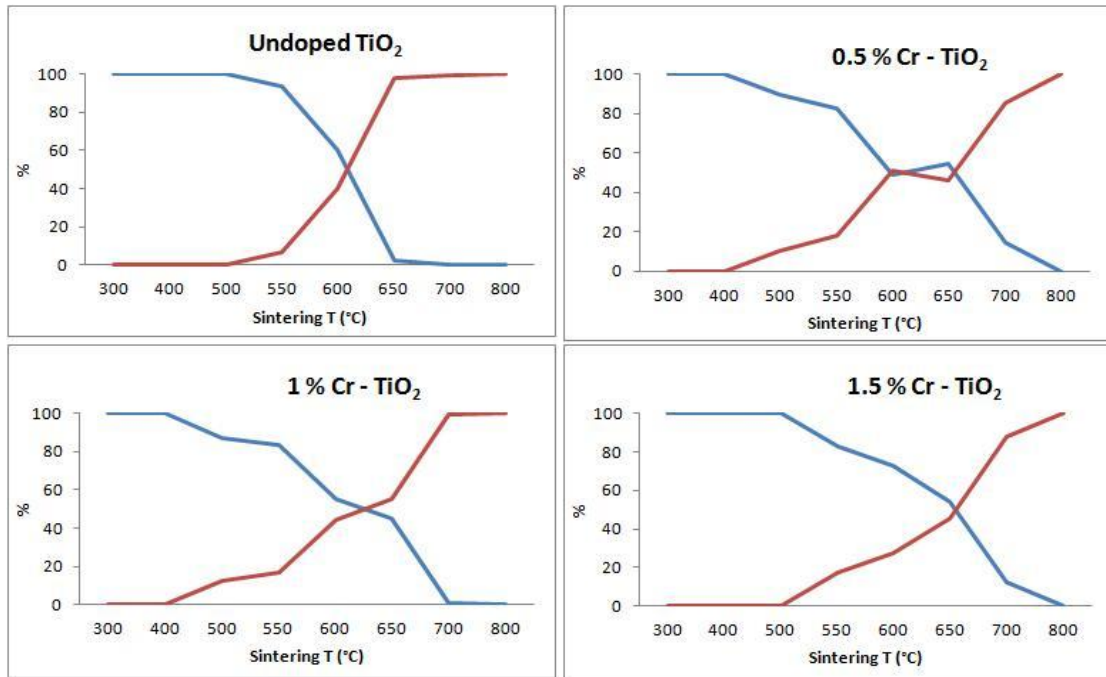


Figure 3.28. Effect of Cr % amount on phase transformation (blue line: anatase, red line: rutile)

3.1.3.4. Effect of dopants on phase transformation

Table 3.4 shows the effect of three dopants; Ag, Zn and Cr on anatase to rutile phase transformation when their concentration is 0.5 %.

When sintering temperature is chosen 300 °C and 400 °C, undoped TiO₂ and TiO₂ powders doped with Ag, Zn and Cr consist of only anatase phase. At 500 °C, slight transformation begins for undoped, Ag and Zn doped TiO₂ however compared to these three TiO₂ powders rutile phase transformation starts faster for Cr doped TiO₂. At 550 °C, while the rutile phase percentage of 0.5 % Zn doped TiO₂ remains 0.2 %, rutile percentage of undoped TiO₂, Ag doped and Cr doped TiO₂ increases to 6.7 %, 9 %, 17.8 % respectively. At 600 °C, while 0.5 % Cr doping promotes anatase to rutile transformation, 0.5 % Ag and 0.5 % Zn doping inhibit anatase to rutile transformation. At 650 °C, rutile phase percentage of 0.5 % Cr doped TiO₂ nearly remains the same. Rutile phase percentage of 0.5 % Ag and 0.5 % Zn doped TiO₂ increase approximately to 50 % while undoped TiO₂ has a rutile percentage of 97.6 %. When sintering temperature is 650 °C, it is obvious that all three dopants inhibit anatase to rutile phase transformation.

Table 3.4. Effect of dopants on phase transformation (0.5 %)

	TiO ₂		0.5 % Ag-TiO ₂		0.5 % Zn-TiO ₂		0.5 % Cr-TiO ₂	
	A ¹ (%)	R ² (%)	A(%)	R(%)	A(%)	R(%)	A(%)	R(%)
300 °C	100	0	100	0	100	0	100	0
400 °C	100	0	100	0	100	0	100	0
500 °C	99.8	0.2	100	0	99.8	0.2	89.6	10.4
550 °C	93.3	6.7	91	9	99.8	0.2	82.2	17.8
600 °C	60.1	39.9	73.5	26.5	79	21	49	51
650 °C	2.4	97.6	49.1	50.9	45.6	54.4	54.2	45.8
700 °C	0.7	99.3	0.6	99.4	5.7	94.3	14.4	85.6
800 °C	0	100	0	100	0	100	0	100

¹Anatase, ²Rutile

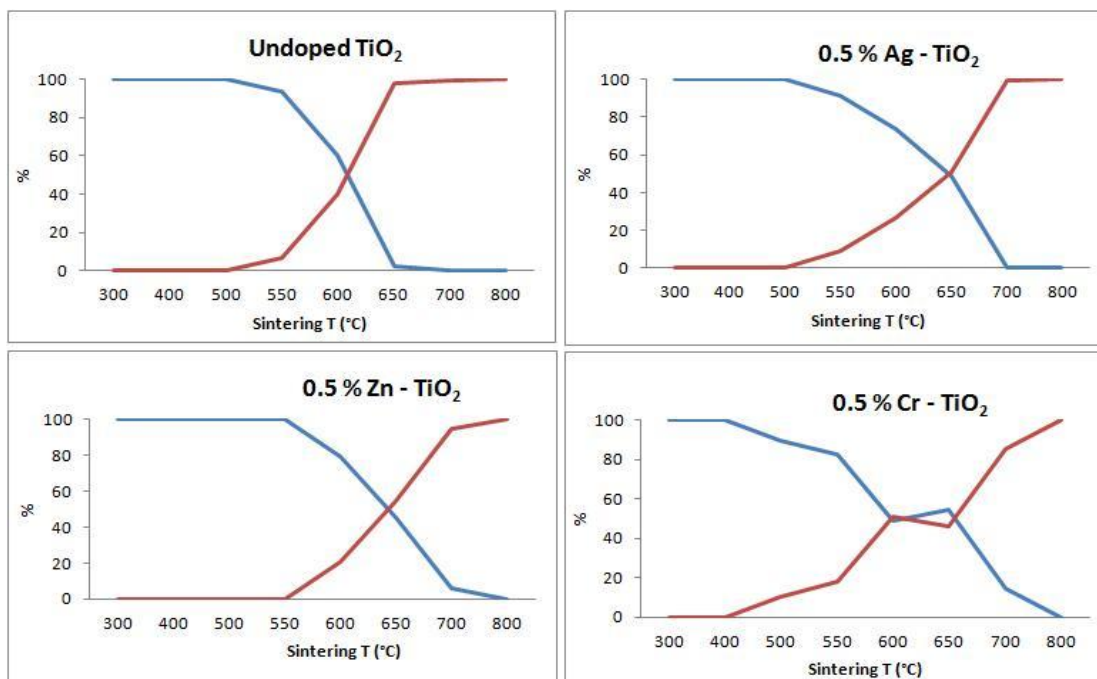


Figure 3.29. Effect of dopants on phase transformation (0.5 %) (blue line: anatase, red line: rutile)

At 700 °C, undoped and Ag doped TiO₂ approximately have same amount of rutile phase; 99.3 % and 99.4 % respectively. Inhibition of anatase to rutile phase transformation of Zn and Cr doped TiO₂ still continues; Zn doped TiO₂ consists of 94.3 % rutile phase while Cr doped TiO₂ consists of 85.6 % rutile phase. At 800 °C, rutile phase transformation is completed for all doped and undoped TiO₂ powders.

Figure 3.29 shows the effects of different dopants on anatase to rutile transformation graphically and it is so obvious from these graphics that Cr is the dopant that affects anatase to rutile transformation more significantly compared to Ag and Zn. Until 650 °C, Cr dopant seems to promote anatase to rutile phase transformation however at 650 °C and 700 °C it behaves like an anatase to rutile phase transition inhibitor.

Table 3.5 shows the effect of three dopants; Ag, Zn and Cr on anatase to rutile phase transformation when their concentration is 1 %.

Table 3.5. Effect of dopants on phase transformation (1 %)

	TiO ₂		1 % Ag-TiO ₂		1 % Zn-TiO ₂		1% Cr-TiO ₂	
	A ¹ (%)	R ² (%)	A(%)	R(%)	A(%)	R(%)	A(%)	R(%)
300 °C	100	0	100	0	100	0	100	0
400 °C	100	0	100	0	100	0	100	0
500 °C	99.8	0.2	99.9	0.1	90.9	9.1	87.3	12.7
550 °C	93.3	6.7	90.3	9.7	91.9	8.1	83.5	16.5
600 °C	60.1	39.9	75.5	24.5	62.3	37.7	55.4	44.6
650 °C	2.4	97.6	61.8	38.2	25.4	74.6	44.9	55.1
700 °C	0.7	99.3	0	100	0.7	100	0.6	99.4
800 °C	0	100	0	100	0	100	0	100

¹Anatase, ²Rutile

Here same situation can be seen as the one seen when dopant concentration was 0.5 %; for all doped TiO₂ and undoped TiO₂ rutile phase transformation does not start until the sintering temperature is 500 °C. At 500 °C, while percentage of rutile phase of undoped TiO₂ and 1 % Ag doped TiO₂ are 0.2 % and 0.1 % respectively, percentage of rutile phase of 1 % Zn and 1 % Cr doped TiO₂ are 9.1 % and 12.7 % respectively. At this temperature, Zn and Cr dopant seem to promote rutile phase transformation. At 550 °C undoped TiO₂, 1 % Ag doped TiO₂, 1 % Zn doped TiO₂ and 1 % Cr doped TiO₂ consist of 6.7 %, 9.7 %, 8.1 %, 16.5 % rutile respectively.

When sintering temperature is 600 °C, 39.9 % of undoped TiO₂ transforms into rutile phase. With a rutile phase percentage of 24.5 %, 1 % Ag dopant seems to inhibit rutile phase transformation at this temperature while 1 % Zn seems not to have an significant effect with a rutile percentage of 37.7 % and 1 % Cr dopant seems to promote rutile phase transformation with the rutile percentage of 44.6 %. Coming up to 650 °C, a large amount of anatase phase transforms into rutile phase when TiO₂ is undoped. Still 61.8 %, 25.4 % and 44.9 % anatase phase remains when TiO₂ is doped with 1 % Ag, 1 % Zn and 1 % Cr respectively. At 700 °C, dopants do not have an significant effect on phase

transformation and at 800 °C, anatase to rutile phase transformation seems to be completed for all TiO₂ powders.

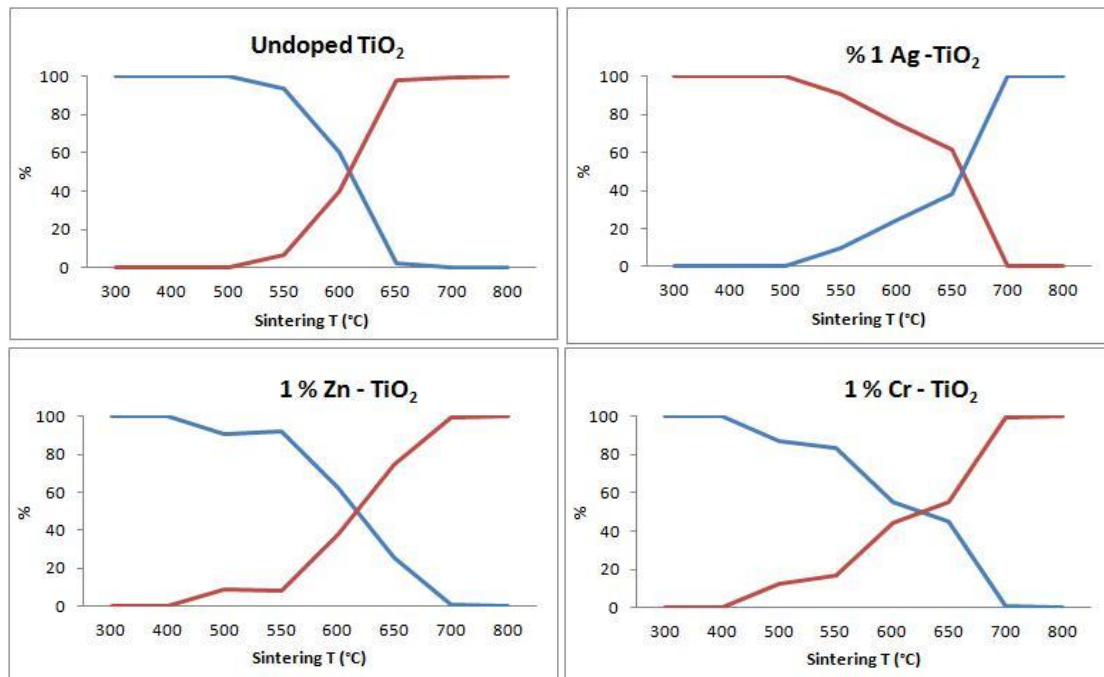


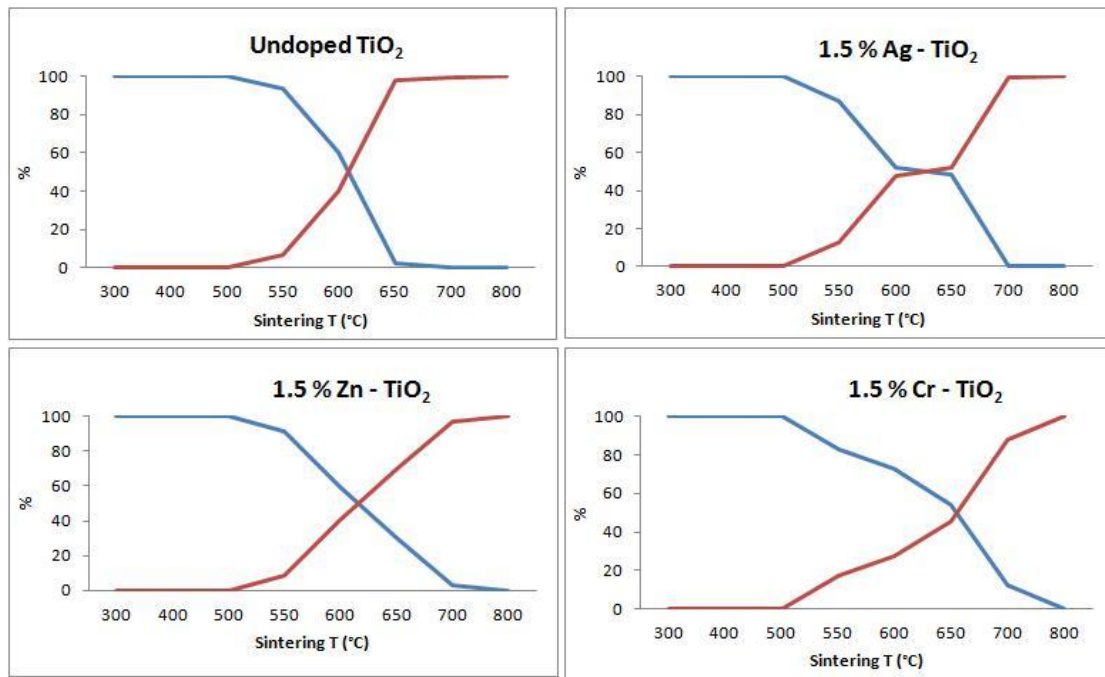
Figure 3.30. Effect of dopants on phase transformation (1%) (blue line: anatase, red line: rutile)

It can be seen from Figure 3.30 that all three dopants first seem to promote anatase to rutile phase transformation however by increasing sintering temperature they start to inhibit anatase to rutile phase transformation. Looking at the sintering temperature 550 °C, while it is obvious that all three dopants promote anatase to rutile phase transformation, at 650 °C, they seem to promote anatase to rutile phase transformation. This inhibition and promotion effects are especially dominant for Cr dopant.

Table 3.6 shows the effect of three dopants; Ag, Zn and Cr on anatase to rutile phase transformation when their concentration is 1.5 %. Rutile phase transformation starts slightly when sintering temperature is 500 °C. At this temperature it can be said that dopants do not have any effect on phase transformation. At 550 °C, all three dopants promote anatase to rutile phase transformation. Cr is the most promotive dopant with a rutile percentage of 17.2 % and Zn is the less promotive dopant with a rutile percentage of 8.7 %.

Table 3.6. Effect of dopants on phase transformation (1.5 %)

	TiO ₂		1.5% Ag-TiO ₂		1.5% Zn-TiO ₂		1.5% Cr-TiO ₂	
	A ¹ (%)	R ² (%)	A(%)	R(%)	A(%)	R(%)	A(%)	R(%)
300 °C	100	0	100	0	100	0	100	0
400 °C	100	0	100	0	100	0	100	0
500 °C	99.8	0.2	99.9	0.1	99.8	0.2	99.9	0.1
550 °C	93.3	6.7	87.3	12.7	91.3	8.7	82.8	17.2
600 °C	60.1	39.9	52.1	47.9	59.6	40.4	72.8	27.2
650 °C	2.4	97.6	48.2	51.8	30.2	69.8	54.3	45.7
700 °C	0.7	99.3	0	100	3.4	96.6	12.2	87.8
800 °C	0	100	0	100	0	100	0	100

¹Anatase, ²Rutile**Figure 3.31.** Effect of dopants on phase transformation (1.5 %) (blue line: anatase, red line: rutile)

At 600 °C, while both Ag and Zn dopants still act as promotive, Cr dopant inhibits anatase to rutile phase transformation. At this temperature, percentages of rutile phase for undoped, 1.5 % Ag doped, 1.5 % Zn doped and 1.5 % Cr doped TiO₂ are 39.9 %, 47.9 %, 40.4 %, 27.2 % respectively. At 650 °C, it is seen that all three dopants inhibit anatase to rutile phase transformation seriously. At this temperature rutile phase percentages of undoped, 1.5 % Ag doped, 1.5 % Zn doped and 1.5 % Cr doped TiO₂ are 97.6 %, 48.2 %, 69.8 %, 45.7 % respectively. At 700 °C, 1.5 % Ag doped TiO₂ completes anatase to rutile phase transformation. Undoped TiO₂ has only 0.7 % and Zn doped TiO₂ has only 3.4 % anatase phase while 1.5 % Cr doped TiO₂ has 12.2 % anatase phase. At 800 °C anatase to rutile phase transformation is completed for undoped, 1.5 % Zn doped and 1.5 % Cr doped TiO₂.

From Figure 3.31, it is possible to see that when concentration is chosen 1.5 %, Ag dopant does not affect phase transformation until the sintering temperature reaches to 550 °C. While at 550 °C Ag dopant promotes, at 600 °C and 650 °C it inhibits rutile phase transformation. Also it is interesting that there is not a big difference at rutile % phase of 1.5 % Ag doped TiO₂ between 600 °C and 650 °C which can not be seen for other dopants. Cr dopant acts like Ag dopant; It does not affect phase transformation until the sintering temperature is 550 °C. While at 550 °C Ag dopant promotes, at 600 °C, 650 °C and different from Ag dopant also at 700 °C it inhibits rutile phase transformation significantly. Zn dopant does not affect phase transformation seriously until the sintering temperature is 650 °C. At 650 °C and 700 °C, it inhibits anatase to rutile phase transformation.

3.1.3.5. Effect of dopant amounts on crystallite size

Table 3.7 and Figure 3.32 show the effect of Ag dopant amount on crystallite size of anatase and rutile phase.

When sintering temperature is 300 °C and 400 °C, there is no big difference between the anatase crystallite size of undoped and doped TiO₂. At 500 °C, Ag dopant at every concentration seems to reduce crystallite size significantly. While the anatase crystallite size of undoped TiO₂ is 29.18 nm, anatase crystallite sizes of 0.5 % Ag, 1 % Ag and 1.5 % Ag doped TiO₂ are 16.96 nm, 17.78 nm, 17.23 nm respectively at 500 °C. At 550 °C, 0.5 %, 1 % and 1.5 % Ag doping do not have a significant effect on anatase and rutile

crystallite size of TiO₂. At 600 °C, Ag doping causes approximately 23 % reduction at anatase and 57 % reduction at rutile crystallite size. Among three different concentrations of Ag dopant while 0.5 % Ag doped TiO₂ has the smallest crystallite size of anatase and rutile, 1 % Ag doped TiO₂ has the biggest crystallite size of anatase and rutile. At 650 °C, from the crystallite size results it is also possible to find out again that at this sintering temperature, Ag dopant inhibits anatase to rutile phase transformation since it is not possible to measure anatase crystallite size of undoped TiO₂ while it is possible to measure anatase crystallite size 0.5 %, 1 % and 1.5 % Ag doped TiO₂.

Anatase and rutile crystallite sizes of Ag doped TiO₂ seem not to be affected so much from the different concentrations of Ag dopant at 650 °C. At this temperature it can be said that Ag doping reduces crystallite size of rutile approximately 42 %. At 700 °C, while 0.5 % and 1 % Ag doping seems to reduce rutile crystallite size, 1.5 % Ag doping seems to increase rutile crystallite size. At 800 °C while 1 % and 1.5 % Ag doping increase rutile crystallite size, 0.5 % Ag doping reduces rutile crystallite size.

Table 3.7. Effect of Ag % amount on crystallite size

	TiO ₂		0.5 % Ag-TiO ₂		1 % Ag-TiO ₂		1.5 % Ag-TiO ₂	
	A ¹ (nm)	R ² (nm)	A(nm)	R(nm)	A(nm)	R(nm)	A(nm)	R(nm)
300 °C	9.10	-	12.23	-	11.80	-	9.96	-
400 °C	12.00	-	12.17	-	10.69	-	11.86	-
500 °C	29.18	-	16.96	-	17.78	-	17.23	-
550 °C	25.90	32.15	25.45	34.24	26.47	33.99	24.92	30.20
600 °C	48.31	96.89	36.72	52.28	37.48	56.68	37.23	55.42
650 °C	-	119.98	40.03	68.36	36.81	72.85	40.73	69.88
700 °C	-	152.20	-	91.16	-	119.50	-	348.50
800 °C	-	218.80	-	183.34	-	393.06	-	330.57

¹Anatase, ²Rutile

Although it is a well known fact that doping with Ag reduces the anatase crystallite size of TiO₂ [75, 76, 87] it is possible to find studies reported that while at lower

concentrations (up to 8 %) Ag dopant reduced, at higher concentrations it increased anatase crystallite size of TiO_2 [85]. The reason of the reduction at anatase crystallite size caused by the Ag dopant is believed to be due to the large ionic radius of Ag^+ (ca. 129 pm) compared to Ti^{4+} (ca. 74.5 pm). As explained in Section 3.1.3.3 because of its large ionic radius Ag^+ can not enter into the lattice of TiO_2 and form a stable sol. Besides, by sintering process diffusion of Ag^+ from the bulk of anatase grains to the surface of anatase grains and to the surface of film is promoted. Consequently being suppressed by Ag^+ grain, size growth of anatase is inhibited [87].

In literature nothing is reported about the effect of Ag dopant on crystallite size growth of rutile phase.

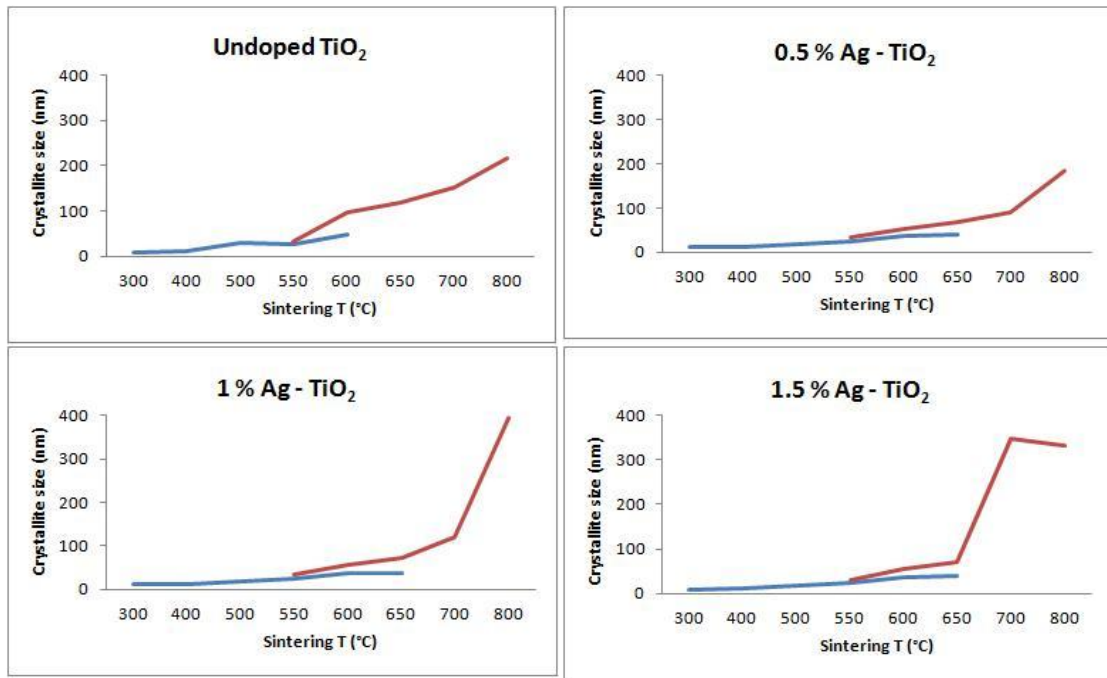


Figure 3.32. Effect of Ag % on crystallite size (blue line: anatase, red line: rutile)

Table 3.8 and Figure 3.33 show the effect of Zn dopant amount on crystallite size of anatase and rutile phase. At 300 °C and 400 °C, while 1 % and 1.5 % Zn seem to reduce anatase crystallite size, 0.5 % Zn seems to increase anatase crystallite size. At 500 °C all three concentrations of Zn seem to reduce anatase crystallite size; anatase crystallite size of undoped, 0.5 % Zn, 1 % Zn and 1.5 % Zn doped TiO_2 are 29.18 nm, 18.09 nm, 18.28 nm and 16.42 nm respectively. At 550 °C, there is not a big difference between

anatase crystallite size of undoped and Zn doped TiO₂. While rutile crystallite size of 0.5 % Zn doped TiO₂ can not be measured 1 % and 1.5 % Zn doping reduce rutile crystallite size of undoped TiO₂. At 600 °C, Zn doping causes approximately 29 % reduction at anatase crystallite size, changing Zn dopant concentration seems not to make a significant difference at anatase crystallite size. At 600 °C, by increasing Zn dopant concentration, reduction of rutile crystallite size seems to increase. While rutile crystallite size of undoped TiO₂ is 96.89 nm, rutile crystallite sizes of 0.5 %, 1 % and 1.5 % Zn doped TiO₂ are 41.96 nm, 50.05 nm and 56.36 nm respectively.

Table 3.8. Effect of Zn % amount on crystallite size

	TiO ₂		0.5 % Zn-TiO ₂		1 % Zn-TiO ₂		1.5 % Zn-TiO ₂	
	A ¹ (nm)	R ² (nm)	A(nm)	R(nm)	A(nm)	R(nm)	A(nm)	R(nm)
300 °C	9.10	-	10.00	-	6.51	-	7.01	-
400 °C	12.00	-	12.29	-	10.63	-	10.21	-
500 °C	29.18	-	18.09	-	18.28	20.72	16.42	-
550 °C	25.90	32.15	25.00	-	27.27	23.99	25.59	27.01
600 °C	48.31	96.89	33.82	41.96	35.71	50.05	32.92	56.36
650 °C	-	119.98	45.42	70.88	46.21	81.52	42.12	80.14
700 °C	-	152.20	48.07	81.23	-	159.22	-	144.97
800 °C	-	218.80	-	126.93	-	135.98	-	161.73

¹Anatase, ²Rutile

At 650 °C, it is not possible to measure anatase crystallite size of undoped TiO₂ and there is not a significant difference between the anatase crystallite size of 0.5 % and 1 % and 1.5 % Zn doped TiO₂. Looking at the rutile crystallite size of TiO₂ at this temperature, a significant reduction can be seen by Zn doping. Rutile crystallite sizes of undoped, 0.5 % Zn, 1 % Zn and 1.5 % Zn doped TiO₂ at this temperature are 119.98 nm, 70.88 nm, 81.52 nm, 80.14 nm respectively. At 700 °C, while 0.5 % Zn doping reduces rutile crystallite size by 47 %, 1 % Zn doping increases rutile crystallite size by 4.7 % and 1.5 % Zn doping reduces rutile crystallite size by 4.7 %. At 800 °C all three concentrations

of Zn dopant reduce rutile crystallite size. Reducing the concentration of Zn dopant reduces rutile crystallite size.

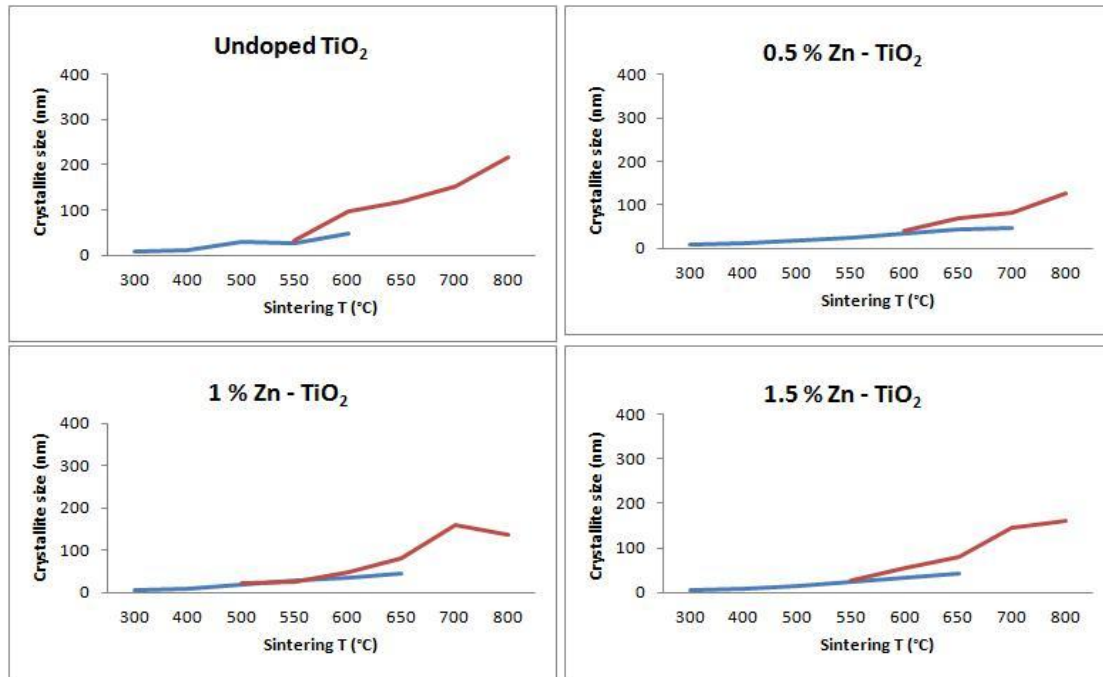


Figure 3.33. Effect of Zn % on crystallite size (blue line: anatase, red line: rutile)

Although in literature it is reported that doping with Zn reduces anatase crystallite size, [126] it is not possible to find a report that investigates the effect of Zn dopant on crystallite size growth of anatase and rutile at a wide sintering temperature range. The reason that Zn reduces the anatase crystallite size is most probably its larger ionic radius (ca. 88 pm) compared to ionic radius of Ti⁴⁺ (ca. 74.5 pm). A similar mechanism as discussed for Ag⁺ can also be seen for Zn²⁺.

Table 3.9 and Figure 3.34 show the effect of Cr dopant amount on crystallite size of anatase and rutile phase.

At 300 °C, 400 °C and 500 °C, by increasing Cr dopant concentration reduction rate of anatase crystallite size of TiO₂ increases. At 550 °C, a little increment occurs at anatase crystallite size of TiO₂ by 0.5 % Cr doping and a little reduction occurs at anatase crystallite size of TiO₂ by 1 % Cr and 1.5 % Cr doping. At same temperature a little increment occurs at rutile crystallite size of TiO₂ by 0.5 % and 1 % Cr doping and a little reduction occurs at rutile crystallite size of TiO₂ by 1.5 % Cr doping. At 600 °C,

Cr doping reduces both anatase and rutile crystallite size of TiO_2 and for both anatase and rutile phase, reduction rate of crystallite size increases by increasing Cr dopant concentration. At this temperature, anatase crystallite sizes of undoped, 0.5 % Cr, 1 % and 1.5 % Cr doped TiO_2 are 48.31 nm, 38.07 nm, 36.94 nm, 27.61 nm respectively and rutile crystallite sizes of undoped, 0.5 % Cr, 1 % and 1.5 % Cr doped TiO_2 are 96.89 nm, 50.96 nm, 50.07 nm, 40.64 nm respectively. Same situation is valid at 650 °C; crystallite size of rutile phase decreases by increasing Cr dopant concentration. Since at this temperature anatase crystallite size of TiO_2 can not be measured it is not possible to say something about effect of Cr dopant on anatase crystallite size however it can be said that by increasing Cr dopant concentration rutile crystallite size decreases. At 700 °C, rutile crystallite sizes of undoped, 0.5 % Cr, 1 % Cr and 1.5 % Cr doped TiO_2 are 152.2 nm, 107.96 nm, 75.97 nm and 83.26 nm respectively. At 800 °C, by increasing Cr dopant concentration rutile crystallite size of TiO_2 decreases. At this temperature rutile crystallite sizes of undoped, 0.5 % Cr, 1 % Cr and 1.5 % Cr doped TiO_2 are 218 nm, 110.18 nm, 107.1 nm and 86.12 nm respectively.

Table 3.9. Effect of Cr % amount on crystallite size

	TiO_2		0.5 % Cr- TiO_2		1 % Cr- TiO_2		1.5 % Cr- TiO_2	
	A ¹ (nm)	R ² (nm)	A(nm)	R(nm)	A(nm)	R(nm)	A(nm)	R(nm)
300 °C	9.10	-	8.40	-	8.18	-	6.88	-
400 °C	12.00	-	11.05	-	10.48	-	9.610	-
500 °C	29.18	-	21.70	25.37	18.84	24.85	17.62	-
550 °C	25.90	32.15	27.20	36.42	25.49	36.52	24.85	31.94
600 °C	48.31	96.89	38.07	50.96	36.94	50.07	27.61	40.64
650 °C	-	119.98	42.49	60.79	38.01	58.87	34.73	52.47
700 °C	-	152.20	64.18	107.96	-	75.97	46.44	83.26
800 °C	-	218.80	-	110.18	-	107.10	-	86.12

¹Anatase, ²Rutile

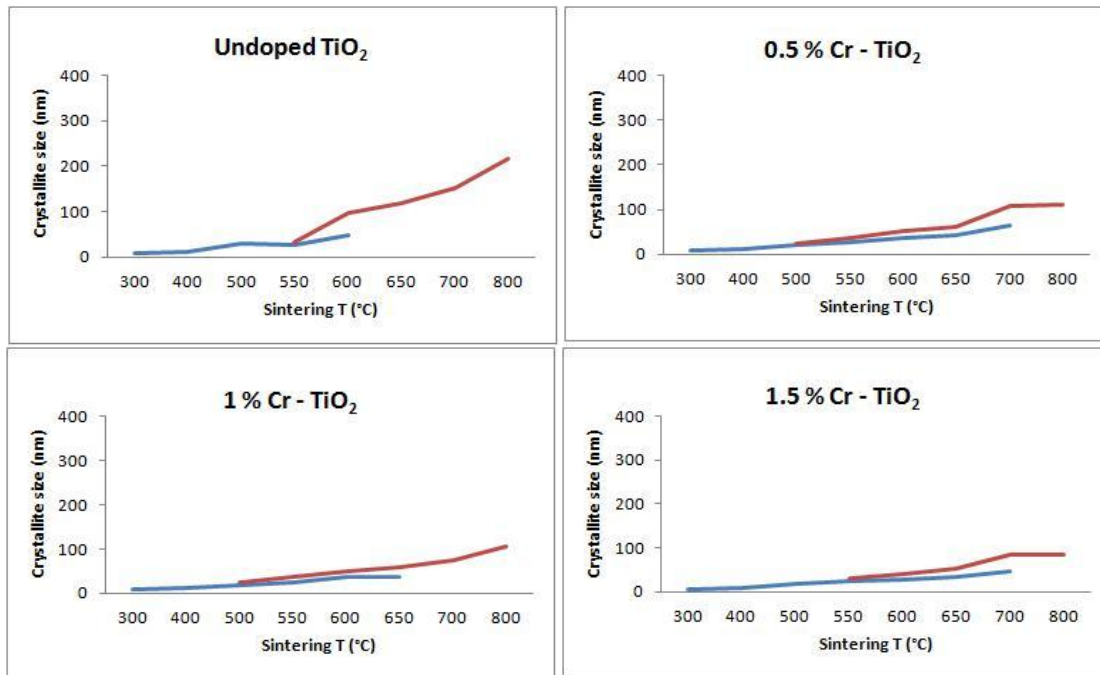


Figure 3.34. Effect of Cr % on crystallite size (blue line: anatase, red line: rutile)

In literature it is reported that Cr dopant reduces anatase crystallite size and it is also noted that the bigger the dopant amount the smallest the anatase crystallite size [127]. However, there is not a study about how the rutile crystallite size is affected by Cr dopant. It is known that ionic radius of Cr^{3+} (ca. 75.5 pm) is similar to the ionic radius of Ti^{4+} (ca. 74.5 pm). According to anatase crystallite size reduction mechanism that is explained for Ag and Zn dopants, Cr should not be expected to reduce anatase crystallite size since its ionic radius is similar to that of Ti^{4+} . The mechanism how Cr^{3+} reduces anatase crystallite size needs to be further understood.

3.1.3.6. Effect of dopants on crystallite size

Table 3.10 and Figure 3.35 show the effect of three dopants; Ag, Zn and Cr on anatase and rutile crystallite size when their concentration is 0.5 %.

When sintering temperature is 300 °C, while 0.5 % Ag and 1.5 % Zn doping increase the anatase crystallite size, 0.5 % Cr doping reduces the anatase crystallite size of TiO_2 . At 400 °C, the only dopant that reduces the anatase crystallite size is 0.5 % Cr. At 500 °C, all three dopants reduce anatase crystallite size, dopant that causes the most reduction is Ag and the least reduction is Cr. At 550 °C, Ag and Zn dopants have not a significant effect on anatase crystallite size while 0.5 % Cr dopant causes a slight

increment at anatase crystallite size. At this temperature it was not possible to measure rutile crystallite size of 0.5 % Zn doped TiO₂.

Table 3.10. Effect dopants on crystallite size (0.5 %)

	TiO ₂		0.5 % Ag-TiO ₂		0.5 % Zn-TiO ₂		0.5 % Cr-TiO ₂	
	A ¹ (nm)	R ² (nm)	A(nm)	R(nm)	A(nm)	R(nm)	A(nm)	R(nm)
300 °C	9.10	-	12.23	-	10.00	-	8.40	-
400 °C	12.00	-	12.17	-	12.29	-	11.05	-
500 °C	29.18	-	16.96	-	18.09	-	21.70	25.37
550 °C	25.90	32.15	25.45	34.24	25.00	-	27.20	36.42
600 °C	48.31	96.89	36.72	52.28	33.82	41.96	38.07	50.96
650 °C	-	119.98	40.03	68.36	45.42	70.88	42.49	60.79
700 °C	-	152.20	-	91.16	48.07	81.23	64.18	107.96
800 °C	-	218.80	-	183.34	-	126.93	-	110.18

¹Anatase, ²Rutile

Looking at the other two dopants it can be said that both Ag and Cr dopant increase rutile crystallite size. When sintering T is 600 °C, doping TiO₂ with 0.5 % Ag, 0.5 % Zn and 0.5 % Cr cause reduction at both anatase and rutile crystallite size. Anatase crystallite sizes of undoped, 0.5 % Ag, 0.5 % Zn and 0.5 % Cr doped TiO₂ are 48.31 nm, 36.72 nm, 33.82 nm, 38.07 nm respectively. Rutile crystallite sizes of undoped, 0.5 % Ag, 0.5 % Zn and 0.5 % Cr doped TiO₂ are 96.89 nm, 52.28 nm, 41.96 nm, 50.96 nm respectively. At 650 °C, it is not anymore possible to measure anatase crystallite size of undoped TiO₂. When anatase crystallite sizes of TiO₂ doped with different dopants are compared it can be said that there is not a significant difference between 0.5 % Ag, Zn and Cr doped TiO₂. Looking at the rutile crystallite sizes, it can be said that doping TiO₂ with 0.5 % Ag, 0.5 % Zn and 0.5 % Cr caused 62 %, 41 %, 49 % reduction at rutile crystallite size respectively. While at 700 °C doping with 0.5 % Ag, 0.5 % Zn and 0.5 % Cr caused 40.1 %, 46.6 % and 29.1 % reduction at rutile crystallite size of TiO₂

respectively, at 800 °C doping with 0.5 % Ag, 0.5 % Zn and 0.5 % Cr caused 16.2 %, 42.0 % and 49.6 % reduction at rutile crystallite size of TiO₂ respectively.

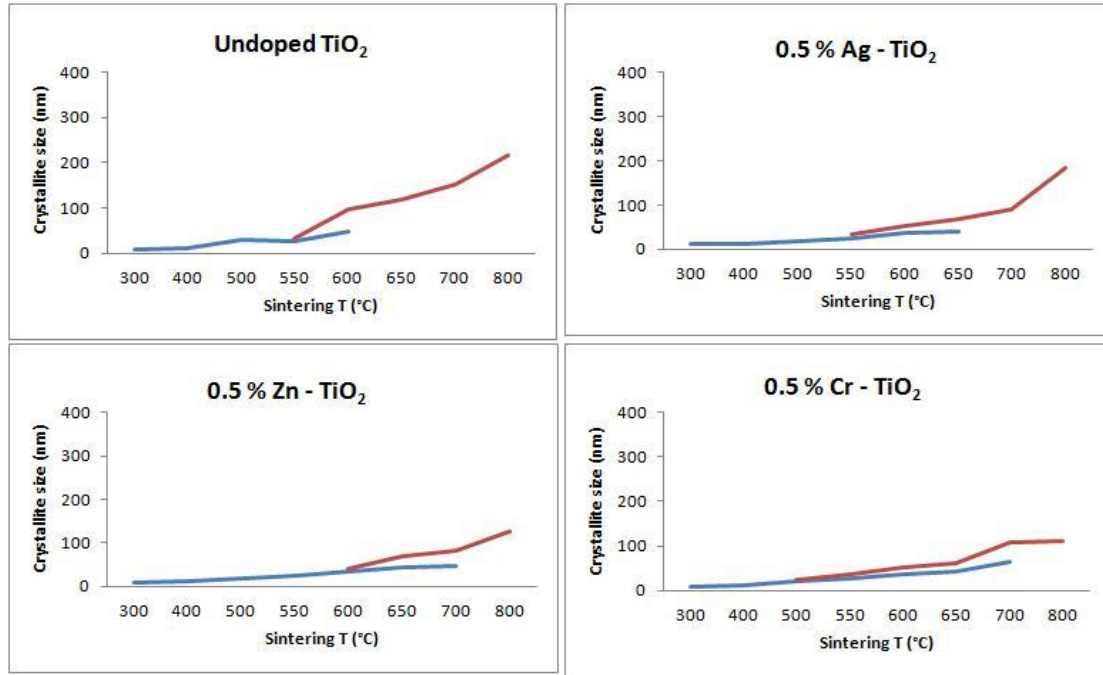
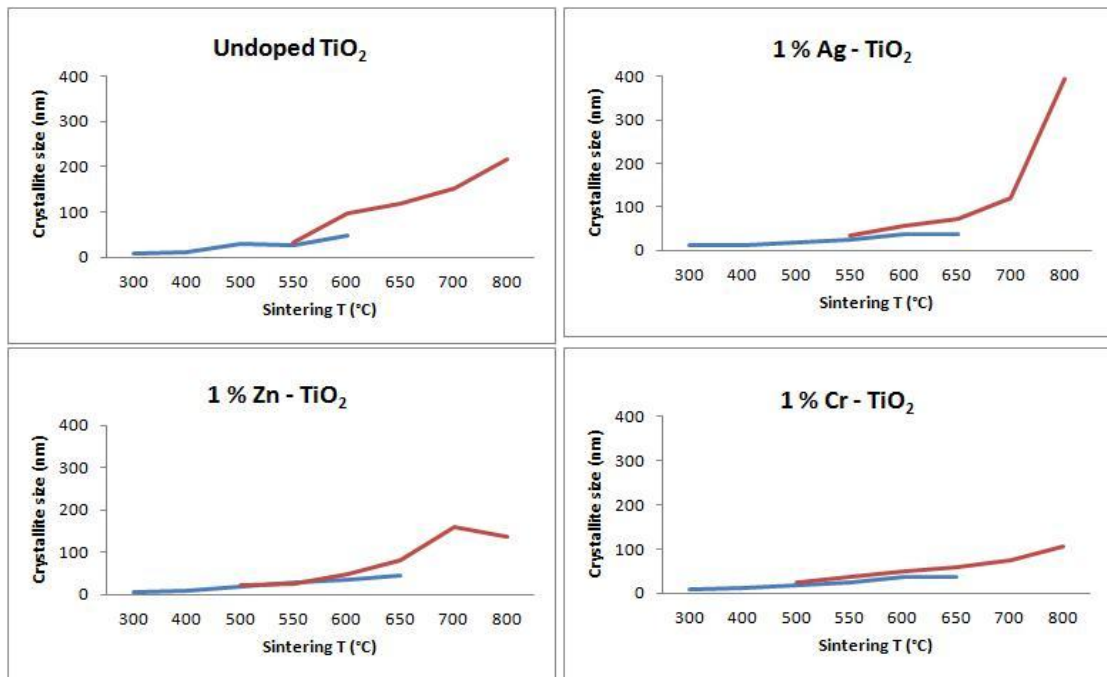


Figure 3.35. Effect of dopants on crystallite size (0.5 %) (blue line: anatase, red line: rutile)

Table 3.11 and Figure 3.36 show the effect of three dopants; Ag, Zn and Cr on anatase and rutile crystallite size when their concentration is 1 %. When sintering temperature is 300 °C, the anatase crystallite sizes of undoped and 1 % Ag, 1 % Zn and 1 % Cr doped TiO₂ are 9.1 nm, 11.80 nm, 6.51 nm and 8.18 nm respectively. It can be said that the most reduction occurs at anatase crystallite size by 1 % Zn doping. When sintering temperature is 400 °C, all three dopants cause approximately the same slight reduction of 11 % at anatase crystallite size. Same situation can be seen when sintering temperature is 500 °C, at this temperature all three dopants cause approximately 38 % reduction at anatase crystallite size.

Table 3.11. Effect dopants on crystallite size (1 %)

	TiO ₂		1 % Ag-TiO ₂		1 % Zn-TiO ₂		1 % Cr-TiO ₂	
	A ¹ (nm)	R ² (nm)	A(nm)	R(nm)	A(nm)	R(nm)	A(nm)	R(nm)
300 °C	9.10	-	11.80	-	6.51	-	8.18	-
400 °C	12.00	-	10.69	-	10.63	-	10.48	-
500 °C	29.18	-	17.78	-	18.28	20.72	18.84	24.85
550 °C	25.90	32.15	26.47	33.99	27.27	23.99	25.49	36.52
600 °C	48.31	96.89	37.48	56.68	35.71	50.05	36.94	50.07
650 °C	-	119.98	36.81	72.85	46.21	81.52	38.01	58.87
700 °C	-	152.20	-	119.50	-	159.22	-	75.97
800 °C	-	218.80	-	393.06	-	135.98	-	107.10

¹Anatase, ²Rutile**Figure 3.36.** Effect of dopants on crystallite size (1 %) (blue line: anatase, red line: rutile)

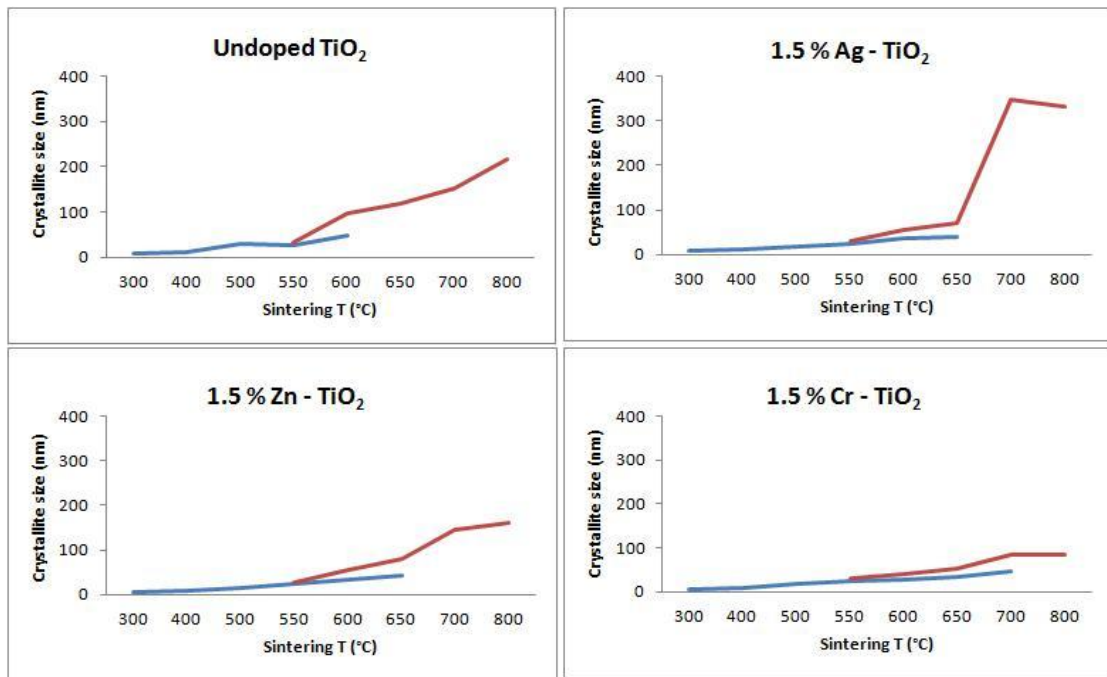
At 550 °C, it can be seen that dopants do not have an effect on anatase crystallite size of TiO₂ and while doping with 1 % Zn reduces, 1 % Ag and 1 % Cr doping increase rutile crystallite size of TiO₂. At 600 °C, doping with 1 % Ag, 1 % Zn and 1 % Cr reduce anatase crystallite size of TiO₂ by 22.4 %, 26 %, 23.5 % respectively and doping with 1 % Ag, 1 % Zn and 1 % Cr reduce rutile crystallite size of TiO₂ by 41.5 %, 48 %, 48 % respectively. When sintering temperature is 650 °C, rutile crystallite size of TiO₂ reduces by 39.2 %, 32.0 % and 50.9 % with 1 % Ag, 1 % Zn and 1 % Cr doping respectively. At this temperature it is possible to say that anatase crystallite sizes of 1 % Ag and 1 % Cr doped TiO₂ are approximately same while anatase crystallite size of 1 % Zn doped TiO₂ is 17 % bigger than anatase crystallite size of 1 % Ag and 1 % Cr doped TiO₂. At 700 °C, 1 % Zn doping causes a slight increment at rutile crystallite size of TiO₂, 1 % Ag doping causes 21 %, 1 % Cr doping causes 50 % reduction at rutile crystallite size of TiO₂. At 800 °C, 1 % Ag doping causes 79.6 % increment, 1 % Zn doping causes 37 % and 1 % Cr doping causes 51 % reduction at rutile crystallite size of TiO₂.

Table 3.12 and Figure 3.37 show the effect of three dopants; Ag, Zn and Cr on anatase and rutile crystallite size when their concentration is 1.5 %.

When sintering temperature is 300 °C, it can be said that while doping with 1.5 % Ag increases anatase crystallite size, doping with 1.5 % Zn and 1.5 % Cr reduce anatase crystallite size slightly. At 400 °C, all three dopants cause slight reduction at anatase crystallite size. Ag dopant causes the smallest and Cr dopant causes the biggest reduction. When 500 °C is chosen as sintering temperature, approximately 41 % reduction is seen at anatase crystallite size of TiO₂ by doping 1.5 % Ag, 1.5 % Zn and 1.5 % Cr. At 550 °C doping with 1.5 % Ag, 1.5 % Zn and 1.5 % Cr do not change anatase crystallite size of TiO₂ too much and doping with 1.5 % Ag, 1.5 % Zn and 1.5 % Cr reduce rutile crystallite size of TiO₂ by 6 %, 16 % and 0.6 % respectively. At 600 °C, 1.5 % Ag, 1.5 % Zn and 1.5 % Cr doping cause respectively 22.9 %, 31.8 %, 42.8 % reduction at anatase crystallite size of TiO₂ and cause respectively 42.8 %, 41.8 %, 58 % reduction at rutile crystallite size of TiO₂.

Table 3.12. Effect dopants on crystallite size (1.5 %)

	TiO ₂		1.5 % Ag-TiO ₂		1.5 % Zn-TiO ₂		1.5 % Cr-TiO ₂	
	A ¹ (nm)	R ² (nm)	A(nm)	R(nm)	A(nm)	R(nm)	A(nm)	R(nm)
300 °C	9.10	-	9.96	-	7.15	-	6.88	-
400 °C	12.00	-	11.86	-	10.21	-	9.61	-
500 °C	29.18	-	17.23	-	16.42	-	17.62	-
550 °C	25.90	32.15	24.92	30.20	25.59	27.01	24.85	31.94
600 °C	48.31	96.89	37.23	55.42	32.92	56.36	27.61	40.64
650 °C	-	119.98	40.73	69.88	42.12	80.14	34.73	52.47
700 °C	-	152.20	-	348.50	-	144.97	46.44	83.26
800 °C	-	218.80	-	330.57	-	161.73	-	86.12

¹Anatase, ²Rutile**Figure 3.37.** Effect of dopants on crystallite size (1.5 %) (blue line: anatase, red line: rutile)

At 650 °C, the biggest anatase crystallite size belongs to 1.5 % Zn doped TiO₂ while the smallest anatase crystallite size belongs to 1.5 % Cr doped TiO₂. At this sintering temperature, 1.5 % Ag, 1.5 % Zn and 1.5 % Cr doping cause 41.7 %, 33.2 % and 56.3 % reduction at rutile crystallite size of TiO₂ respectively. At 700 °C, 1.5 % Ag doping causes 129 % increment at rutile crystallite size of TiO₂ while 1.5 % Zn doping causes 4.7 %, 1.5 % Cr doping causes 45.2 % reduction at rutile crystallite size of TiO₂. At 800 °C, 1.5 % Ag doping causes 51 % increment, 1.5 % Zn doping causes 26 % and 1.5 % Cr doping causes 60.6 % reduction at rutile crystallite size of TiO₂.

3.1.4. TEM results of TiO₂ powders

Figure 3.38 and Figure 3.39 show TEM images and EDS analysis of undoped TiO₂, 0.5 %, 1 %, 1.5 % Ag doped TiO₂ powders that were sintered at 400 °C for 1 hour respectively.

The undoped TiO₂ and 0.5 % Ag doped TiO₂, 1 % Ag doped TiO₂, 1.5 % Ag doped TiO₂ particles have nearly spherical morphology. The average diameters of undoped, 0.5 %, 1 % and 1.5 % Ag doped TiO₂ particles are approximately 11-12 nm. It can be said that these results are in good agreement with XRD results.

Figure 3.41 proves that undoped powder exists as TiO₂. From the same figure while it is possible to see Ag peak at 0.5 % Ag and 1 % Ag doped TiO₂ powder, Ag peak can not be seen at 1.5 % Ag doped TiO₂ powder. The incorrect amounts of Ag detected in all three Ag doped TiO₂ powders can be due to the slight amount of Ag that was added into TiO₂. The Cu peak that is seen at all four spectrum is due to the Cu grid that was used for sample preparation.

SAED patterns given within the TEM images show that undoped TiO₂, 0.5 %, 1 %, 1.5 % Ag doped TiO₂ consist of anatase phase and this shows that SAED patterns are in good agreement with XRD measurements.

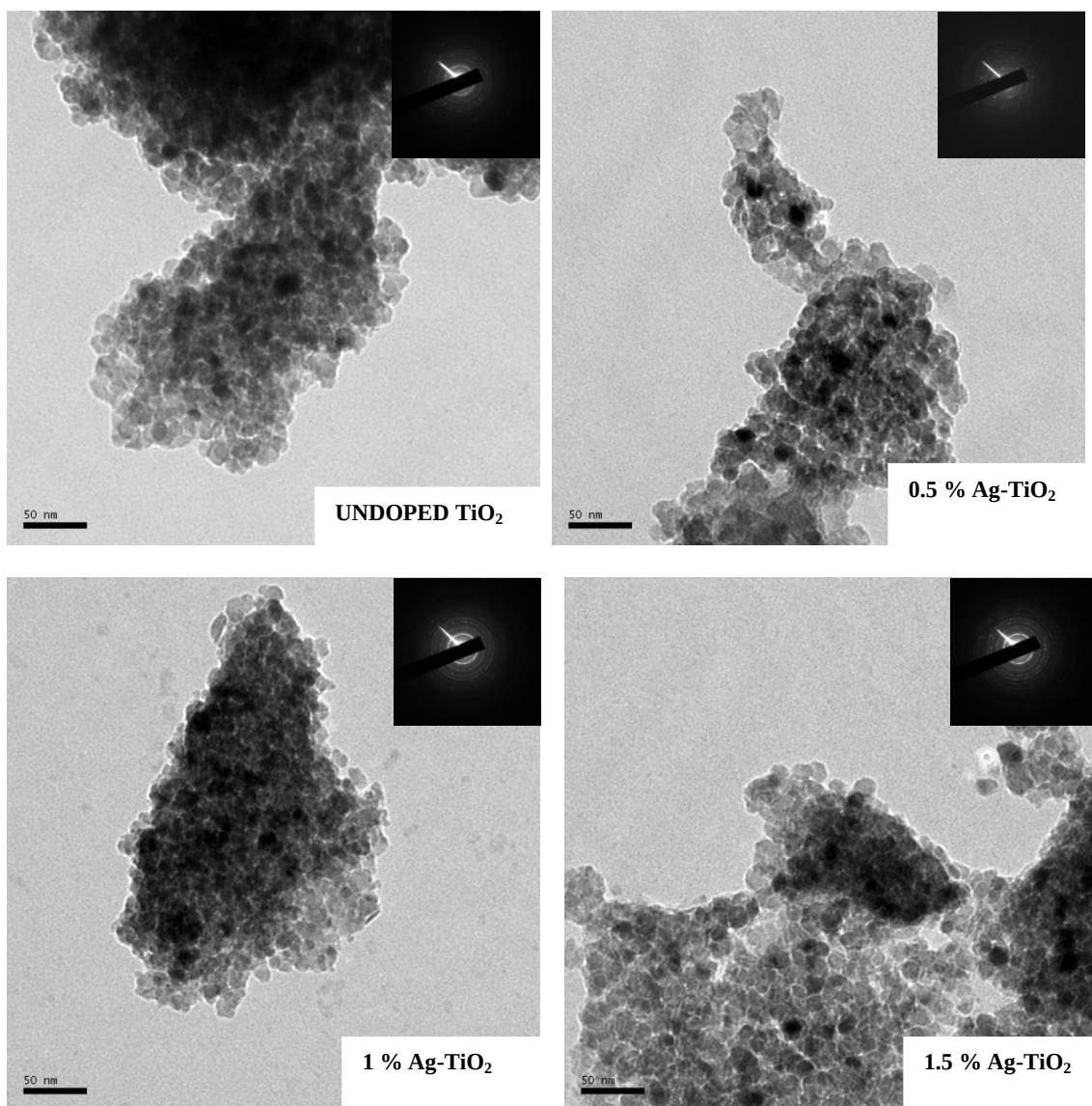
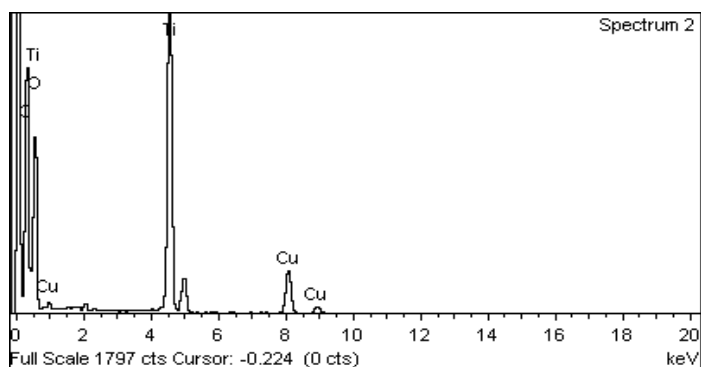
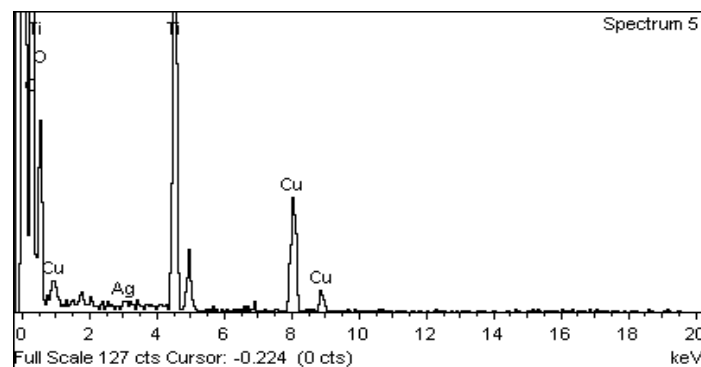


Figure 3.38. TEM images of undoped TiO₂, 0.5 % Ag-TiO₂, 1 % Ag-TiO₂, 1.5 % Ag-TiO₂



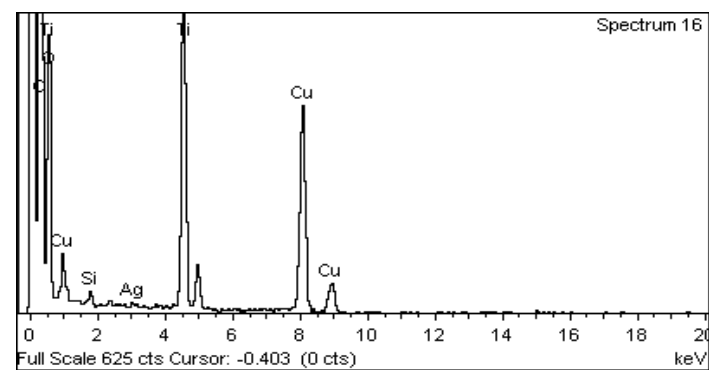
UNDOPED TiO_2

Element	Weight%	Atomic%
O K	40.70	67.26
Ti K	59.30	32.74



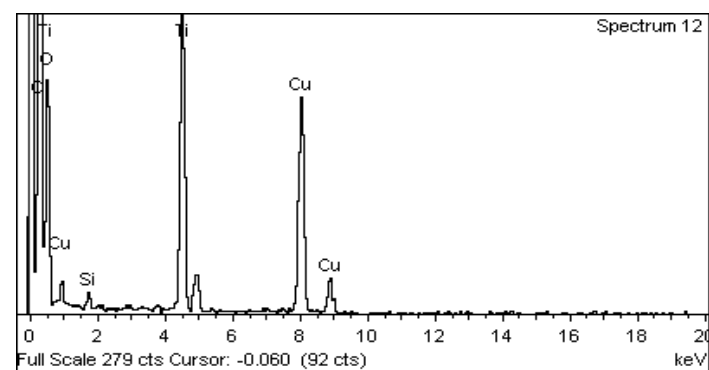
0.5 % Ag- TiO_2

Element	Weight%	Atomic%
O K	28.76	55.07
Ti K	69.47	44.43
Ag L	1.77	0.50



1 % Ag- TiO_2

Element	Weight%	Atomic%
O K	36.83	64.02
Ti K	61.03	35.43
Ag L	2.14	0.55



1.5 % Ag- TiO_2

Element	Weight%	Atomic%
O K	40.19	66.80
Ti K	59.81	33.20

Figure 3.39. EDS analysis of undoped TiO_2 , 0.5 % Ag- TiO_2 , 1 % Ag- TiO_2 , 1.5 % Ag- TiO_2

Figure 3.40 and Figure 3.41 show TEM images and EDS analysis of undoped TiO_2 , 0.5 % Zn, 1 % Zn, 1.5 % Zn doped TiO_2 powders that were sintered at 400 °C for 1 hour respectively.

The undoped TiO_2 and 0.5 % Zn, 1 % Zn, 1.5 % Zn doped TiO_2 particles have nearly spherical morphology. It is obvious that the average diameter of undoped TiO_2 (approximately 12 nm) is slightly bigger than the average diameter of 0.5 %, 1 % and 1.5 % Zn doped TiO_2 (approximately 10-11 nm).

Figure 3.41 proves that undoped powder exists as TiO_2 . It is possible to see Zn peak at 0.5 %, 1 % and 1.5 % Zn doped TiO_2 powder. The Zn amounts that were detected by EDS analysis are not the expected amounts when compared to the added ones. EDS analysis might not detect Zn dopant correctly since the amount is very small. The Cu peak that is seen at all four spectrum is due to the Cu grid that is used for sample preparation.

SAED patterns given within the TEM images show that undoped TiO_2 , 0.5 %, 1 % Zn doped TiO_2 and 1.5 % Zn doped TiO_2 consist of anatase phase and this shows that SAED patterns are in good agreement with XRD measurements.

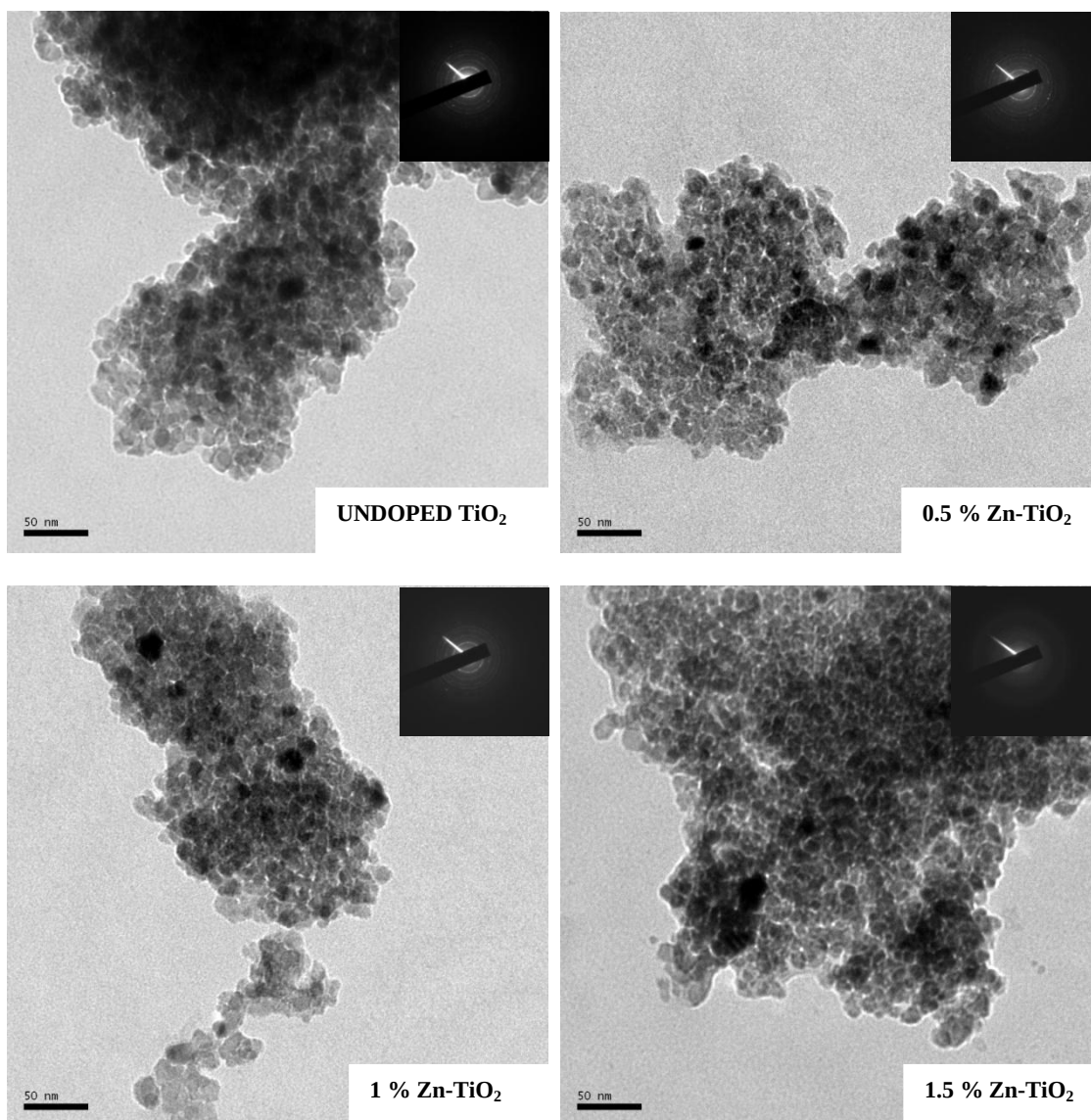
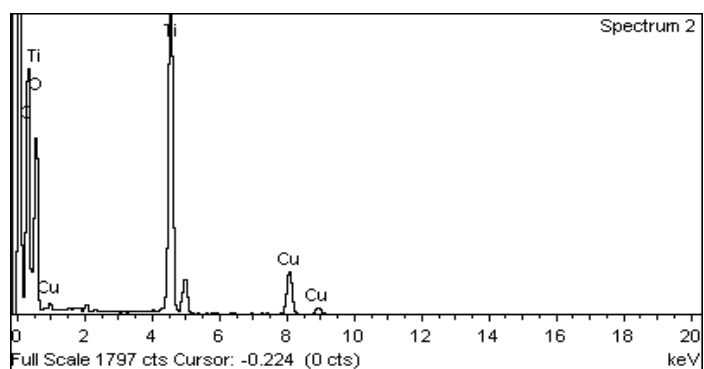
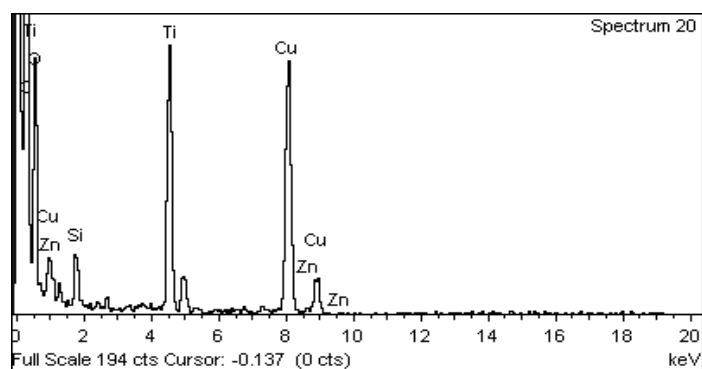


Figure 3.40. TEM images of undoped TiO₂, 0.5 % Zn-TiO₂, 1 % Zn-TiO₂, 1.5 % Zn-TiO₂



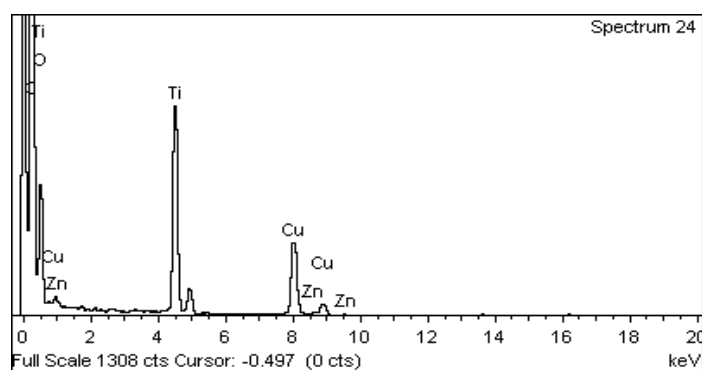
UNDOPED TiO₂

Element	Weight%	Atomic%
O K	40.70	67.26
Ti K	59.30	32.74



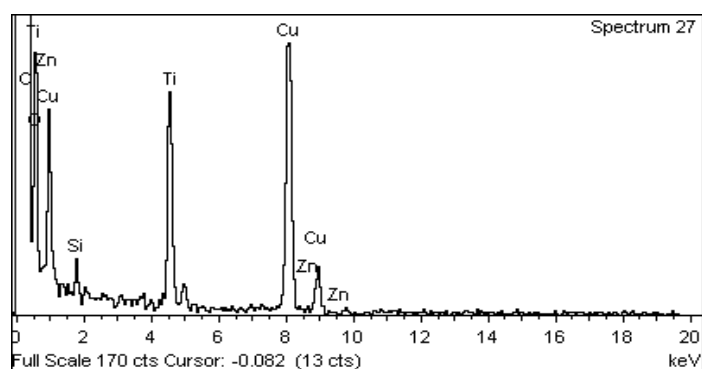
0.5 % Zn-TiO₂

Element	Weight%	Atomic%
O K	26.74	52.39
Ti K	71.41	46.73
Zn K	1.84	0.88



1 % Zn-TiO₂

Element	Weight%	Atomic%
O K	40.19	66.91
Ti K	58.71	32.64
Zn K	1.10	0.45



1.5 % Zn-TiO₂

Element	Weight%	Atomic%
O K	40.12	66.92
Ti K	58.06	32.34
Zn K	1.82	0.74

Figure 3.41. EDS analysis of undoped TiO₂, 0.5 % Zn-TiO₂, 1 % Zn-TiO₂, 1.5 % Zn-TiO₂

Figure 3.42 and Figure 3.43 show TEM images and EDS analysis of undoped TiO_2 , 0.5 %, 1 %, 1.5 % Cr doped TiO_2 powders that were sintered at 400 °C for 1 hour respectively.

The undoped TiO_2 and 0.5 % Cr doped TiO_2 , 1 % Cr doped TiO_2 , 1.5 % Cr doped TiO_2 particles have nearly spherical morphology. It can be seen from Figure 3.42 that the powder that has the smallest diameter is 1.5 % Cr doped TiO_2 and all Cr doped TiO_2 particles have smaller diameters compared to the diameter of undoped TiO_2 particles and these results are in good agreement with XRD results given in section 3.1.3.5.

Figure 3.43 proves that undoped powder exists as TiO_2 . It is possible to see Cr peak at all three TiO_2 powders that are doped with Cr. The Cr amounts that were detected by EDS analysis are not the correct amounts. However it is an expected thing since the amount of Cr dopant is very small so it is hard to detect it at EDS analysis correctly. The Cu peak that is seen at all four spectrum is due to the Cu grid.

SAED patterns given within the TEM images show that undoped TiO_2 , 0.5 %, 1 %, 1.5 % Cr doped TiO_2 consist of anatase phase and this shows that SAED patterns are in good agreement with XRD measurements.

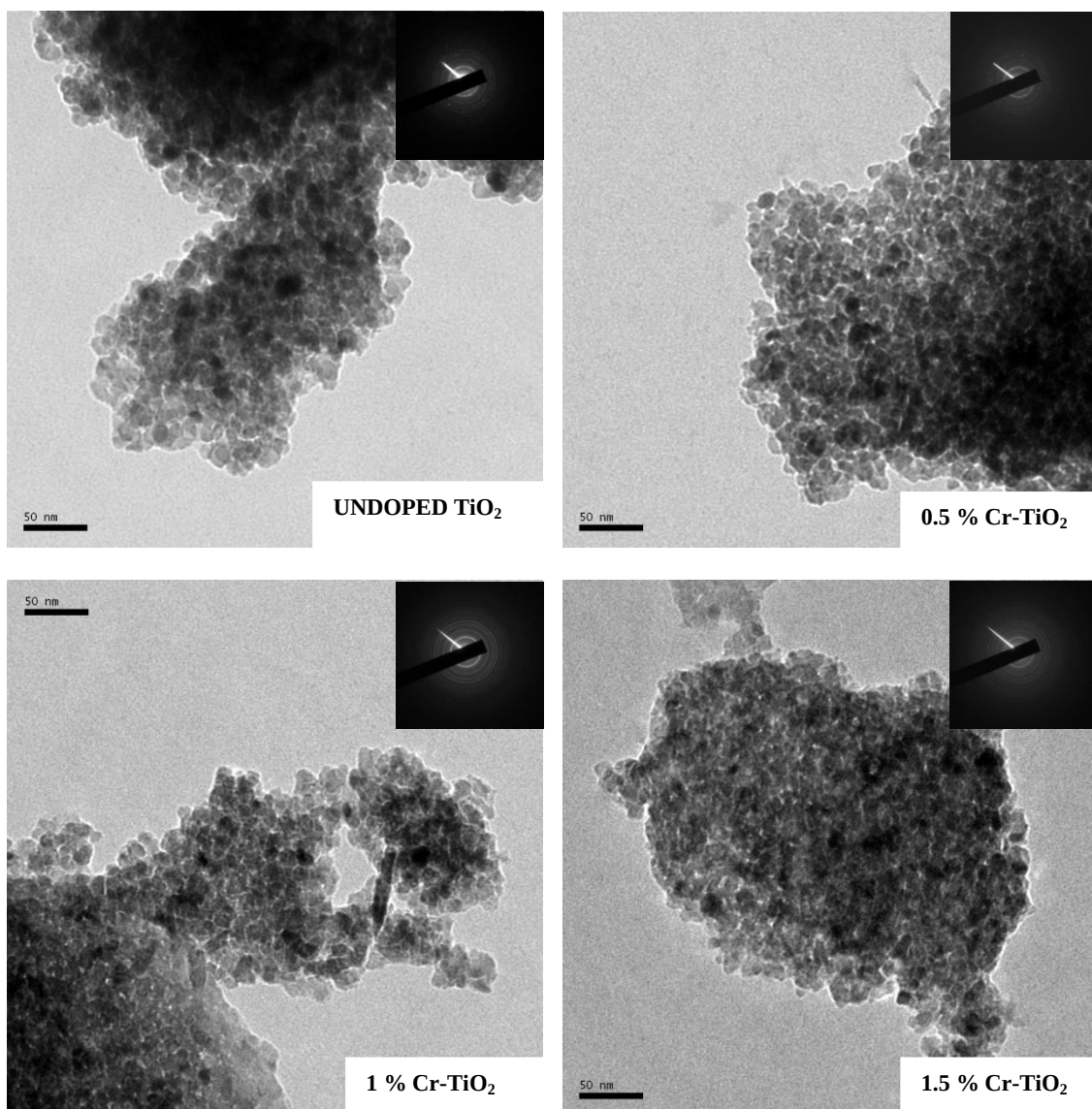
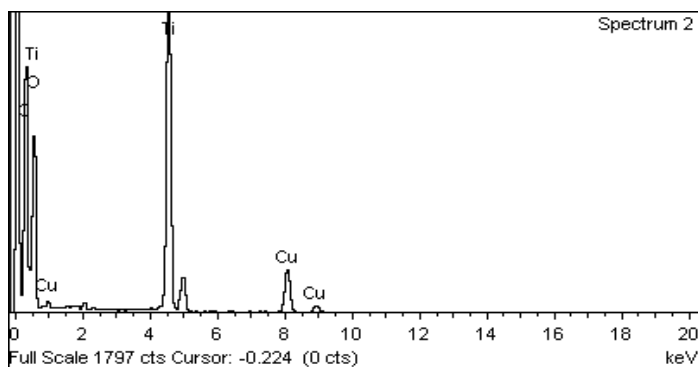
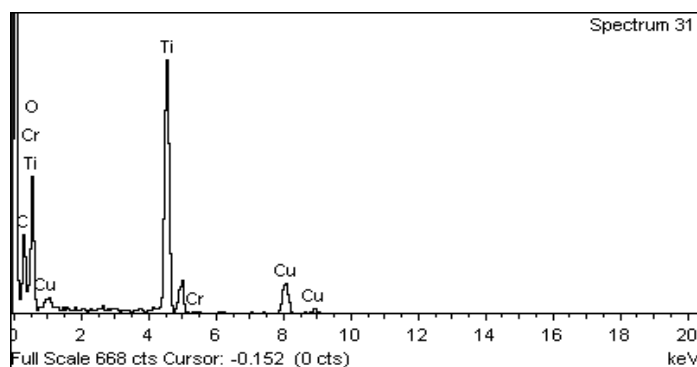


Figure 3.42. TEM images of undoped TiO₂, 0.5 % Cr-TiO₂, 1 % Cr-TiO₂, 1.5 % Cr-TiO₂



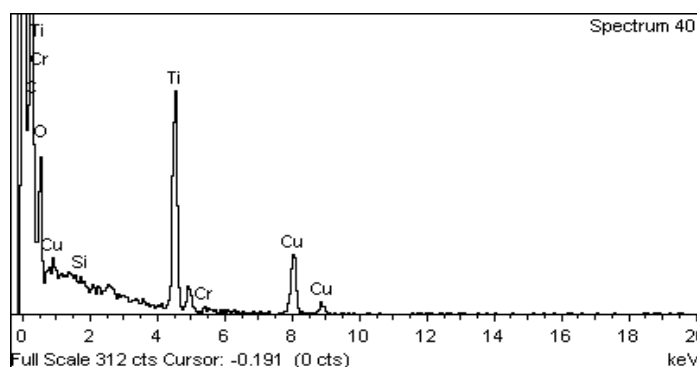
UNDOPED TiO_2

Element	Weight%	Atomic%
O K	40.70	67.26
Ti K	59.30	32.74



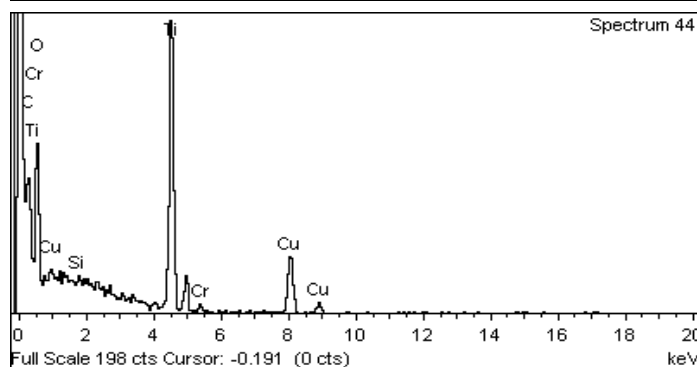
0.5 % Cr- TiO_2

Element	Weight%	Atomic%
O K	35.85	62.60
Ti K	63.92	37.28
Cr K	0.22	0.12



1 % Cr- TiO_2

Element	Weight%	Atomic%
O K	39.88	66.55
Ti K	58.88	32.81
Cr K	1.24	0.64



1.5 % Cr- TiO_2

Element	Weight%	Atomic%
O K	36.98	63.75
Ti K	62.28	35.86
Cr K	0.74	0.39

Figure 3.43. TEM images of undoped TiO_2 , 0.5 % Cr- TiO_2 , 1 % Cr- TiO_2 , 1.5 % Cr- TiO_2

3.1.5. BET results of TiO₂ powders

In Table 3.13 surface areas of undoped and 0.5 % Ag, 1 % Ag, 1.5 % Ag, 0.5 % Zn, 1 % Zn, 1.5 % Zn, 0.5 % Cr, 1 % Cr, 1.5 % Cr doped TiO₂ powders that were sintered at 400 °C for 1 hour are given.

Table 3.13. Surface area of TiO₂ powders

Powder name	Surface area (m ² /gr)
Undoped TiO ₂	25.85
0.5 % Ag-TiO ₂	21.06
1 % Ag-TiO ₂	38.60
1.5 % Ag-TiO ₂	53.58
0.5 % Zn-TiO ₂	31.39
1 % Zn-TiO ₂	40.43
1.5 % Zn-TiO ₂	44.80
0.5 % Cr-TiO ₂	29.73
1 % Cr-TiO ₂	34.96
1.5 % Cr-TiO ₂	24.65

Looking at the Ag dopant, it is possible to say that by increasing the amount of Ag dopant, surface area of the doped TiO₂ powder increases. When its amount is 0.5 %, Ag dopant causes TiO₂ surface area to decrease and when its amount is 1 % and 1.5 %, Ag dopant causes TiO₂ surface area to increase. While the surface area of undoped TiO₂ is 25.85 m²/gr, surface areas of 0.5 % Ag, 1 % Ag and 1.5 % Ag doped TiO₂ powders are 21.06 m²/gr, 38.60 m²/gr, 53.58 m²/gr respectively.

Looking at the Zn dopant, as it was said for Ag dopant for Zn dopant it can be also said that by increasing the amount of Zn dopant surface area of the doped TiO₂ powder increases. All three concentrations of Zn dopant promote surface area of TiO₂. While

the surface area of undoped TiO₂ is 25.85 m²/gr, surface areas of 0.5 % Zn, 1 % Zn and 1.5 % Zn doped TiO₂ powder are 31.39 m²/gr, 40.43 m²/gr, 44.80 m²/gr respectively.

Looking at the Cr dopant, it is not possible to say that increasing dopant amount increases surface area. The surface area of 1 % Cr doped TiO₂ is higher than both the surface areas of 0.5 % Cr doped TiO₂ and 1.5 % Cr doped TiO₂ and surface area of 0.5 % Cr doped TiO₂ is slightly bigger than the surface area of 1.5 % Cr doped TiO₂. While the surface area of undoped TiO₂ is 25.85 m²/gr, surface areas of 0.5 % Cr, 1 % Cr and 1.5 % Cr doped TiO₂ powder are 29.73 m²/gr, 34.96 m²/gr, 24.65 m²/gr respectively.

It is a well known fact that specific surface area increases by decreasing of crystallite size and all three dopants; Ag, Zn and Cr were reported that they reduced crystallite size of TiO₂ [76, 85, 122, 126, 127]. Looking at Section 3.1.3.5, to the crystallite size of undoped TiO₂ (12 nm) and 0.5 % Ag (12.17 nm), 1 % Ag (10.69 nm), 1.5 % Ag (11.86 nm), 0.5 % Zn (12.29 nm), 1 % Zn (10.63 nm) 1.5 % Zn (10.21 nm), 0.5 % Cr (11.05 nm), 1 % Cr (10.48 nm) and 1.5 % Cr (9.61 nm) doped TiO₂ powders sintered at 400 °C for 1 hour, it can be seen that there is a slight difference between crystallite sizes. Besides, if these small differences are taken into consideration it can be said that crystallite size results almost support the surface area results.

3.2. Characterization Of The TiO₂ Films

3.2.1. Roughness results

Table 3.14 and Figure 3.44 show roughness results and AFM images over an area of 40 µm x 40 µm of undoped TiO₂, 0.5 % Ag-TiO₂, 1 % Ag-TiO₂, 1.5 % Ag-TiO₂, 0.5 % Zn-TiO₂, 1 % Zn-TiO₂, 1.5 % Zn-TiO₂, 0.5 % Cr-TiO₂, 1 % Cr-TiO₂, 1.5 % Cr-TiO₂ films respectively.

It can be seen from Table 3.14 that more or less all three dopants increased roughness value of undoped TiO₂ film. Increasing the dopant concentration seems not to change roughness significantly for Ag dopant, seems to decrease roughness for Zn dopant and seems to increase roughness for Cr dopant.

Table 3.14. Roughness results of TiO₂ films

Film name	Ra (nm)
Undoped TiO ₂	2.01
0.5 % Ag-TiO ₂	3.89
1 % Ag-TiO ₂	4.10
1.5 % Ag-TiO ₂	3.61
0.5 % Zn-TiO ₂	3.62
1 % Zn-TiO ₂	2.40
1.5 % Zn-TiO ₂	2.08
0.5 % Cr-TiO ₂	2.11
1 % Cr-TiO ₂	3.48
1.5 % Cr-TiO ₂	4.76

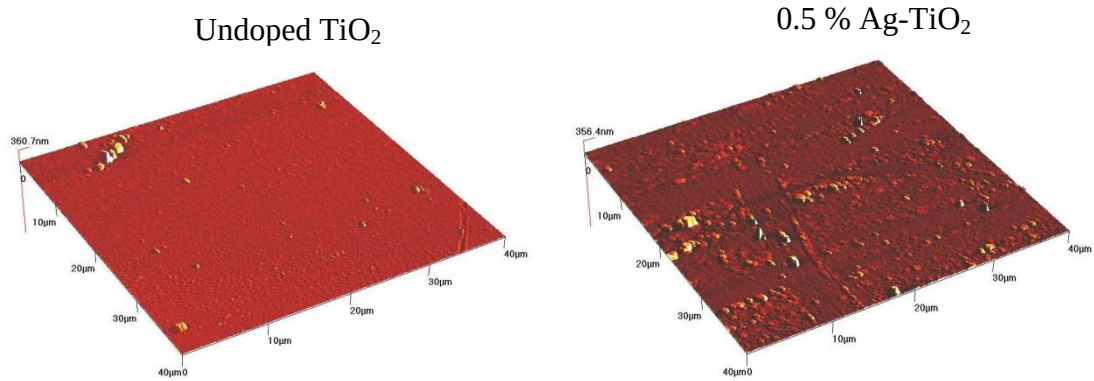


Figure 3.44. AFM images of undoped TiO₂, 0.5 % Ag-TiO₂, 1 % Ag-TiO₂, 1.5 % Ag-TiO₂, 0.5 % Zn-TiO₂, 1 % Zn-TiO₂, 1.5 % Zn-TiO₂, 0.5 % Cr-TiO₂, 1 % Cr-TiO₂, 1.5 % Cr-TiO₂ films.

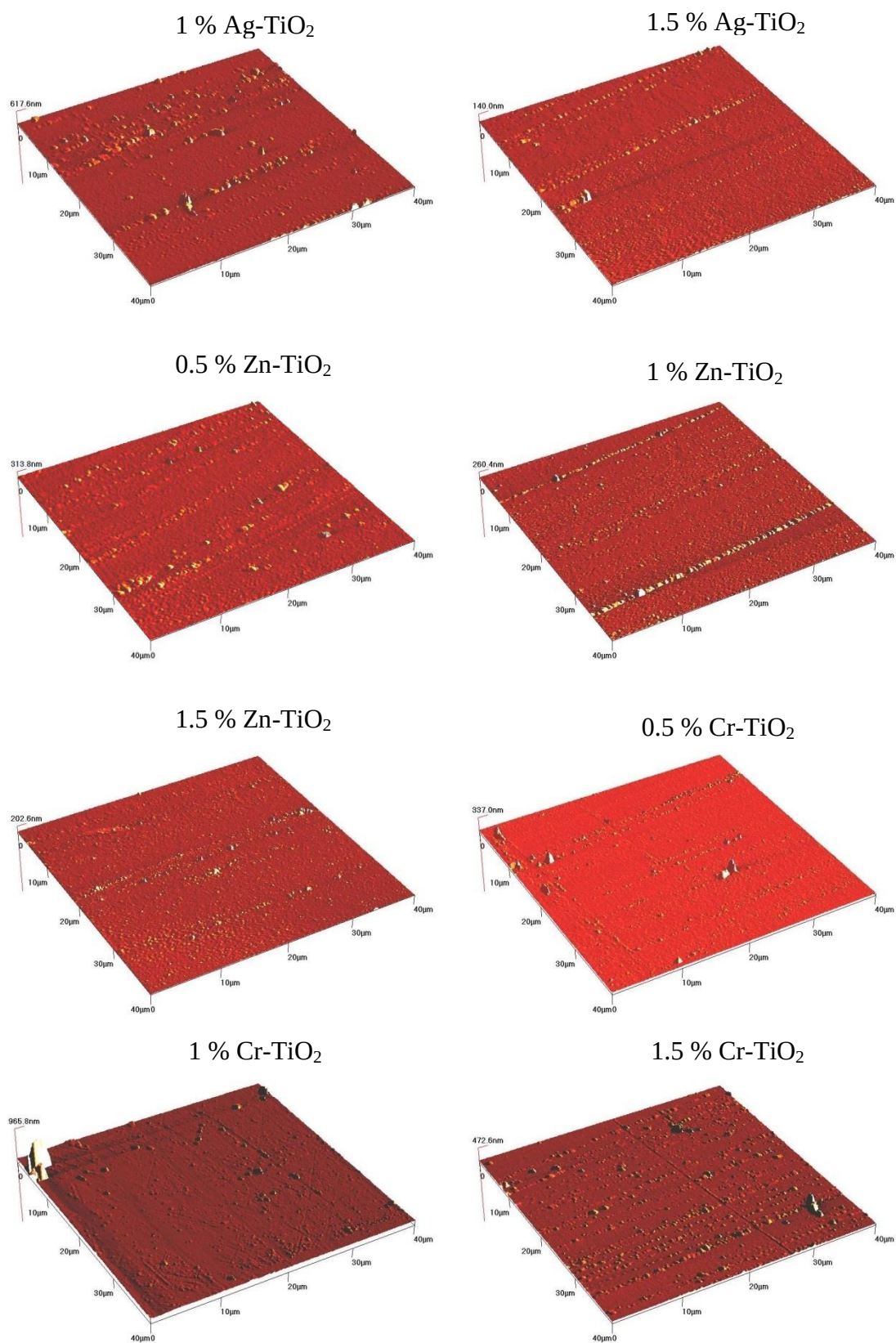


Figure 3.44. Continues

When initial (before UV irradiated) contact angles of undoped TiO₂, 0.5 % Ag-TiO₂, 1 % Ag-TiO₂, 1.5 % Ag-TiO₂, 0.5 % Zn-TiO₂, 1 % Zn-TiO₂, 1.5 % Zn-TiO₂, 0.5 % Cr-TiO₂, 1 % Cr-TiO₂, 1.5 % Cr-TiO₂ films given in Section 3.3.1 are evaluated taking roughness results given in Table 3.14. into consideration, it is possible to say that roughness and hydrophobicity are directly proportional. Although increment is not too much, the films that have higher roughness values also have higher contact angle values.

In literature two models are used to explain the effect of surface roughness on hydrophobicity and hydrophilicity. The Wenzel Model assumes that no air is entrapped between the protrusions of the surface and the spaces of these protrusions are filled with liquid. On the other hand Cassie-Baxter Model assumes that air is entrapped between the protrusions and drop sits on the surface made of air and protrusions [128, 129].

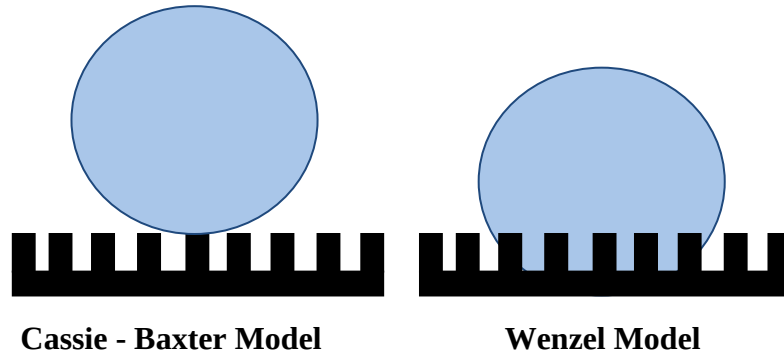


Figure 3.45. The effect of surface roughness on hydrophobicity and hydrophilicity

In Wenzel's Model, Young's contact angle (Θ_Y) is multiplied with roughness factor (r) which is always bigger than 1 to get Wenzel's contact angle (Θ_W).

$$\cos \Theta_W = r \cos \Theta_Y \quad (3.10)$$

According to this model both hydrophilicity and hydrophobicity can be reinforced depending on the Young's contact angle (Θ_Y) value.

Young's contact angle (Θ_Y) is calculated by using the relationship between solid-gas (γ_{SG}), solid-liquid (γ_{SL}) and liquid-gas (γ_{LG}) interfacial tensions. While calculating Young's contact angle, surfaces are assumed to be smooth and chemically homogenous.

$$\cos \Theta_Y = (\gamma_{SG} - \gamma_{SL}) / \gamma_{LG} \quad (3.11)$$

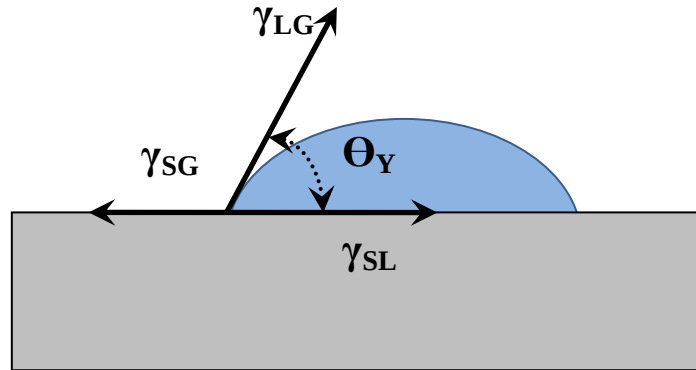


Figure 3.46. Young contact angle (Θ_y)

In Cassi-Baxter's Model, different than Wenzel's Model the roughness factor of the wetted area (r_f) and area fraction of the projected wet area (f) are included in the calculation of apparent contact angle (Θ_{CB}).

$$\cos \Theta_{CB} = r_f f \cos \Theta_y + f - 1 \quad (3.12)$$

Besides the studies that can be explained with Wenzel Model [130] or with Cassie-Baxter Model [131], it is possible to come across with different ideas being reported that if roughness is less than 100 nm, it does not have a significant effect on contact angle values [132].

3.3. Determination The Physical Properties Of TiO_2 Films

3.3.1. Contact angle measurement and photoinduced wettability test

In this section initial contact angle values and photoinduced wettability test results of undoped TiO_2 , 0.5 % Ag- TiO_2 , 1 % Ag- TiO_2 , 1.5 % Ag- TiO_2 , 0.5 % Zn- TiO_2 , 1 % Zn- TiO_2 , 1.5 % Zn- TiO_2 , 0.5 % Cr- TiO_2 , 1 % Cr- TiO_2 , 1.5 % Cr- TiO_2 films are given.

Photoinduced wettability tests were done under exactly the same conditions of photocatalytic activity tests (Light source = Xenon Lamp, Filter type = UV Filter, Black standart temperature = 35 °C, Irradiation rate = 765 W/m²).

Photoinduced wettability is known to occur due to the adsorption of water molecules on the photogenerated surface defective sites. When TiO₂ film is radiated with UV light, photogenerated electron-hole pairs are formed.



If their recombination can be prevented, these pairs move to the surface of TiO₂ film and react with adsorbed species on the surface of TiO₂ film. While electrons react with Ti⁴⁺ to form Ti³⁺ defective sites and react with adsorbed O₂ on the surface to form O₂⁻, holes react with formed O₂⁻ and causes oxygen vacancies (Vo) to occur.



Water molecules are adsorbed on the surface through these oxygen vacancies and number of hydroxyl groups on TiO₂ film is increased making TiO₂ film hydrophilic under UV radiation [133, 134].

Contact angle values of this TiO₂ film that became hydrophilic under UV light irradiation start to increase after storage in dark is thought to be due the replacement of oxygen atoms with adsorbed hydroxyl groups in the darkness which reduces the density of hydroxyl groups on the TiO₂ film surface [131, 135].

3.3.1.1. Effect of Ag dopant

Figure 3.47 shows contact angle of water droplet on SLS glasses coated with undoped, 0.5 % Ag, 1 % Ag and 1.5 % Ag doped TiO₂ solution.

Results which are arithmetic mean of three measurements show that 0.5 %, 1 %, 1.5 % Ag doping slightly increase the initial contact angle value of TiO₂ film. Increasing Ag concentration from 0.5 % to 1 % increases initial contact angle and further increasing Ag concentration from 1 % to 1.5 % decreases initial contact angle. However it should be noted that these reductions and increments at contact angle of Ag doped TiO₂ films are very slight that they can be ignored.

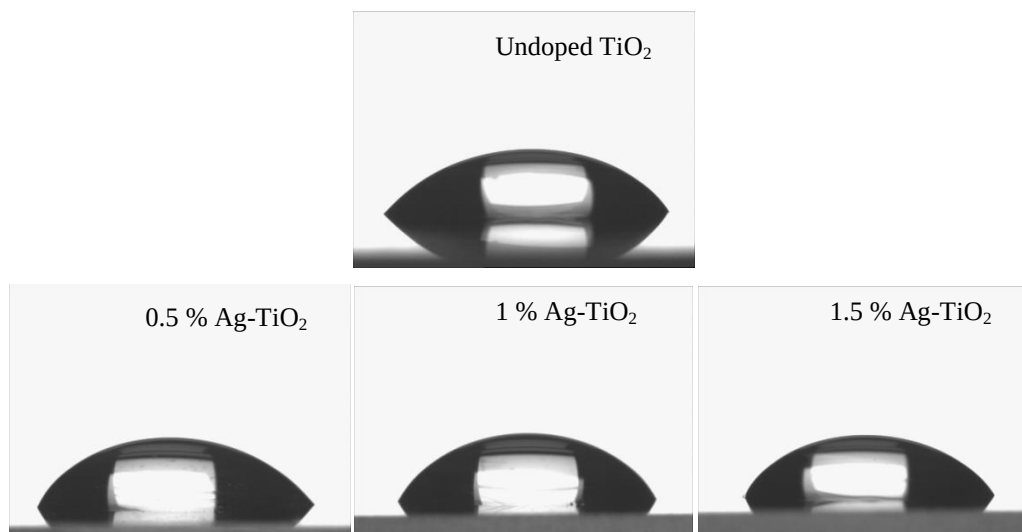


Figure 3.47. Contact angle measurement of SLS glasses coated with undoped TiO_2 , 0.5 % Ag- TiO_2 , 1 % Ag- TiO_2 , 1.5 % Ag- TiO_2

Table 3.15 and Figure 3.48 show changes in contact angles of uncoated SLS glass and SLS glasses coated with undoped, 0.5 % Ag, 1 % Ag, 1.5 % Ag doped TiO_2 solutions during UV irradiation and storage in dark. In literature Ag doping is reported to improve photoinduced wettability of TiO_2 film [133] due to the increase of Ti^{3+} defective sites [135].

It can be seen from Table 3.15 that after 60 minutes UV irradiation, contact angles of Ag doped TiO_2 films, reach smaller contact angle values than that of undoped TiO_2 film. 1.5 % seems to be the optimum concentration of Ag that shows the highest photoinduced wettability. Among three different concentrations of Ag, 1 % which is given to be the best concentration for photocatalytic activity in Section 3.4.2.1, shows the lowest photoinduced wettability. After all it should be taken into consideration that neither the contact angle values of 0.5 %, 1 %, 1.5 % Ag doped TiO_2 films after 60 minutes irradiation given in Table 3.15 nor the absorbance values of 0.5 %, 1 %, 1.5 % Ag doped TiO_2 films given in Section 3.4.2.1 show remarkable differences. So it can still be said that photocatalytic activity and photoinduced wettability are related to each other [136].

Table 3.15. Changes in contact angles of uncoated SLS glass, SLS glasses coated with undoped TiO_2 , 0.5 % Ag- TiO_2 , 1 % Ag- TiO_2 , 1.5 % Ag- TiO_2 during UV irradiation and storage in dark.

	0 min. UV	15 min. UV	30 min. UV	45 min. UV	60 min. UV	18 hrs. Dark	24 hrs. Dark	48 hrs. Dark
Uncoated glass	45°	63°	57°	58°	65°	52°	63°	56°
Undoped TiO_2	54°	13°	10°	9°	8.2°	28°	42°	56°
0.5 % Ag- TiO_2	59°	10.6°	10.3°	8°	7.2°	25°	38°	51°
1 % Ag- TiO_2	62°	17°	11.1°	10°	8°	30°	47°	64°
1.5 % Ag- TiO_2	61°	12°	8.5°	8°	6.3°	32°	42°	62°

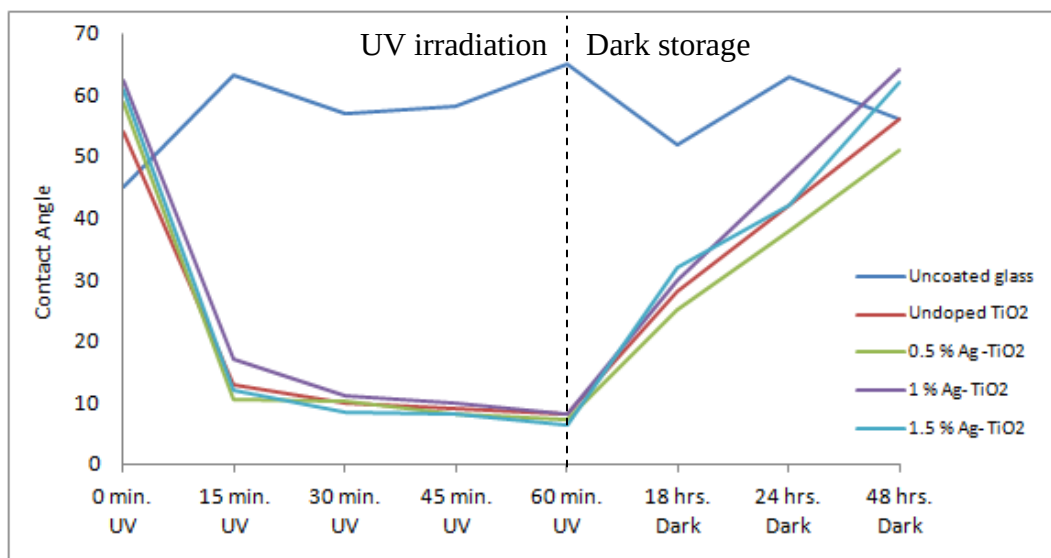


Figure 3.48. Changes in contact angles of uncoated SLS glass, SLS glasses coated with undoped TiO_2 , 0.5 % Ag- TiO_2 , 1 % Ag- TiO_2 , 1.5 % Ag- TiO_2 during UV irradiation and storage in dark.

Figure 3.48 indicates that almost all TiO_2 films gain their first contact angle values after storage in the dark for 48 hours.

Looking at contact angle values of uncoated SLS glass during UV irradiation and storage in dark it is possible to say that there is a slight and inconsistent change which

can also be a proof for the photocatalytic activity test result of uncoated SLS glass that is discussed in Section 3.4.2.

3.3.1.2. Effect of Zn dopant

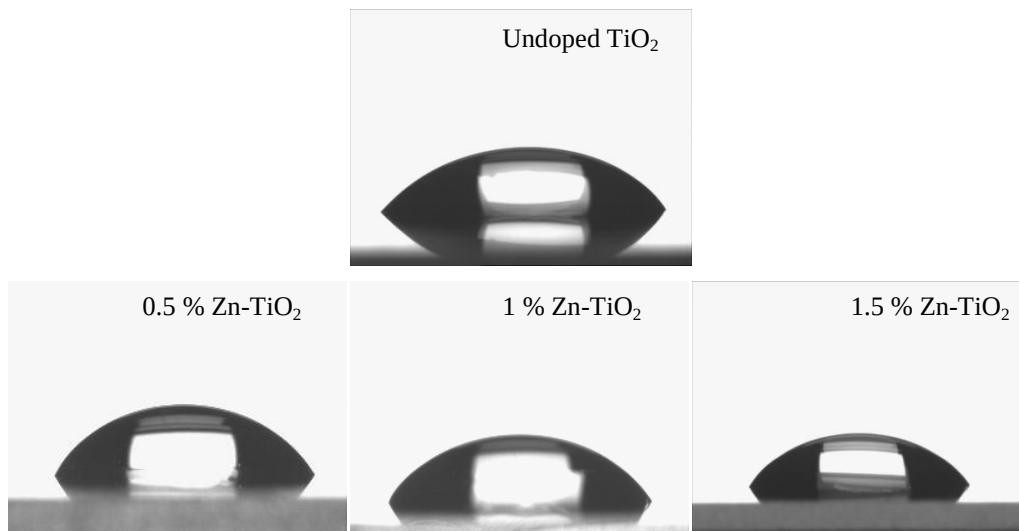


Figure 3.49. Contact angle measurement of SLS glasses coated with undoped TiO_2 , 0.5 % Zn- TiO_2 , 1 % Zn- TiO_2 , 1.5 % Zn- TiO_2

Figure 3.49 shows contact angle of water droplet on SLS glasses coated with undoped, 0.5 % Zn, 1 % Zn and 1.5 % Zn doped TiO_2 . Results which are arithmetic mean of three measurements show that 0.5 %, 1 %, 1.5 % Zn doping slightly increase the initial contact angle value of TiO_2 film. While increasing Zn dopant concentration from 0.5 % to 1 % decreases initial contact angle value of 0.5 % Zn doped TiO_2 film, increasing Zn concentration from 1 % to 1.5 % almost has no effect on initial contact angle of 1 % Zn doped TiO_2 film. As said before for Ag dopant it should also be noted for Zn dopant that differences between the contact angles are very slight that they can be ignored.

Table 3.16 and Figure 3.50 show changes in contact angles of uncoated SLS glass and SLS glasses coated with undoped, 0.5 % Zn, 1 % Zn, 1.5 % Zn doped TiO_2 during UV irradiation and storage in dark. It can be seen that after 60 minutes UV irradiation, contact angle of all TiO_2 films decreases approximately to 8.2° - 9° and after storage in the dark for 48 hours all of them approximately gain their first contact angle values.

Table 3.16. Changes in contact angles of uncoated SLS glass, SLS glasses coated with undoped TiO_2 , 0.5 % Zn- TiO_2 , 1 % Zn- TiO_2 , 1.5 % Zn- TiO_2 during UV irradiation and storage in dark.

	0 min. UV	15 min. UV	30 min. UV	45 min. UV	60 min. UV	18 hrs. Dark	24 hrs. Dark	48 hrs. Dark
Uncoated glass	45°	63°	57°	58°	65°	52°	63°	56°
Undoped TiO_2	54°	13°	10°	9°	8.2°	28°	42°	56°
0.5 % Zn- TiO_2	61°	9.7°	9.5°	9.3°	9°	31°	41°	63°
1 % Zn- TiO_2	57°	11.9°	11.5°	10°	8.5°	34°	51°	59°
1.5 % Zn- TiO_2	58°	17.4°	13.3°	13°	8.5°	38°	51°	60°

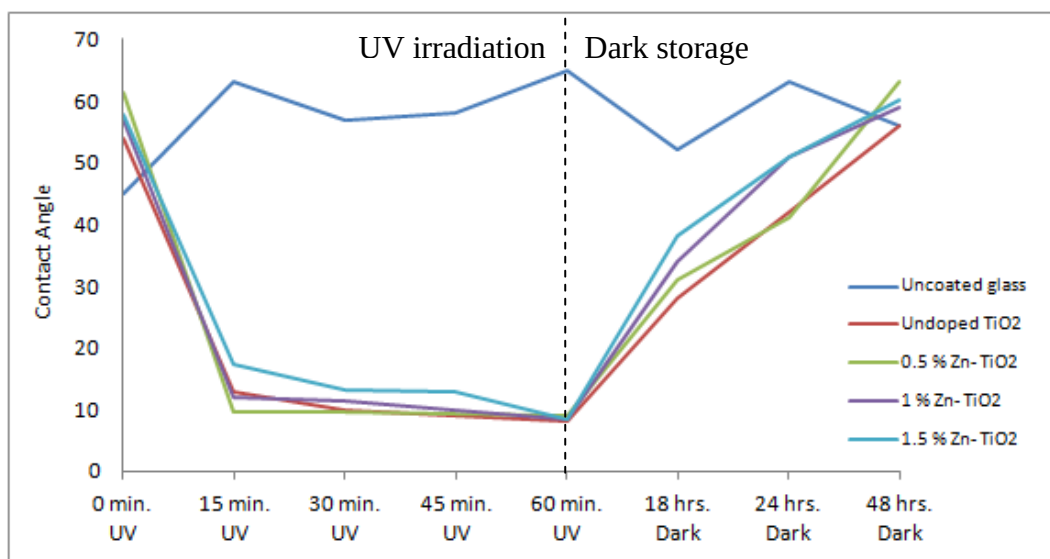


Figure 3.50. Changes in contact angles of uncoated SLS glass, SLS glasses coated with undoped TiO_2 , 0.5 % Zn- TiO_2 , 1 % Zn- TiO_2 , 1.5 % Zn- TiO_2 during UV irradiation and storage in dark.

Effect of Zn dopant on photocatalytic activity that is discussed in Section 3.4.2.2 also supports the effect of Zn dopant on photoinduced wettability. 0.5 % Zn doped TiO_2 film that shows the lowest photocatalytic activity also shows the lowest photoinduced wettability after 60 minutes UV irradiation and undoped TiO_2 film has both better

photoinduced wettability and better photocatalytic activity than Zn doped TiO_2 films. Among Zn dopants 1 % Zn is given in Section 3.4.2.2 to be the one that shows the highest photocatalytic activity, it also together with 1.5 % Zn show the highest photoinduced wettability.

3.3.1.3. Effect of Cr dopant

Figure 3.51 shows contact angle of water droplet on SLS glasses coated with undoped, 0.5 % Cr, 1 % Cr and 1.5 % Cr doped TiO_2 . Results which are arithmetic mean of three measurements show that 1 % Cr and 1.5 % Cr doping increase the initial contact angle value of TiO_2 film while 0.5 % Cr has no effect on initial contact angle of TiO_2 film. Also it should be noted that increasing the Cr dopant concentration increases initial contact angle value.

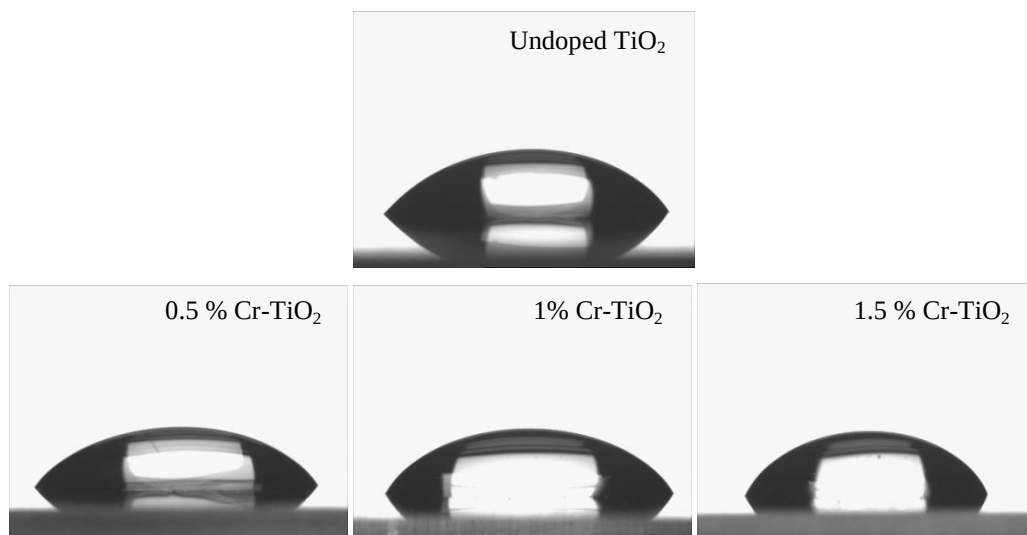


Figure 3.51. Contact angle measurement of SLS glasses coated with undoped TiO_2 , 0.5 % Cr- TiO_2 , 1 % Cr- TiO_2 , 1.5 % Cr- TiO_2

Table 3.17 and Figure 3.52 show changes in contact angles of uncoated SLS glass and SLS glasses coated with undoped, 0.5 % Cr, 1 % Cr, 1.5 % Cr doped TiO_2 during UV irradiation and storage in dark. Looking at the contact angle values it is so obvious that Cr dopant causes TiO_2 film to lose its photoinduced wettability behaviour. When doped with 0.5 % Cr, 1 % Cr and 1.5 % Cr, contact angle of TiO_2 film no more decreases under UV irradiation. Similar to uncoated SLS glass contact angle of Cr doped TiO_2 films change inconsistently during UV irradiation and storage in dark.

Table 3.17. Changes in contact angles of uncoated SLS glass, SLS glasses coated with undoped TiO_2 , 0.5 % Cr- TiO_2 , 1 % Cr- TiO_2 , 1.5 % Cr- TiO_2 during UV irradiation and storage in dark.

	0 min. UV	15 min. UV	30 min. UV	45 min. UV	60 min. UV	18 hrs. Dark	24 hrs. Dark	48 hrs. Dark
Uncoated glass	45°	63°	57°	58°	65°	52°	63°	56°
Undoped TiO_2	54°	13°	10°	9°	8.2°	28°	42°	56°
0.5 % Cr- TiO_2	54°	40°	40°	39°	40°	49°	64°	63°
1 % Cr- TiO_2	61°	55°	40°	40°	45°	54°	60°	65°
1.5 % Cr- TiO_2	65°	55°	54°	55°	60°	62°	63°	68°

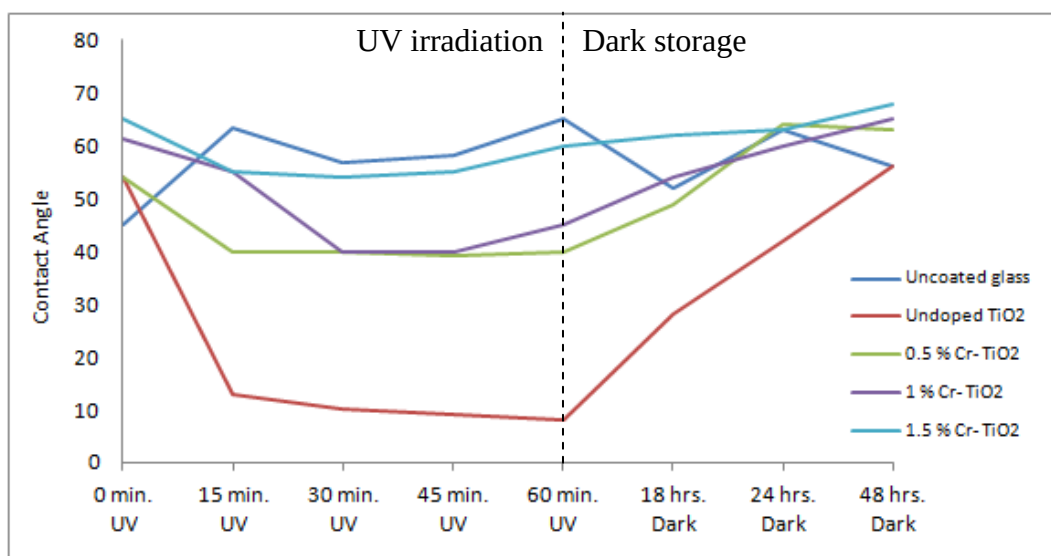


Figure 3.52. Changes in contact angles of uncoated SLS glass, SLS glasses coated with undoped TiO_2 , 0.5 % Cr- TiO_2 , 1 % Cr- TiO_2 , 1.5 % Cr- TiO_2 during UV irradiation and storage in dark.

These results verify the photocatalytic activity results discussed in Section. 3.4.2.3. It can be concluded that Cr dopant causes TiO_2 film to lose both its photoinduced wettability and photocatalytic activity. This result supports the idea that photocatalytic and photoinduced wettability properties are correlated [136].

In literature reason of this detrimental effect of Cr dopant on photoinduced wettability of TiO_2 film was found to be Cr_2O_3 phase [137] which was also supposed to be the reason of detrimental effect of Cr dopant on photocatalytic activity of TiO_2 film [138] which is discussed in Section 3.4.2.3. Besides, in literature it is possible to find reports that are telling exactly the opposite that Cr doping improves photoinduced hydrophilicity of TiO_2 film [139-141]. It should be noted that different synthesizing methods, different substrates, different Cr dopant concentrations were reported in these studies each of which can be a reason of this difference.

3.3.1.4. Effect of dopant concentration (0.5 %)

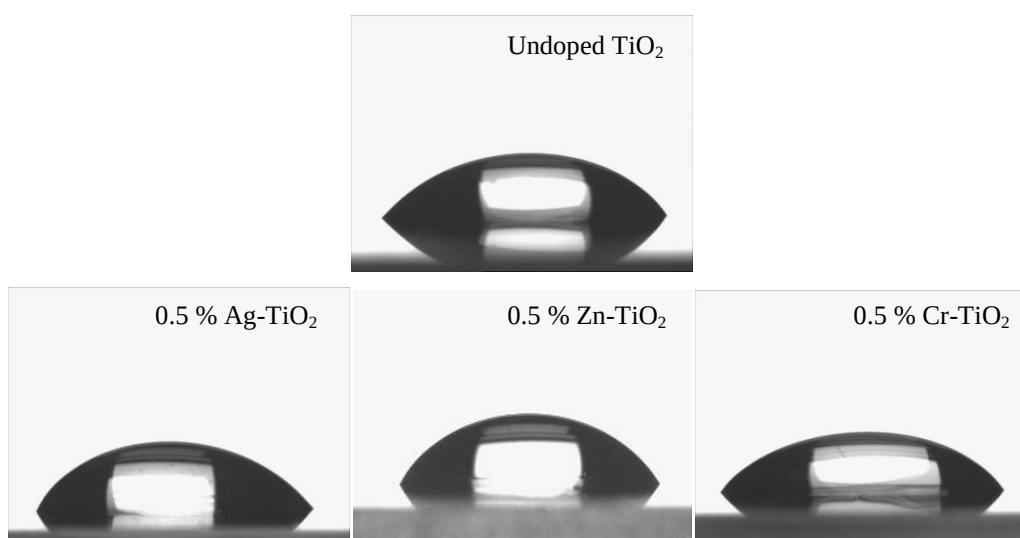


Figure 3.53. Contact angle measurement of SLS glasses coated with undoped TiO_2 , 0.5 % Ag- TiO_2 , 0.5 % Zn- TiO_2 , 0.5 % Cr- TiO_2

Figure 3.53 shows contact angle of water droplet on SLS glasses coated with undoped, 0.5 % Ag, 0.5 % Zn and 0.5 % Cr doped TiO_2 . Results which are arithmetic mean of three measurements show that when their concentration is chosen 0.5 %, Ag and Zn dopants slightly increase and Cr dopant does not affect initial hydrophilicity of TiO_2 film.

Table 3.18 and Figure 3.54 show changes in contact angles of uncoated SLS glass and SLS glasses coated with undoped, 0.5 % Ag, 0.5 % Zn, 0.5 % Cr doped TiO_2 during UV irradiation and storage in dark. While 0.5 % Ag and 0.5 % Zn dopants do not make a

big difference at photoinduced wettability mechanism of TiO_2 , 0.5 % Cr dopant causes photoinduced wettability mechanism of TiO_2 not to work.

Table 3.18. Changes in contact angles of uncoated SLS glass, SLS glasses coated with undoped TiO_2 , 0.5 % Ag-TiO_2 , 0.5 % Zn-TiO_2 , 0.5 % Cr-TiO_2 during UV irradiation and storage in dark.

	0 min. UV	15 min. UV	30 min. UV	45 min. UV	60 min. UV	18 hrs. Dark	24 hrs. Dark	48 hrs. Dark
Uncoated glass	45°	63°	57°	58°	65°	52°	63°	56°
Undoped TiO_2	54°	13°	10°	9°	8.2°	28°	42°	56°
0.5 % Ag-TiO_2	59°	10.6°	10.3°	8°	7.2°	25°	38°	51°
0.5 % Zn-TiO_2	61°	9.7°	9.5°	9.3°	9°	31°	41°	63°
0.5 % Cr-TiO_2	54°	40°	40°	39°	40°	49°	64°	63°

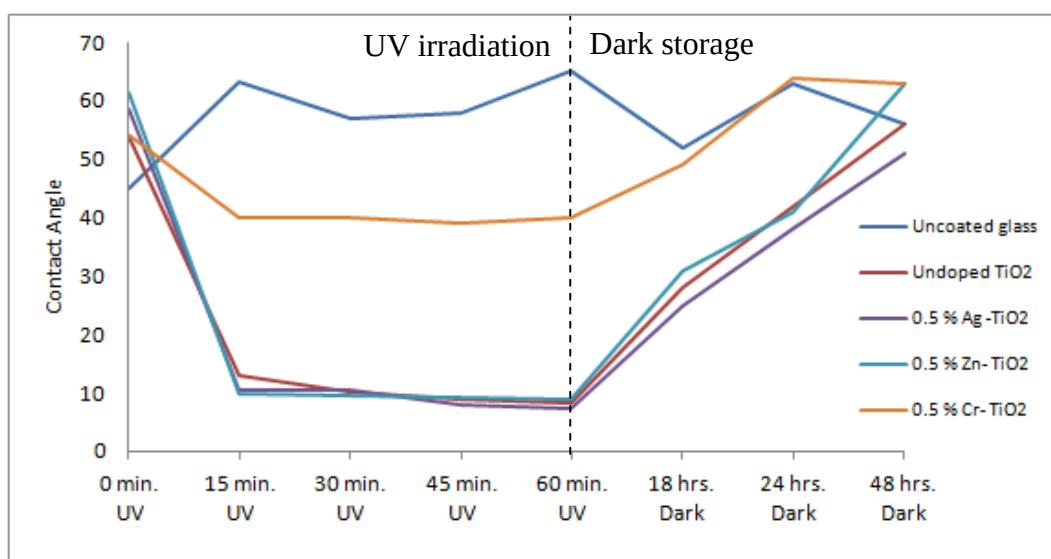


Figure 3.54. Changes in contact angles of uncoated SLS glass, SLS glasses coated with undoped TiO_2 , 0.5 % Ag-TiO_2 , 0.5 % Zn-TiO_2 , 0.5 % Cr-TiO_2 during UV irradiation and storage in dark.

3.3.1.5. Effect of dopant concentration (1 %)

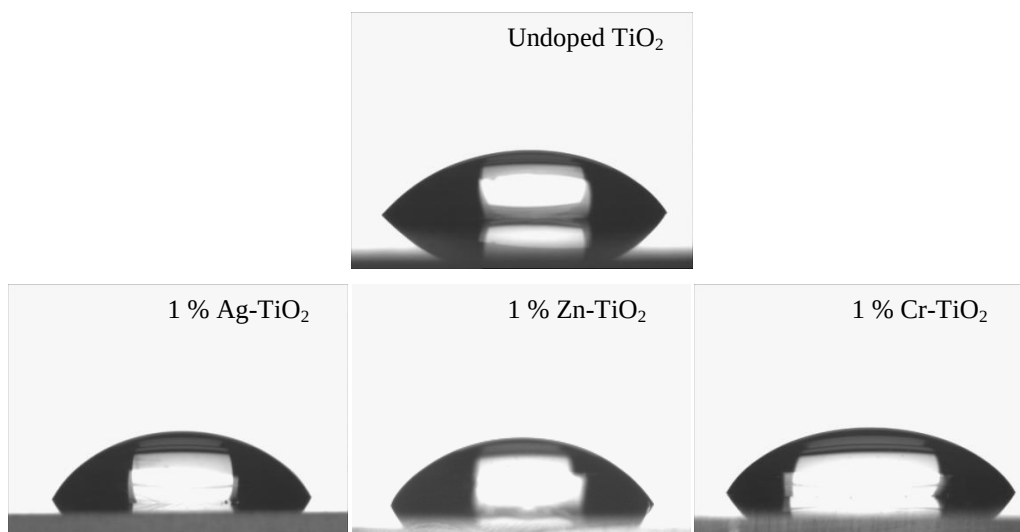


Figure 3.55. Contact angle measurement of SLS glasses coated with undoped TiO_2 , 1 % Ag-TiO_2 , 1 % Zn-TiO_2 , 1 % Cr-TiO_2

Figure 3.55 shows contact angle of water droplet on SLS glasses coated with undoped 1 % Ag , 1 % Zn and 1 % Cr doped TiO_2 . Results which are arithmetic mean of three measurements show that when their concentration is chosen 1 %, all of the three dopants slightly increase initial hydrophilicity of TiO_2 film.

Table 3.19. Changes in contact angles of uncoated SLS glass, SLS glasses coated with undoped TiO_2 , 1 % Ag-TiO_2 , 1 % Zn-TiO_2 , 1 % Cr-TiO_2 during UV irradiation and storage in dark.

	0 min. UV	15 min. UV	30 min. UV	45 min. UV	60 min. UV	18 hrs. Dark	24 hrs. Dark	48 hrs. Dark
Uncoated glass	45°	63°	57°	58°	65°	52°	63°	56°
Undoped TiO_2	54°	13°	10°	9°	8.2°	28°	42°	56°
1 % Ag-TiO_2	62°	17°	11.1°	10°	8°	30°	47°	64°
1 % Zn-TiO_2	57°	11.9°	11.5°	10°	8.5°	34°	51°	59°
1 % Cr-TiO_2	61°	55°	40°	40°	45°	54°	60°	65°

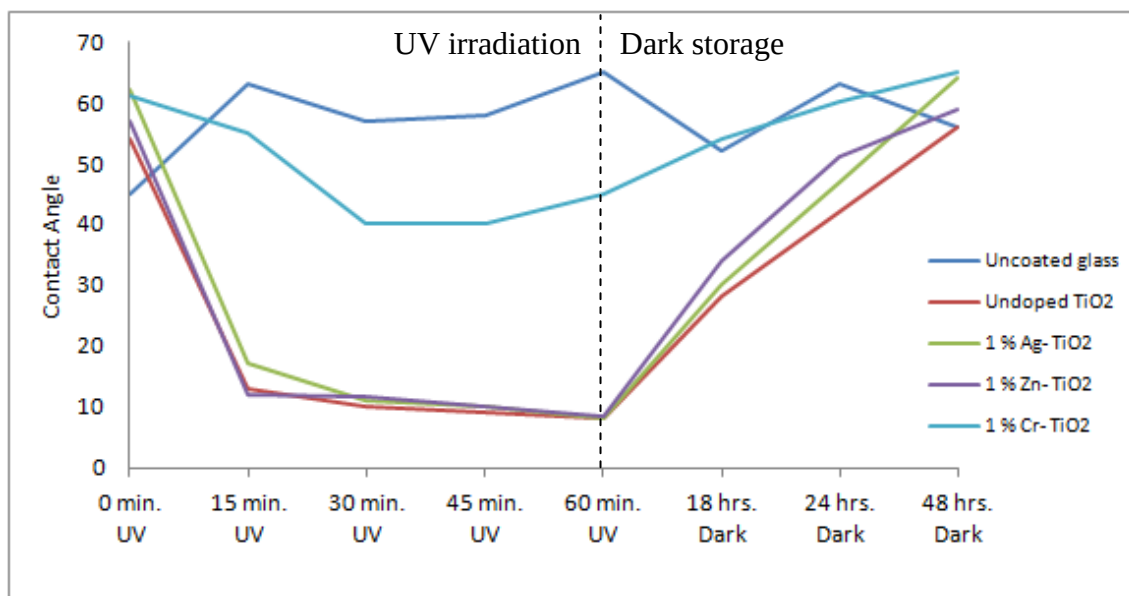


Figure 3.56. Changes in contact angles of uncoated SLS glass, SLS glasses coated with undoped TiO₂, 1 % Ag-TiO₂, 1 % Zn-TiO₂, 1 % Cr-TiO₂ during UV irradiation and storage in dark.

Table 3.19 and Figure 3.56 show changes in contact angles of uncoated SLS glass and SLS glasses coated with undoped, 1 % Ag, 1 % Zn, 1 % Cr doped TiO₂ during UV irradiation and storage in dark. While 1 % Ag and 1 % Zn dopants do not make a big difference at photoinduced wettability mechanism of TiO₂, 1 % Cr dopant causes photoinduced wettability mechanism of TiO₂ not to work.

3.3.1.6. Effect of dopant concentration (1.5 %)

Figure 3.57 shows contact angle of water droplet on SLS glasses coated with undoped 1.5 % Ag, 1.5 % Zn and 1.5 % Cr doped TiO₂. Results which are arithmetic mean of three measurements show that when their concentration is chosen 1.5 %, all three dopants increase initial hydrophilicity of TiO₂ film. Cr is the one that causes the highest increment at the initial contact angle of undoped TiO₂ film.

Table 3.20 and Figure 3.58 show changes in contact angles of uncoated SLS glass, SLS glasses coated with undoped, 1.5 % Ag, 1.5 % Zn, 1.5 % Cr doped TiO₂ during UV irradiation and storage in dark. While 1.5 % Ag and 1.5 % Zn dopants do not make a big difference at photoinduced wettability mechanism of TiO₂, 1.5 % Cr dopant causes photoinduced wettability mechanism of TiO₂ not to work.

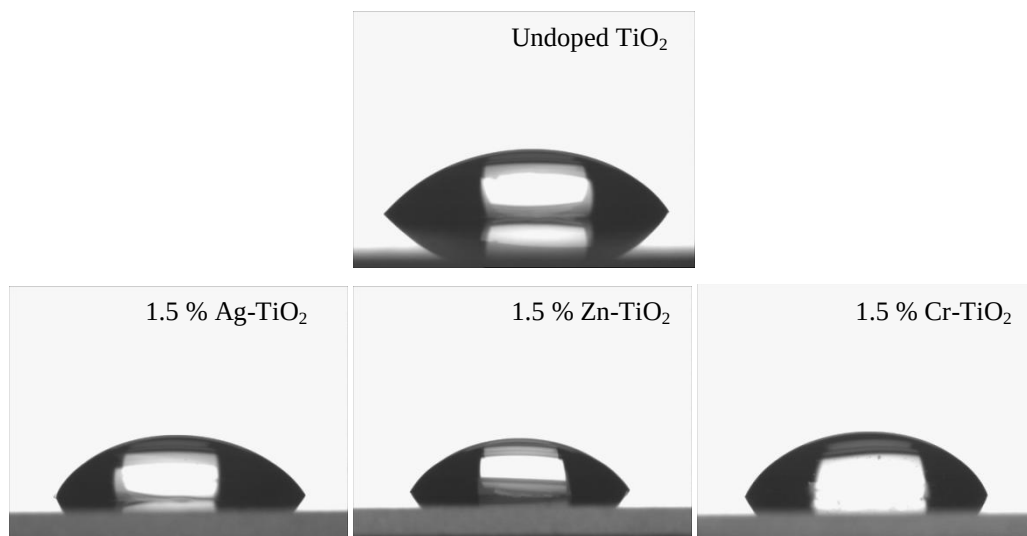


Figure 3.57. Contact angle measurement of SLS glasses coated with undoped TiO_2 , 1.5 % Ag-TiO_2 , 1.5 % Zn-TiO_2 , 1.5 % Cr-TiO_2

Table 3.20. Changes in contact angles of uncoated SLS glass, SLS glasses coated with undoped TiO_2 , 1.5 % Ag-TiO_2 , 1.5 % Zn-TiO_2 , 1.5 % Cr-TiO_2 during UV irradiation and storage in dark.

	0 min. UV	15 min. UV	30 min. UV	45 min. UV	60 min. UV	18 hrs. Dark	24 hrs. Dark	48 hrs. Dark
Uncoated glass	45°	63°	57°	58°	65°	52°	63°	56°
Undoped TiO_2	54°	13°	10°	9°	8.2°	28°	42°	56°
1.5 % Ag-TiO_2	61°	12°	8.5°	8°	6.3°	32°	42°	62°
1.5 % Zn-TiO_2	58°	17.4°	13.3°	13°	8.5°	38°	51°	60°
1.5 % Cr-TiO_2	65°	55°	54°	55°	60°	62°	63°	68°

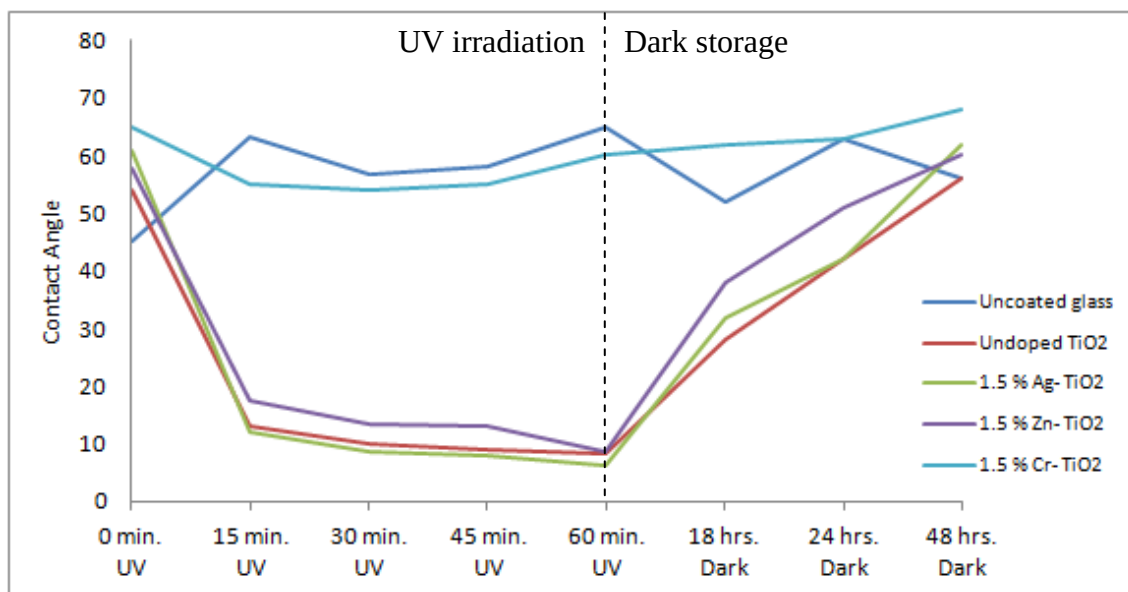


Figure 3.58. Changes in contact angles of uncoated SLS glass, SLS glasses coated with undoped TiO₂, 1.5 % Ag-TiO₂, 1.5 % Zn-TiO₂, 1.5 % Cr-TiO₂ during UV irradiation and storage in dark

3.3.2. Transmittance measurement

3.3.2.1. Effect of Ag dopant

Figure 3.59 shows the transmission spectra of uncoated SLS glass and SLS glasses that were coated with undoped TiO₂, 0.5 % Ag doped TiO₂, 1 % Ag doped TiO₂, 1.5 % Ag doped TiO₂ and Figure 3.60 shows the transmission spectra of uncoated SLS glass and SLS glasses first coated with SiO₂ then coated with undoped TiO₂, 0.5 % Ag doped TiO₂, 1 % Ag doped TiO₂, 1.5 % Ag doped TiO₂.

In the absence of SiO₂ layer absorption edge of TiO₂ film seems to shift neither to shorter nor to longer wavelength ranges when doped with 0.5 % Ag, 1 % Ag and 1.5 % Ag. In the presence of SiO₂ layer absorption edge of TiO₂ film seems to shift to shorter wavelength ranges when doped with 0.5 % Ag, 1 % Ag and 1.5 % Ag.

This shift is ascribed to the difference in crystallite size. It is known that films that contain smaller crystallites show blue shift and films that contain larger crystallites show red shift [63, 142-145].

Transmittances of uncoated SLS glass and SLS glasses that were coated with undoped TiO_2 , 0.5 % Ag doped, 1 % Ag doped, 1.5 % Ag doped TiO_2 at 400 nm and at 450 nm are 93 %, 88 %, 92 %, 92 %, 93 % and 92 %, 91 %, 88 %, 88 %, 88 % respectively.

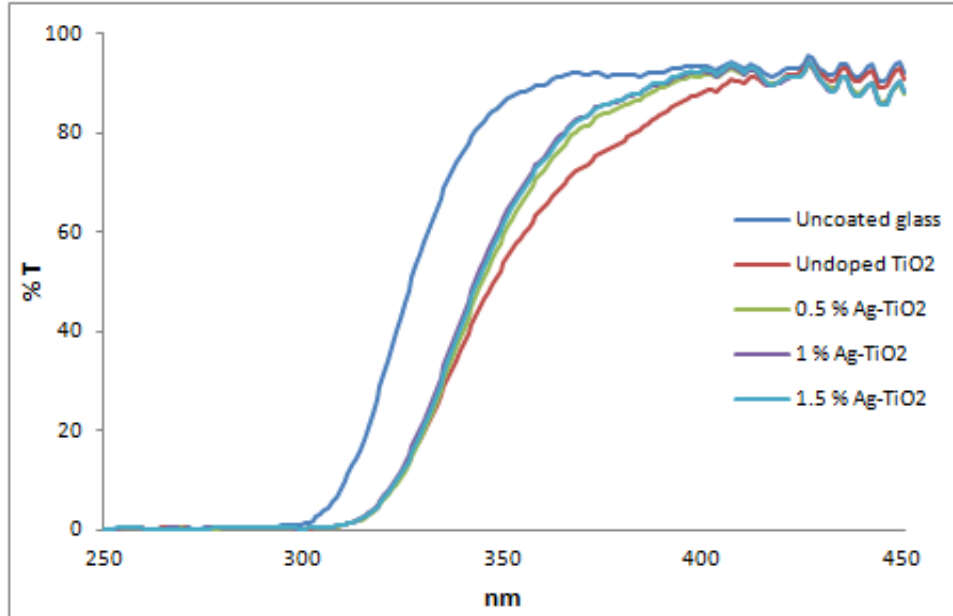


Figure 3.59. Transmission spectra of uncoated SLS glass and SLS glasses coated with undoped TiO_2 , 0.5 % Ag- TiO_2 , 1 % Ag- TiO_2 , 1.5 % Ag- TiO_2

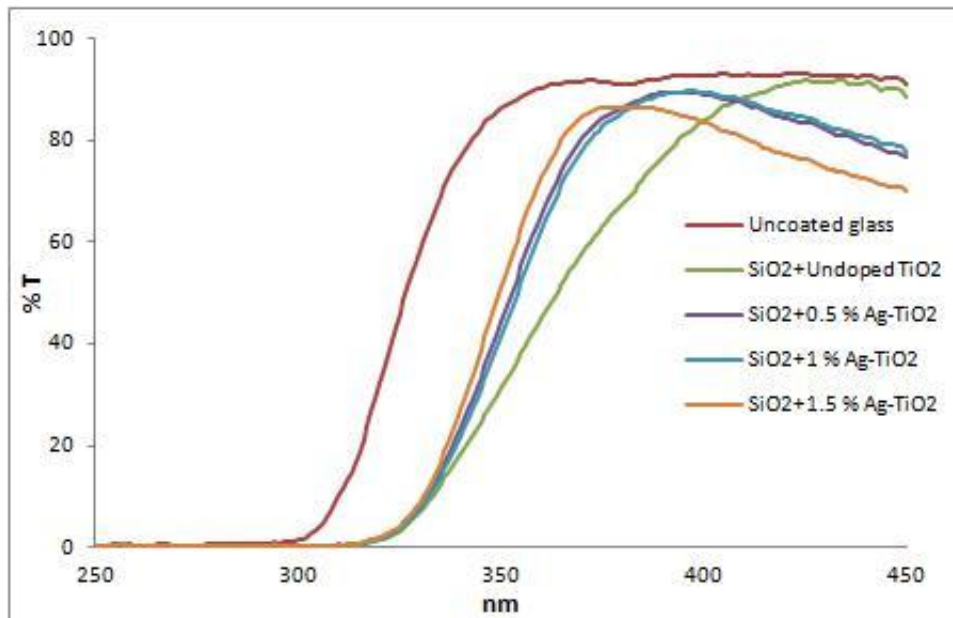


Figure 3.60. Transmission spectra of uncoated SLS glass and SLS glasses coated with SiO_2 +undoped TiO_2 , SiO_2 +0.5 % Ag- TiO_2 , SiO_2 +1 % Ag- TiO_2 , SiO_2 +1.5 % Ag- TiO_2

Transmittances of uncoated SLS glass and SLS glasses that were first coated with SiO₂ then coated with undoped TiO₂, 0.5 % Ag doped, 1 % Ag doped, 1.5 % Ag doped TiO₂ at 400 nm and at 450 nm are 93 %, 84 %, 89 %, 89 %, 83 % and 92 %, 88 %, 77 %, 78 %, 70 % respectively.

While in the absence of SiO₂ layer Ag dopant does not cause a significant difference at transmittance of SLS glass coated with TiO₂, in the presence of SiO₂ layer Ag dopant causes transmittance of SLS glass coated with TiO₂ to reduce remarkably above 400 nm and between three different concentrations of Ag dopant, 1.5 % is the concentration at which the biggest reduction is seen.

From Figure 3.59 and Figure 3.60 it is also possible to see that undoped TiO₂, 0.5 % Ag doped, 1 % Ag doped and 1.5 % Ag doped TiO₂ films behave like UV blockers and this behaviour becomes stronger when SLS glasses are first coated with SiO₂.

Transmittances of uncoated SLS glass and SLS glasses that were coated with undoped TiO₂, 0.5 % Ag doped, 1 % Ag doped and 1.5 % Ag doped TiO₂ at 350 nm are 86 %, 53 %, 59 %, 63 %, 62 % respectively.

Transmittances of uncoated SLS glass and SLS glasses that were first coated with SiO₂ then coated with undoped TiO₂ 0.5 % Ag doped, 1 % Ag doped and 1.5 % Ag doped TiO₂ at 350 nm are 86 %, 31 %, 44 %, 41 %, 51 % respectively.

3.3.2.2. Effect of Zn dopant

Figure 3.61 shows the transmission spectra of uncoated SLS glass and SLS glasses that were coated with undoped TiO₂, 0.5 % Zn doped TiO₂, 1 % Zn doped TiO₂ and 1.5 % Zn doped TiO₂ and Figure 3.62 shows the transmission spectra of uncoated SLS glass and SLS glasses first coated with SiO₂ then coated with undoped TiO₂, 0.5 % Zn doped TiO₂, 1 % Zn doped TiO₂ and 1.5 % Zn doped TiO₂.

Transmittances of uncoated SLS glass and SLS glasses that were coated with undoped TiO₂, 0.5 % Zn doped, 1 % Zn doped and 1.5 % Zn doped TiO₂ at 400 nm and at 450 nm are 93 %, 88 %, 77 %, 93 %, 92 % and 92 %, 91 %, 90 %, 88 %, 88 % respectively.

Transmittances of uncoated SLS glass and SLS glasses that were first coated with SiO₂ then coated with undoped TiO₂, 0.5 % Zn doped, 1 % Zn doped, 1.5 % Zn doped TiO₂

at 400 nm and at 450 nm are 93 %, 84 %, 88 %, 88 %, 88 % and 92 %, 88 %, 88 %, 74 %, 74 % respectively.

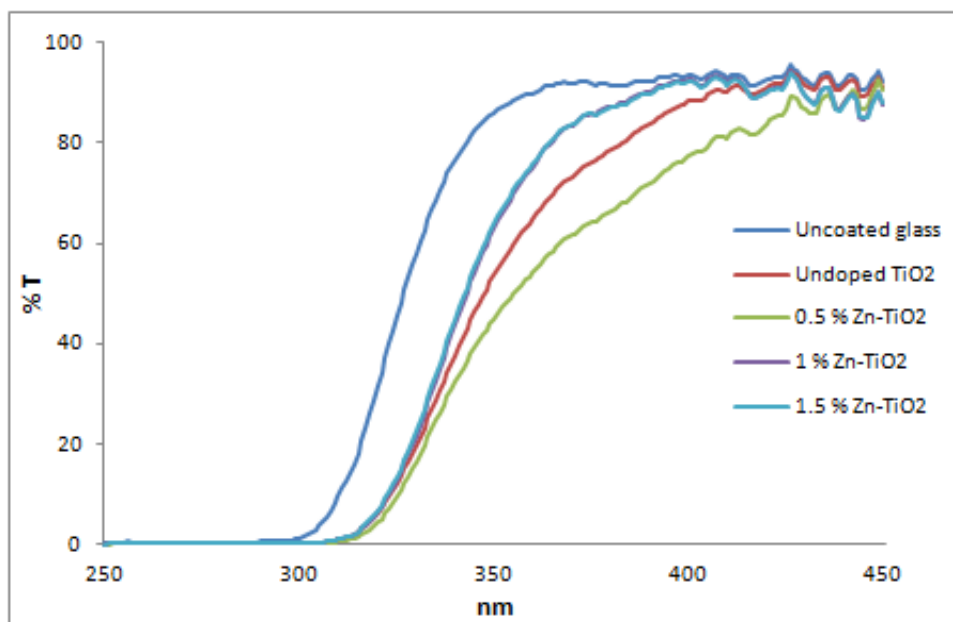


Figure 3.61. Transmission spectra of uncoated SLS glass and SLS glasses coated with undoped TiO₂, 0.5 % Zn-TiO₂, 1 % Zn-TiO₂, 1.5 % Zn-TiO₂

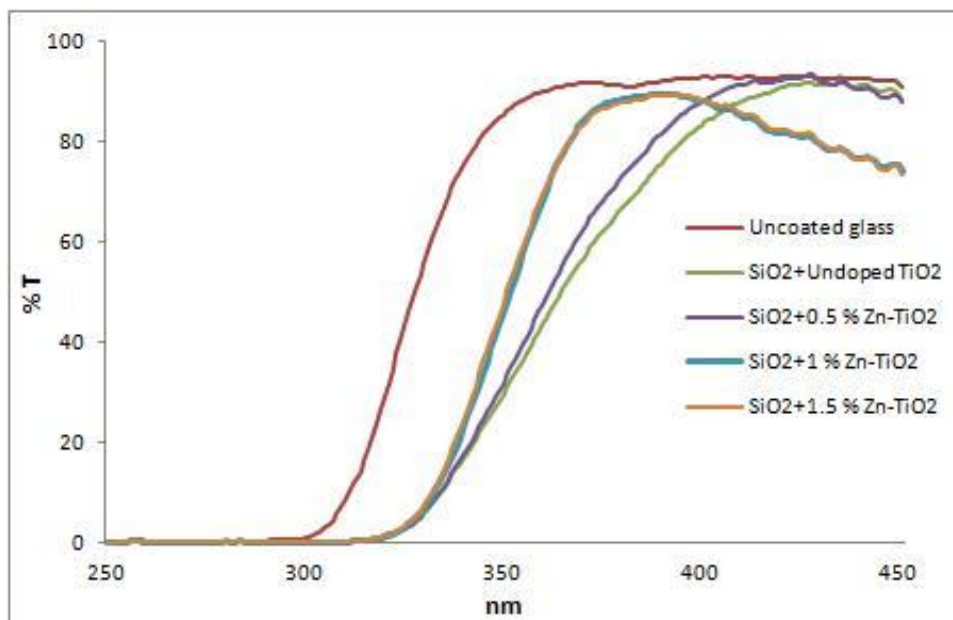


Figure 3.62. Transmission spectra of uncoated SLS glass and SLS glasses coated with SiO₂+undoped TiO₂, SiO₂+0.5 % Zn-TiO₂, SiO₂+1 % Zn-TiO₂, SiO₂+1.5 % Zn-TiO₂

While in the absence of SiO_2 layer Zn dopant does not cause a significant difference at transmittance of SLS glass coated with TiO_2 , in the presence of SiO_2 layer 1 % Zn and 1.5 % Zn dopants cause transmittance of SLS glass coated with TiO_2 to reduce remarkably and 0.5 % Zn dopant does not cause a significant difference at transmittance of SLS glass coated with TiO_2 above 400 nm.

In the absence of SiO_2 layer, absorption edge of TiO_2 film seems to shift neither to shorter nor to longer wavelength ranges when doped with 0.5 % Zn, 1 % Zn and 1.5 % Zn. In the presence of SiO_2 layer absorption edge of TiO_2 film seems to shift to shorter wavelength ranges when doped with 1 % Zn and 1.5 % Zn. 0.5 % Zn seems not to shift the absorption edge of TiO_2 film.

From Figure 3.61 and Figure 3.62 it is also possible to see that undoped TiO_2 , 0.5 % Zn doped, 1 % Zn doped and 1.5 % Zn doped TiO_2 films behave like UV blockers and this behaviour becomes stronger when SLS glasses are first coated with SiO_2 .

Transmittances of uncoated SLS glass and SLS glasses that were coated with undoped TiO_2 , 0.5 % Zn doped, 1 % Zn doped and 1.5 % Zn doped TiO_2 at 350 nm are 86 %, 53 %, 45 %, 63 %, 64 % respectively. Transmittances of uncoated SLS glass and SLS glasses that were first coated with SiO_2 then coated with undoped TiO_2 0.5 % Zn doped, 1 % Zn doped, 1.5 % Zn doped TiO_2 at 350 nm are 86 %, 31 %, 33 %, 48 %, 50 % respectively.

3.3.2.3. Effect of Cr dopant

Figure 3.63 shows the transmission spectra of uncoated SLS glass and SLS glasses that were coated with undoped TiO_2 , 0.5 % Cr doped TiO_2 , 1 % Cr doped TiO_2 and 1.5 % Cr doped TiO_2 and and Figure 3.64 shows the transmission spectra of uncoated SLS glass and SLS glasses first coated with SiO_2 then coated with undoped TiO_2 , 0.5 % Cr doped TiO_2 , 1 % Cr doped TiO_2 and 1.5 % Cr doped TiO_2 .

Transmittances of uncoated SLS glass and SLS glasses that were coated with undoped TiO_2 , 0.5 % Cr doped, 1 % Cr doped, 1.5 % Cr doped TiO_2 at 400 nm and at 450 nm are 93 %, 88 %, 76 %, 90 %, 90 % and 92 %, 91 %, 91 %, 88 %, 88 % respectively.

Transmittances of uncoated SLS glass and SLS glasses that were first coated with SiO_2 then coated with undoped TiO_2 , 0.5 % Cr doped, 1 % Cr doped, 1.5 % Cr doped TiO_2 at

400 nm and at 450 nm are 93 %, 84 %, 83 %, 85 %, 88 % and 92 %, 88 %, 88 %, 72 %, 72 % respectively.

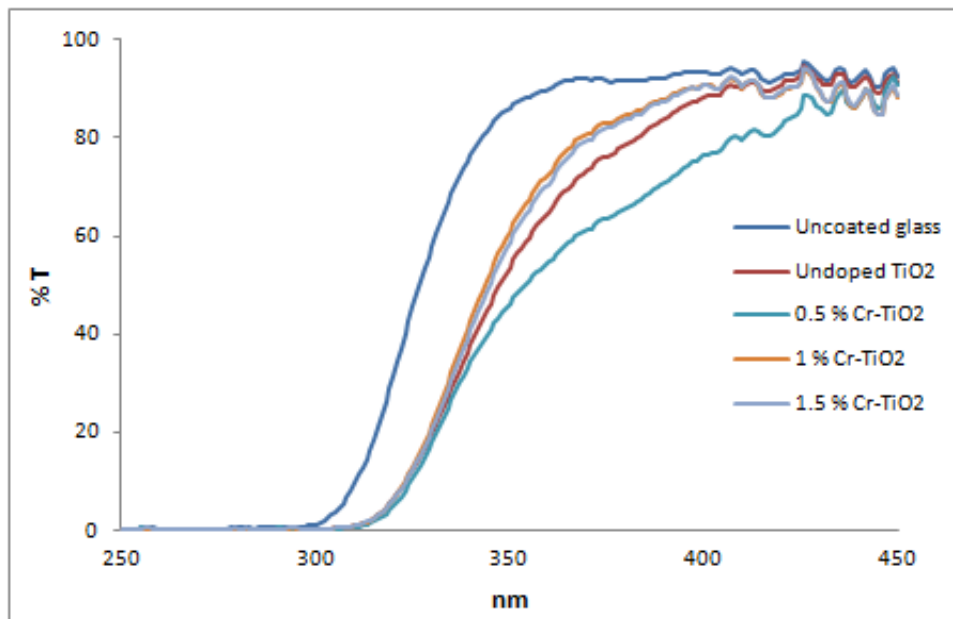


Figure 3.63. Transmission spectra of uncoated SLS glass and SLS glasses coated with undoped TiO₂, 0.5 % Cr-TiO₂, 1 % Cr-TiO₂, 1.5 % Cr-TiO₂

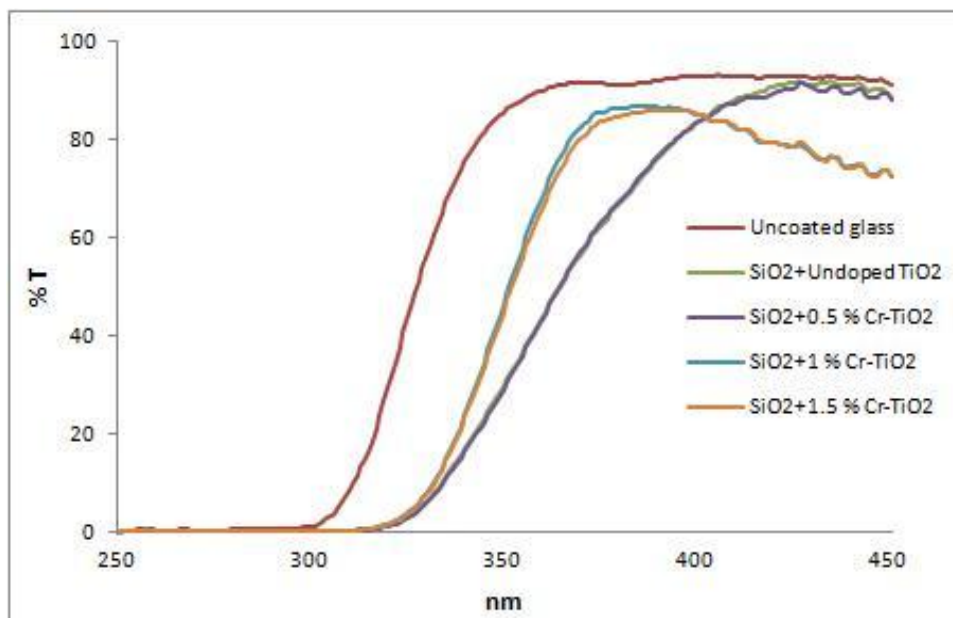


Figure 3.64. Transmission spectra of uncoated SLS glass and SLS glasses coated with SiO₂+undoped TiO₂, SiO₂+0.5 % Cr-TiO₂, SiO₂+1 % Cr-TiO₂, SiO₂+1.5 % Cr-TiO₂

While in the absence of SiO₂ layer Cr dopant does not cause a significant difference at transmittance of SLS glass coated with TiO₂, in the presence of SiO₂ layer 1 % Cr and 1.5 % Cr dopants cause transmittance of SLS glass coated with TiO₂ to reduce remarkably and 0.5 % Cr does not cause a significant difference at transmittance of SLS glass coated with TiO₂ above 400 nm.

In the absence of SiO₂ layer absorption edge of TiO₂ film seems to shift neither to shorter nor to longer wavelength ranges when doped with 0.5 % Cr, 1 % Cr and 1.5 % Cr.

In the presence of SiO₂ layer while absorption edge of TiO₂ film seems to shift to shorter wavelength ranges when doped with 1 % Cr and 1.5 % Cr, 0.5 % Cr causes neither blue nor red shift.

From Figure 3.63 and Figure 3.64 it is also possible to see that undoped TiO₂, 0.5 % Cr doped, 1 % Cr doped and 1.5 % Cr doped TiO₂ films behave like UV blockers and this behaviour becomes stronger when SLS glasses are first coated with SiO₂.

Transmittances of uncoated SLS glass and SLS glasses that were coated with undoped TiO₂, 0.5 % Cr doped, 1 % Cr doped, 1.5 % Cr doped TiO₂ at 350 nm are 86 %, 53 %, 46 %, 61 %, 59 % respectively. Transmittances of uncoated SLS glass and SLS glasses that were first coated with SiO₂ then coated with undoped TiO₂ 0.5 % Cr doped, 1 % Cr doped, 1.5 % Cr doped TiO₂ at 350 nm are 86 %, 31 %, 30 %, 49 %, 47 % respectively.

3.3.2.4. Effect of dopant concentration (0.5 %)

Figure 3.65 shows the transmission spectra of uncoated SLS glass and SLS glasses that were coated with undoped TiO₂, 0.5 % Ag doped TiO₂, 0.5 % Zn doped TiO₂, 0.5 % Cr doped TiO₂ and Figure 3.66 shows the transmission spectra of uncoated SLS glass and SLS glasses first coated with SiO₂ then coated with undoped TiO₂, 0.5 % Ag TiO₂ doped, 0.5 % Zn doped TiO₂, 0.5 % Cr doped TiO₂.

Transmittances of uncoated SLS glass and SLS glasses that were coated with undoped TiO₂, 0.5 % Ag doped, 0.5 % Zn doped, 0.5 % Cr doped TiO₂ at 400 nm and at 450 nm are 93 %, 88 %, 92 %, 77 %, 76 % and 92 %, 91 %, 88 %, 90 %, 91 % respectively.

Transmittances of uncoated SLS glass and SLS glasses that were first coated with SiO₂ then coated with undoped TiO₂, 0.5 % Ag doped, 0.5 % Zn doped, 0.5 % Cr doped TiO₂

at 400 nm and at 450 nm are 93 %, 84 %, 89 %, 88 %, 83 % and 92 %, 88 %, 77 %, 88 % respectively.

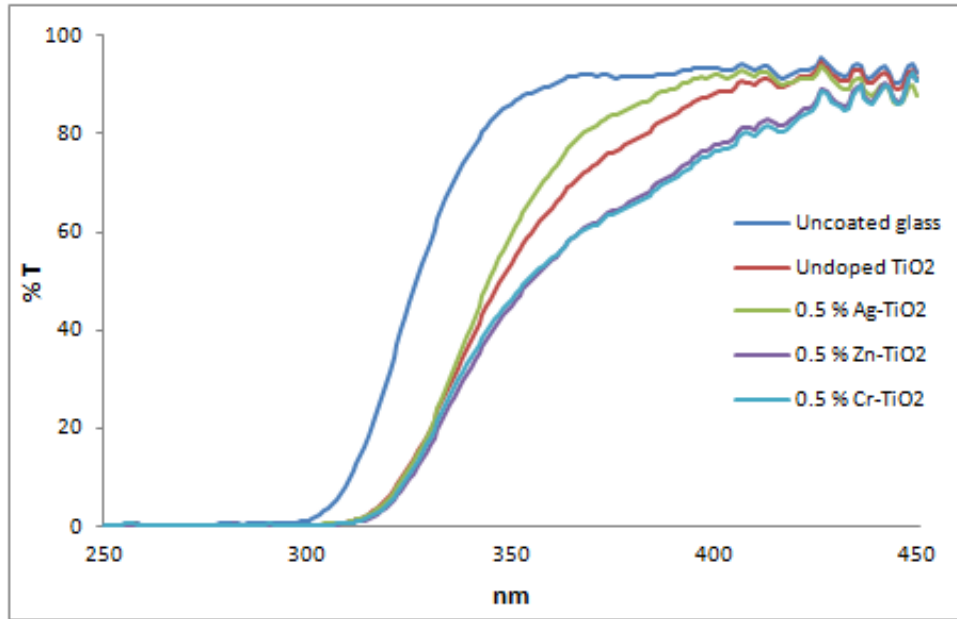


Figure 3.65. Transmission spectra of uncoated SLS glass and SLS glasses coated with undoped TiO_2 , 0.5 % Ag-TiO_2 , 0.5 % Zn-TiO_2 , 0.5 % Cr-TiO_2

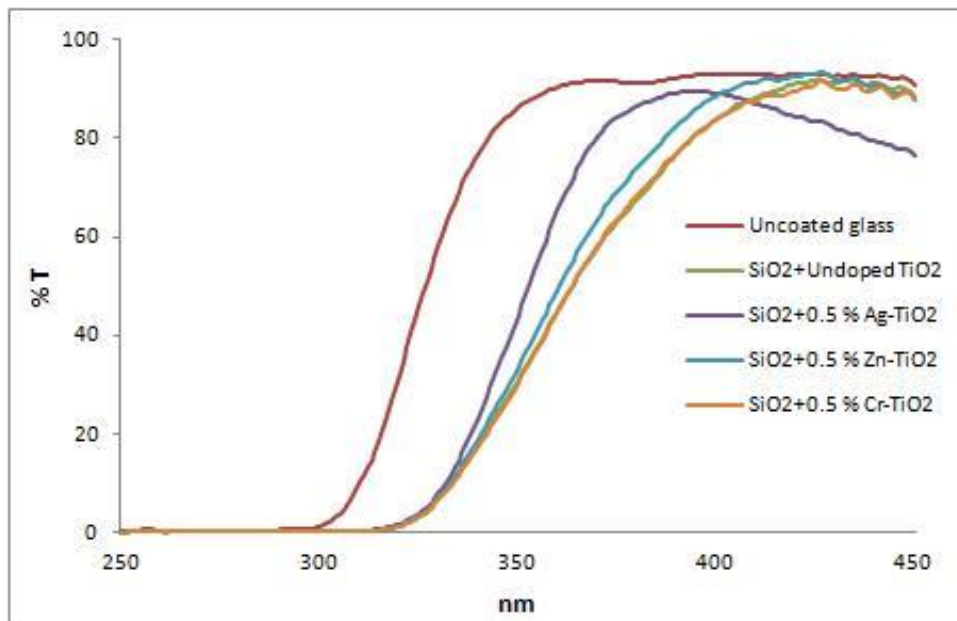


Figure 3.66. Transmission spectra of uncoated SLS glass and SLS glasses coated with SiO_2 + undoped TiO_2 , SiO_2 +0.5 % Ag-TiO_2 , SiO_2 +% 0.5 % Zn-TiO_2 , SiO_2 +% 0.5 % Cr-TiO_2

While in the absence of SiO_2 layer 0.5 % concentration of all three dopants do not cause a significant difference at transmittance of SLS glass coated with TiO_2 , in the presence of SiO_2 layer, 0.5 % Ag dopant causes transmittance of SLS glass coated with TiO_2 to reduce remarkably, 0.5 % Zn and 0.5 % Cr dopants do not cause a significant difference at transmittance of SLS glass coated with TiO_2 above 400 nm.

In the absence of SiO_2 layer, absorption edge of TiO_2 film seems to shift neither to shorter nor to longer wavelength ranges when doped with 0.5 % Ag, 0.5 % Zn and 0.5 % Cr. In the presence of SiO_2 layer, while absorption edge of TiO_2 film seems to shift to shorter wavelength ranges when doped with 0.5 % Ag and 0.5 % Zn, 0.5 % Cr causes neither blue nor red shift.

3.3.2.5. Effect of dopant concentration (1 %)

Figure 3.67 shows the transmission spectra of uncoated SLS glass and SLS glasses that were coated with undoped TiO_2 , 1 % Ag doped TiO_2 , 1 % Zn doped TiO_2 , 1 % Cr doped TiO_2 and Figure 3.68 shows the transmission spectra of uncoated SLS glass and SLS glasses first coated with SiO_2 then coated with undoped TiO_2 , 1 % Ag doped TiO_2 , 1 % Zn doped TiO_2 , 1 % Cr doped TiO_2 .

Transmittances of uncoated SLS glass and SLS glasses that were first coated with SiO_2 then coated with undoped TiO_2 , 1 % Ag doped, 1 % Zn doped, 1 % Cr doped TiO_2 at 400 nm and at 450 nm are 93 %, 84 %, 89 %, 88 %, 85 % and 92 %, 88 %, 78 %, 74 %, 72 % respectively. While in the absence of SiO_2 layer 1 % concentration of all three dopants do not cause a significant difference at transmittance of SLS glass coated with TiO_2 , in the presence of SiO_2 layer 1 % concentration of all three dopants cause transmittance of SLS glass coated with TiO_2 to reduce above 400 nm.

Transmittances of uncoated SLS glass and SLS glasses that were coated with undoped TiO_2 , 1 % Ag doped, 1 % Zn doped, 1 % Cr doped TiO_2 at 400 nm and at 450 nm are 93 %, 88 %, 92 %, 93 %, 90 % and 92 %, 91 %, 88 %, 88 %, 88 % respectively.

In the presence of SiO_2 layer absorption edge of TiO_2 film seems to shift to shorter wavelength ranges when doped with 1 % Ag, 1 % Zn and 1 % Cr while in the absence of SiO_2 layer, absorption edge of TiO_2 film seems to shift neither to shorter nor to longer wavelength ranges when doped with 1 % Ag, 1 % Zn and 1 % Cr.

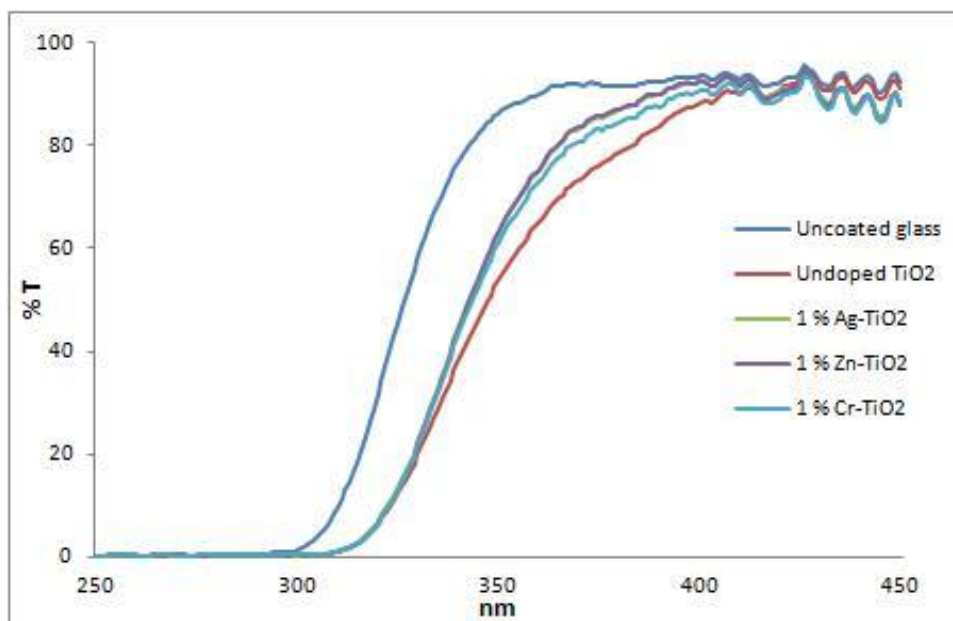


Figure 3.67. Transmission spectra of uncoated SLS glass and SLS glasses coated with undoped TiO_2 , 1 % Ag-TiO_2 , 1 % Zn-TiO_2 , 1 % Cr-TiO_2

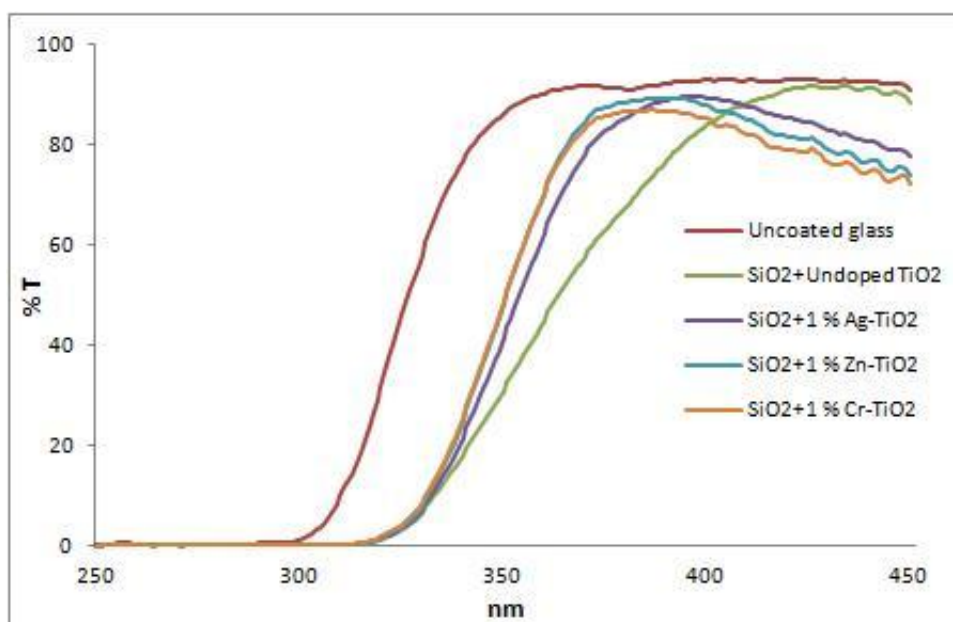


Figure 3.68. Transmission spectra of uncoated SLS glass and SLS glasses coated with SiO_2 + undoped TiO_2 , SiO_2 +1 % Ag-TiO_2 , SiO_2 +1 % Zn-TiO_2 , SiO_2 +1 % Cr-TiO_2

3.3.2.6. Effect of dopant concentration (1.5 %)

Figure 3.69 shows the transmission spectra of uncoated SLS glass and SLS glasses that were coated with undoped TiO_2 , 1.5 % Ag doped, 1.5 % Zn doped, 1.5 % Cr doped TiO_2 and Figure 3.70 shows the transmission spectra of uncoated SLS glass and SLS glasses first coated with SiO_2 then coated with undoped TiO_2 , 1.5 % Ag doped TiO_2 , 1.5 % Zn doped TiO_2 , 1.5 % Cr doped TiO_2 .

Transmittances of uncoated SLS glass and SLS glasses that were coated with undoped TiO_2 , 1.5 % Ag doped, 1.5 % Zn doped, 1.5 % Cr doped TiO_2 at 400 nm and at 450 nm are 93 %, 88 %, 93 %, 92 %, 90 % and 92 %, 91 %, 88 %, 88 %, 88 % respectively.

Transmittances of uncoated SLS glass and SLS glasses that were first coated with SiO_2 then coated with undoped TiO_2 , 1.5 % Ag doped, 1.5 % Zn doped, 1.5 % Cr doped TiO_2 at 400 nm and at 450 nm are 93 %, 84 %, 83 %, 88 %, 85 % and 92 %, 88 %, 70 %, 74 %, 72 % respectively.

While in the absence of SiO_2 layer 1.5 % concentration of all three dopants do not cause a significant difference at transmittance of SLS glass coated with TiO_2 , in the presence of SiO_2 layer 1.5 % concentration of all three dopants cause transmittance of SLS glass coated with TiO_2 to reduce above 400 nm.

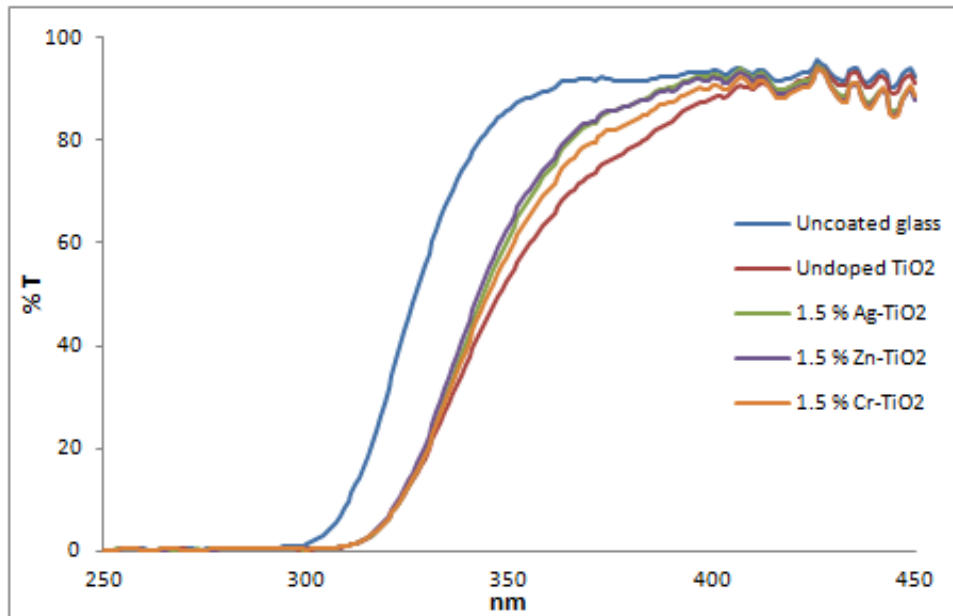


Figure 3.69. Transmission spectra of uncoated SLS glass and SLS glasses coated with undoped TiO_2 , 1.5 % Ag- TiO_2 , 1.5 % Zn- TiO_2 , 1.5 % Cr- TiO_2

In the presence of SiO₂ layer absorption edge of TiO₂ film seems to shift to shorter wavelength ranges when doped with 1.5 % Ag, 1.5 % Zn and 1.5 % Cr while in the absence of SiO₂ layer absorption edge of TiO₂ film seems to shift neither to shorter nor to longer wavelength ranges when doped with 1.5 % Ag, 1.5 % Zn and 1.5 % Cr.

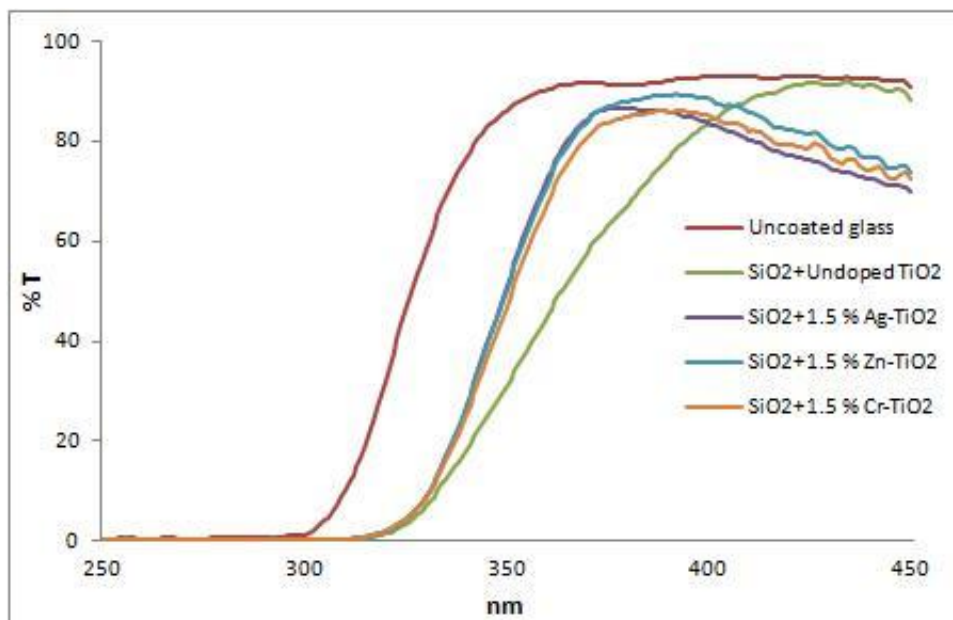


Figure 3.70. Transmission spectra of uncoated SLS glass and SLS glasses coated with SiO₂+undoped TiO₂, SiO₂+1.5 % Ag-TiO₂, SiO₂+1.5 % Zn-TiO₂, SiO₂+1.5 % Cr-TiO₂

3.4. Testing The Photocatalytical Activity Of TiO₂ Films

3.4.1. Choosing proper conditions for photocatalytic activity testing

To choose the sintering temperature, withdrawal speed and pH of Rhodamine B solution at which the TiO₂ film shows the highest photocatalytic activity, a number of experiments were done before studying the effects of dopants and dopant amounts on photocatalytic activity of TiO₂ film.

In the first part of this study sintering temperature and withdrawal speed were chosen constant as 400 °C and 12 cm/min. respectively and the effect of pH of Rhodamine B solution on photocatalytic activity was studied.

In literature there are studies recording the effect of Rhodamine B's pH on photocatalytic activity; Jain and his friends studied the photocatalytic degradation of Rhodamine B in the pH range of 4-11 and they found that degradation rate remained

constant from pH 2 to 6.7 and then started to increase. Finally they concluded that neutral and alkaline media had a positive effect on photocatalytic degradation [146].

Soares and his friends reported a study about process variables for the photocatalytic degradation of Rhodamine B. They prepared Rhodamine B solution with a concentration of 20 mg/L and measured pH of this solution as 4.3. Besides this neutral pH value, they studied pH 6, 7, 9, 10 and 12. 0.01 mol/L NaOH solution was used for pH adjustment. They found out that when pH was within the range of 6 to 10 the degradation rate of Rhodamine B was not affected significantly. However when the pH fell below 6 or increased above 10, the reaction rate was reduced approximately by 28 % [147].

Li and his friends studied photoelectrocatalytic degradation of Rhodamine B at different pH values including 2, 4, 6, 8 and 10. Their experimental results showed that photoelectrocatalytic degradation rate of Rhodamine B increased by increasing pH. They claimed that the first reason for that was the significant effect of pH value on the adsorption behaviour of the organic dye on the catalyst surface; Since the point of zero charge of TiO_2 is known to be at pH 6.4, it is possible to say that TiO_2 surface is positively charged when the pH of the media is less than 6.4 and is negatively charged when the pH of the media is greater than 6.4.

It was also reported that when the pH value of Rhodamine B is below 4 Rhodamine B is in the cationic form, while it is in the zwitterionic form when its pH is greater than 4. When Rhodamine B is in cationic form, its adsorption on the catalyst surface becomes difficult because of an electrostatic repulsive force. On the other hand when Rhodamine is in zwitterionic form it is reported that a certain part of the molecule is attracted by the catalyst surface due to the electrostatic attraction.

Secondly Li and his friends mentioned that by increasing the pH value of the Rhodamine B, photocatalytic degradation rate was increased due to the modification of the position of TiO_2 conduction band and due to the raising the oxidizing ability of photogenerated holes [148]. It should also be noted that during photocatalysis, adsorption of the Rhodamine B on the TiO_2 surface can occur via positively charged diethylamino group (alkylamine adsorption) or negatively charged carboxyl group (carboxyl adsorption). As mentioned above for carboxyl adsorption Rhodamine B

should be in cationic form and TiO_2 should be positively charged ($\text{pH} < 6.4$), for alkylamine adsorption, Rhodamine B should be in zwitterionic form and TiO_2 should be negatively charged ($\text{pH} > 6.4$). It is important that the Rhodamine B adsorbs via its diethylamino or carboxyl group since active oxygen species mostly produced near the adsorption site and these active oxygen species attack the nearer organic groups which are carboxyl groups for carboxyl adsorption and diethylamino groups for alkylamine adsorption [148]. When carboxyl groups are attacked by active oxygen species, ring cleavage occurs and when diethylamino groups are attacked by active oxygen species deethylation occurs which is the rate limiting process for photocatalytic degradation of Rhodamine B [149].

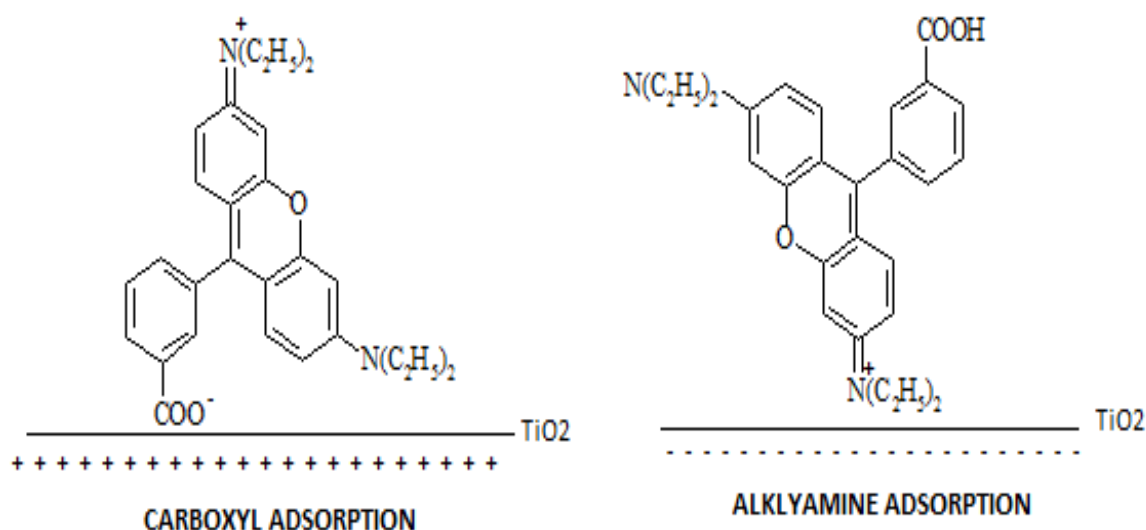


Figure 3.71. Adsorption mechanism of Rhodamine B on TiO_2 surface.

In this study 2 ppm Rhodamine B solution was prepared for photocatalytic activity studies. The natural pH of 2 ppm Rhodamine B was measured approximately 5. Taking results of studies reported in literature into consideration 9 was chosen as the second pH value of Rhodamine B and adjustment was made by anhydrous NaOH. Looking at the Figure 3.72 it is obviously seen that photocatalytic degradation rate increased by increasing the pH of the Rhodamine B. As a result of this study 9 was chosen as the pH of Rhodamine B solution.

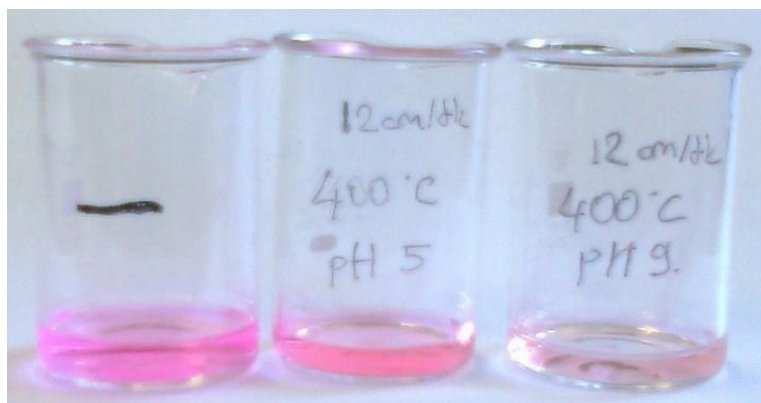


Figure 3.72. Rhodamine B solutions with different pHs after 15 hours radiation, withdrawal speed=12 cm/min, sintering temperature=400 °C (left to right: unirradiated Rhodamine B, Rhodamine B whose pH is 5, Rhodamine B whose pH is 9)

In the second part of this study; glass samples that were coated with undoped TiO_2 are sintered at the same temperatures that were studied at XRD analysis except 600 °C, 650 °C, 700 °C and 800 °C since it is shown at Section 3.5.2.8 that the glasses that was sintered at the temperatures above 550 °C was bended. In this study withdrawal speed was chosen constant as 12 cm/min taking the preliminary study mentioned in “Section 2.2.6 Coating SLS glasses with SiO_2 to prevent Na^+ diffusion” as a reference and pH of Rhodamine B solution was adjusted to 9 as the result of the first part of this study.

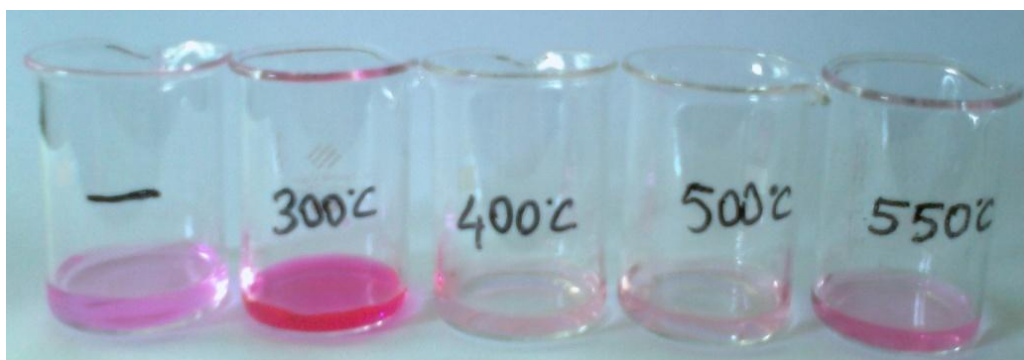


Figure 3.73. Rhodamine B solution after 15 hours radiation, withdrawal speed=12 cm/min, pH of Rhodamine B solution=9 (left to right: unirradiated Rhodamine B, Rhodamine B belongs to the SLS glass sintered at 300 °C, Rhodamine B belongs to the SLS glass sintered at 400 °C, Rhodamine B belongs to the SLS glass sintered at 500 °C, Rhodamine B belongs to the SLS glass sintered at 550 °C)

Looking at the Figure 3.73 which shows the photocatalytic activity test results of SLS glass samples that were coated with undoped TiO_2 at a constant withdrawal speed (12 cm/min) and sintered at four different temperatures (300 °C, 400 °C, 500 °C, 550 °C) it can be seen that the worst sintering temperature for degradation of Rhodamine B is 300 °C. When 300 °C is chosen as sintering temperature the color of rhodamine B becomes darker after radiation. It is because of that at 300 °C TiO_2 film is still amorphous.

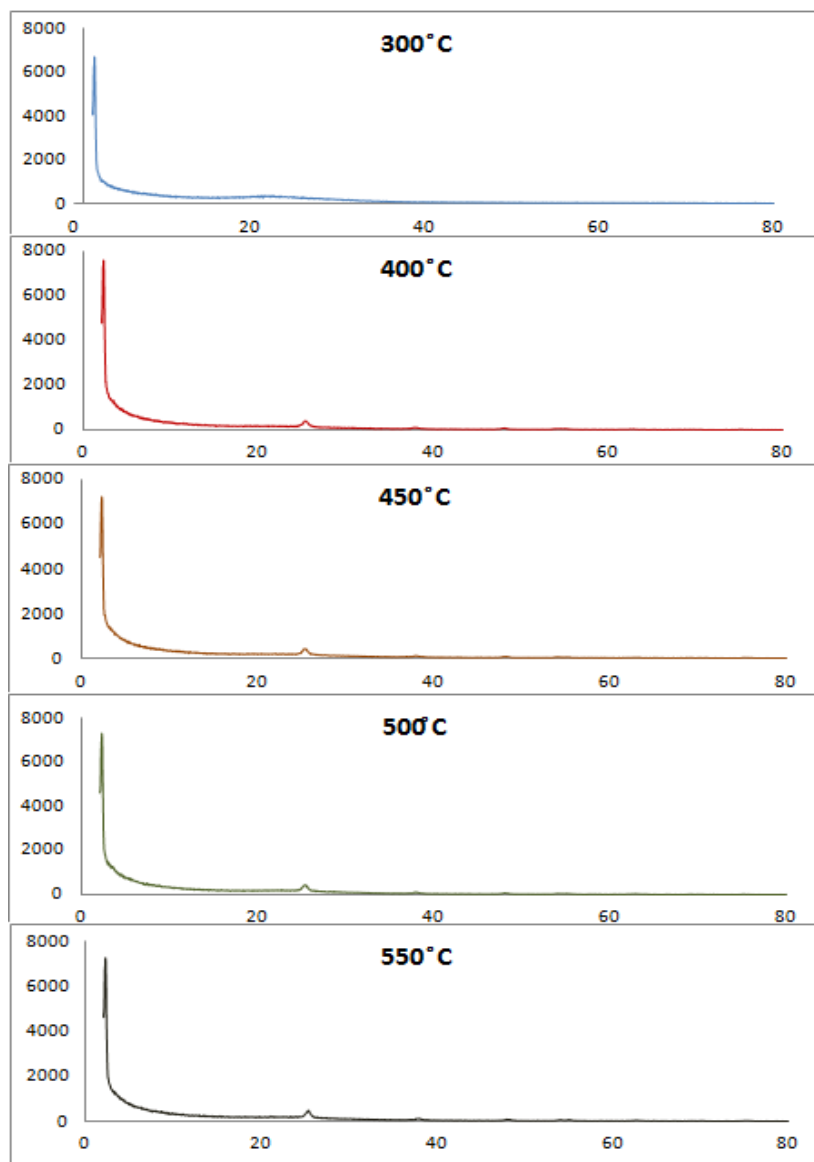


Figure 3.74. Film analysis of undoped TiO_2 coated SLS glasses (sintering temperatures from top to bottom: 300 °C, 400 °C, 500 °C, 550 °C)

Film analysis of SLS glasses coated with undoped TiO_2 and sintered at 300 °C, 400 °C, 500 °C, 550 °C can be seen in Figure 3.74 which also shows that transformation to anatase phase occurs at 400 °C where the best photocatalytic activity is seen and that at 300 °C, TiO_2 film is still amorphous. Looking at Figure 3.38 it can further be said that when sintering temperature is chosen 500 °C a slightly worse and when sintering temperature is chosen 550 °C a considerably worse result is got compared to the Rhodamine B degradation result at sintering temperature of 400 °C. This can not be explained by phase type of TiO_2 film since it is obvious from Figure 3.75 that at all three sintering temperatures, TiO_2 film consists of only anatase phase. This result shows that phase type of TiO_2 film is not the only parameter that affects photocatalytic activity. According to the results of this study 400 °C was chosen as sintering temperature.

After choosing 400 °C as sintering temperature, film analysis is done also for the SLS glasses coated with 0.5 % Ag, 1 % Ag, 1.5 % Ag, 0.5 % Zn, 1 % Zn, 1.5 % Zn, 0.5 % Cr, 1 % Cr, 1.5 % Cr doped TiO_2 solution and sintered at 400 °C for 1 hour. From Figure 3.38, it can be seen that all doped TiO_2 films consist of anatase phase as undoped TiO_2 film.

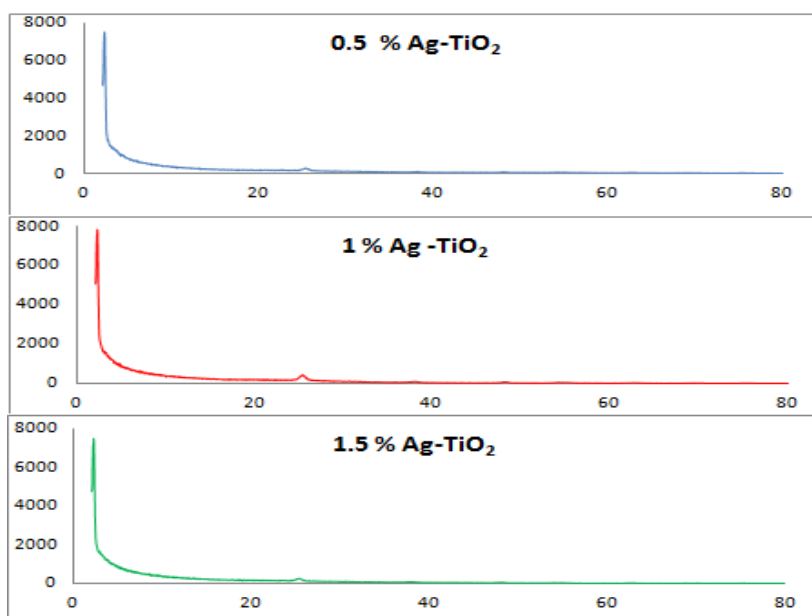


Figure 3.75. Film analysis of 0.5 % Ag-TiO₂, 1 % Ag-TiO₂, 1.5 % Ag-TiO₂, 0.5 % Zn-TiO₂, 1 % Zn-TiO₂, 1.5 % Zn-TiO₂, 0.5 % Cr-TiO₂, 1 % Cr-TiO₂, 1.5 % Cr-TiO₂ at 400 °C sintering temperature.

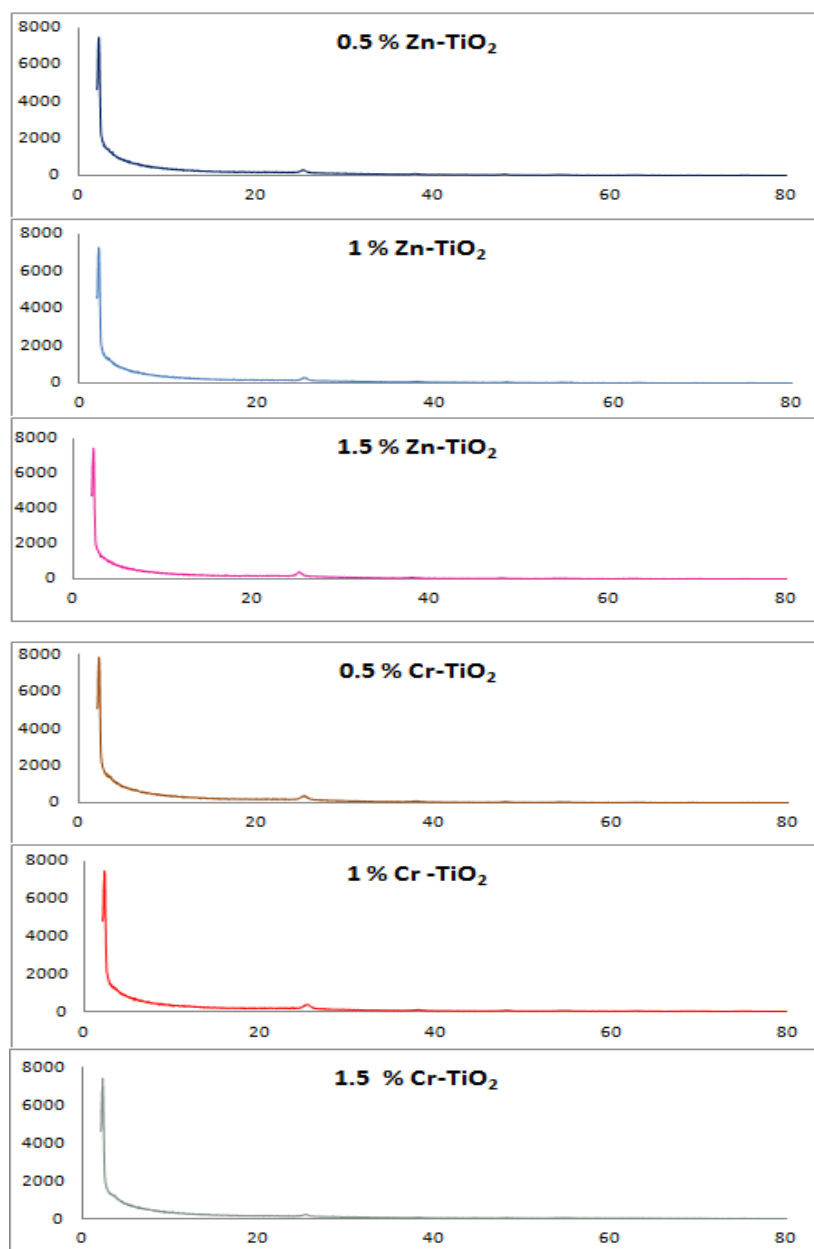


Figure 3.75. Continues

Finally in the last part of this study, effect of withdrawal speed on photocatalytic activity was studied by taking sintering temperature (400 °C) and pH of Rhodamine B solution (9) constant as discussed in the first and second part of this preliminary study.

Since it was mentioned in “Section 2.2.6 Coating SLS glasses with SiO₂ to prevent Na⁺ diffusion” glass samples that were coated with a withdrawal speed of 18 cm/min, 21 cm/min, 24 cm/min had some crackings on their surface after sintering process withdrawal speeds of 18 cm/min, 21 cm/min and 24 cm/min, were not studied in this

part of the study again. Comparison of the withdrawal speeds (12 cm/min and 15 cm/min) that were studied in this part of the study can be seen at Figure 3.76 .

Looking at the Figure 3.76 it is obvious that when withdrawal rate is chosen 15 cm/min, photocatalytic activity is much more better than the photocatalytic activity when withdrawal speed is chosen 12 cm/min since as mentioned in section “1.1.3. Dip coating process” The coating thickness increases by increasing the withdrawal speed.



Figure 3.76. Rhodamine B solution after 15 hours radiation, sintering temperature=400 °C, pH of Rhodamine B solution=9. (left to right: unradiated Rhodamine B, Rhodamine B belongs to the SLS glass coated with a withdrawal speed of 12 cm/min, Rhodamine B belongs to the SLS glass coated with a withdrawal speed of 15 cm/min)

At the end of this preliminary study it was found out that it was possible to have the best photocatalytic activity when pH of Rhodamine B Solution was chosen 9, sintering temperature was chosen 400 °C and withdrawal speed was chosen 15 cm/min and these values are decided to be used while examining the effects of dopants and dopant amounts on photocatalytic activity of TiO₂.

3.4.2. Examination the effects of dopants

Before examination the effect of dopants on photocatalytic activity of undoped TiO₂ film, uncoated SLS glass was radiated in Rhodamine B solution to find out what will happen to a SLS glass without a TiO₂ coating.



Figure 3.77. Unradiated Rhodamine B and Rhodamine B in which uncoated SLS glass is radiated for 15 hours.

Figure 3.77 shows the color of unirradiated Rhodamine B and Rhodamine B in which uncoated SLS glass was radiated for 15 hours. It is obvious that when not coated with TiO_2 , SLS glass causes the color of Rhodamine B to become darker and Figure 3.78 shows that while absorbance value of unirradiated Rhodamine B is 0.443, it increases to 1.314 when an uncoated SLS glass is radiated within Rhodamine B.

Figure 3.79 shows uncoated SLS glass, uncoated SLS glass after 15 hours UV irradiation in Rhodamine B and TiO_2 coated SLS glass after 15 hours UV irradiation in Rhodamine B. It is so obvious that when not coated with TiO_2 , SLS glass becomes dirty while it stays clean when coated with TiO_2 .

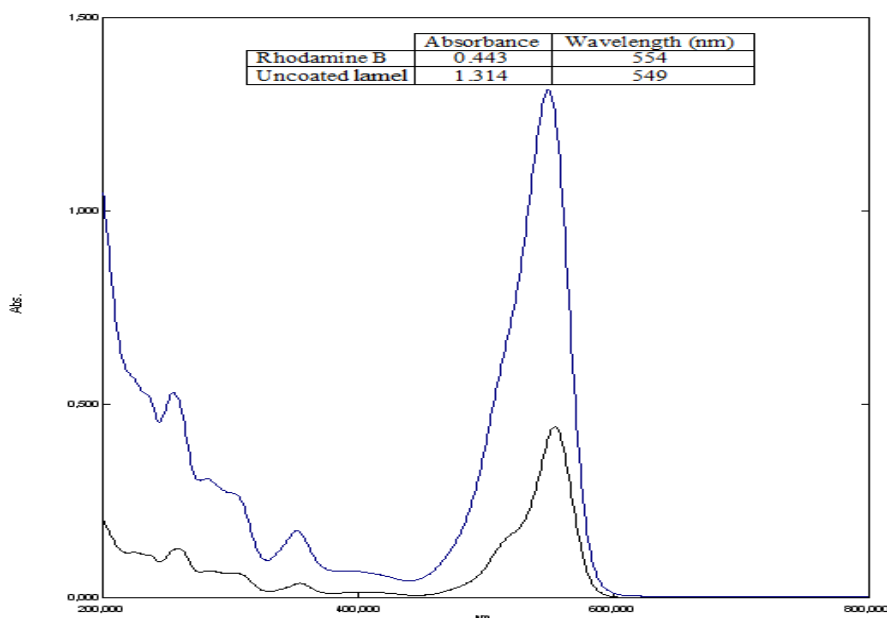


Figure 3.78. Absorbance measurements of unirradiated Rhodamine B and Rhodamine B which belongs to uncoated SLS glass radiated for 15 hours.

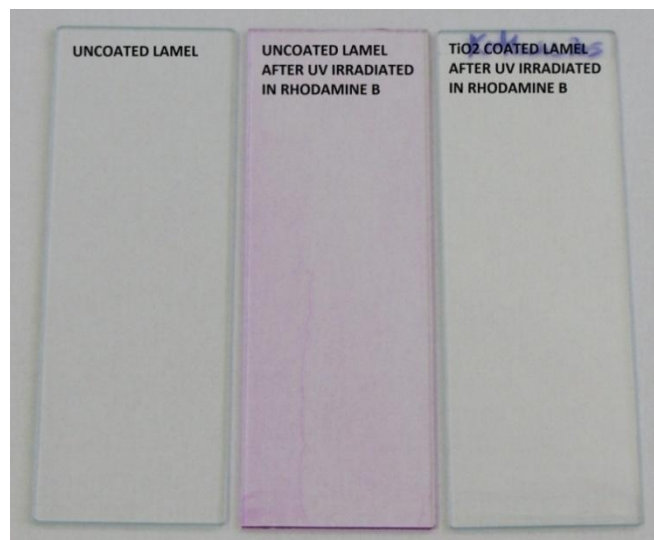


Figure 3.79. Uncoated SLS glass, uncoated SLS glass after 15 hours UV irradiation in Rhodamine B, TiO_2 coated SLS glass after 15 hours UV irradiation in Rhodamine B.

3.4.2.1. Effect of Ag dopant

Figure 3.80, Figure 3.81 and Figure 3.82 show unirradiated Rhodamine B solution and Rhodamine B solutions in which SLS glasses coated with undoped TiO_2 , 0.5 % Ag doped TiO_2 , 1 % Ag doped TiO_2 , 1.5 % Ag doped TiO_2 were radiated for 10, 15 and 20 hours respectively.

When SLS glasses coated with undoped TiO_2 , 0.5 % Ag doped TiO_2 , 1 % Ag doped TiO_2 , 1.5 % Ag doped TiO_2 are radiated within Rhodamine B solution for 10 hours Rhodamine B starts to discolorate and after 20 hours radiation Rhodamine B nearly loses its pink color. Looking at Figure 3.38, 3.39 and 3.40, it is possible to say that doping TiO_2 with Ag slightly increases photocatalytic activity when the concentration of Ag is chosen 0.5 %, 1 % and 1.5 %.

Figure 3.83 shows absorption values of unirradiated Rhodamine B solution and Rhodamine B solutions in which SLS glasses coated with undoped TiO_2 , 0.5 % Ag doped TiO_2 , 1 % Ag doped TiO_2 , 1.5 % Ag doped TiO_2 were radiated for 15 hours.

Maximum absorption of unirradiated Rhodamine B solution is measured 0.443 at 554 nm. Absorbance values of Rhodamine B solutions in which SLS glasses coated with undoped TiO_2 , 0.5 % Ag doped TiO_2 , 1 % Ag doped TiO_2 , 1.5 % Ag doped TiO_2 were radiated for 15 hours are 0.079 at 533 nm, 0.057 at 533 nm, 0.054 at 531 nm and 0.065

at 534 nm respectively. Blue shift in maximum absorption peak that occurs due to N-deethylation of Rhodamine B [149] can be seen at undoped, 0.5 % Ag doped TiO_2 , 1 % Ag doped TiO_2 and 1.5 % Ag doped TiO_2 .

These results show that all three concentrations of Ag dopant cause photocatalytic activity of TiO_2 to increase slightly. Changing the concentration of Ag dopant from 0.5 % to 1.5 % also causes a slight change at the photocatalytic activity of TiO_2 . It is possible to say that 1 % is the optimum concentration of Ag dopant to have the best photocatalytic activity. Besides, Figure 3.83 shows that maximum absorption of Rhodamine B shifted from 554 nm to 531 nm when within undoped TiO_2 , 0.5 % Ag doped TiO_2 , 1 % Ag doped TiO_2 and 1.5 % Ag doped TiO_2 coated SLS glasses were radiated for 15 hours.



Figure 3.80. After 10 hours radiation (left to right: unradiated Rhodamine B, Rhodamine B belongs to undoped TiO_2 , 0.5 % Ag- TiO_2 , 1 % Ag- TiO_2 , 1.5 % Ag- TiO_2)



Figure 3.81. After 15 hours radiation (left to right: unradiated Rhodamine B, Rhodamine B belongs to undoped TiO_2 , 0.5 % Ag- TiO_2 , 1 % Ag- TiO_2 , 1.5 % Ag- TiO_2)

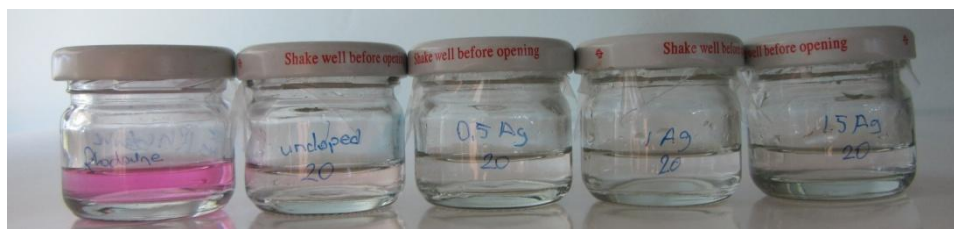


Figure 3.82. After 20 hours radiation (left to right: unradiated Rhodamine B, Rhodamine B belongs to undoped TiO_2 , 0.5 % Ag- TiO_2 , 1 % Ag- TiO_2 , 1.5 % Ag- TiO_2)

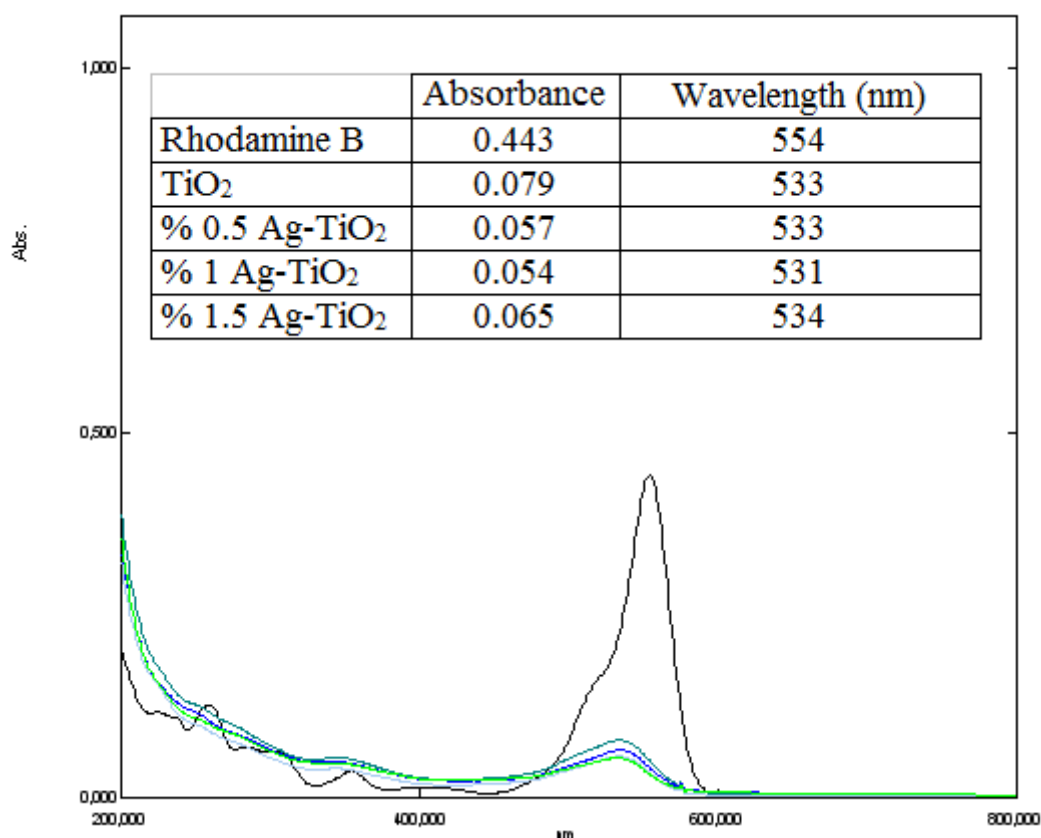


Figure 3.83. Absorbance measurement after 15 hours radiation (Ag dopant)

It was discussed in Sections 3.1.3.1 and 3.1.5 respectively that doping with Ag decreases the anatase grain size and this reduction at anatase grain size causes the specific surface area of doped TiO₂ to increase and it is a known fact that the higher the surface area the higher the photocatalytic activity [76].

Also at Section 3.1.3.1, it was explained that due to its larger ionic radius (ca. 129 pm) compared to ionic radius of Ti⁴⁺ (ca. 74.5 pm), Ag can not enter into the lattice of TiO₂ and deposited on the surface of TiO₂. These Ag particles deposited on the surface of TiO₂ act as electron hole separation centers. Photogenerated electrons transfer from the conduction band of TiO₂ to these metallic silver particles deposited on the surface of TiO₂.

Then these Ag particles react with the adsorbed O₂ or Ti⁴⁺ and form reactive species; O₂⁻ and Ti³⁺. Adsorbed O₂ can also play a role in the formation of other active species such as H₂O₂ and HO₂⁻ which promote photocatalytic activity.

Since electron-hole recombination is being inhibited by Ag doping, the holes at valance band can react with the water molecules adsorbed on TiO_2 surface to form hydroxyl radicals which play an important role in photocatalytic degradation mechanism.

However it should be noted that when concentration of Ag is increased it starts behaving exactly the opposite way and becomes an electron-hole recombination center.

One other reason for that the higher concentrations of Ag inhibits photocatalytic activity is that it can prevent the contact of TiO_2 with the organic molecule, which is wanted to be degraded, by covering the surface of TiO_2 and so by increasing the diffusion distance [75, 85, 87, 150].

3.4.2.2. Effect of Zn dopant

Figure 3.84, Figure 3.85 and Figure 3.86 show unirradiated Rhodamine B solution and Rhodamine B solutions in which SLS glasses coated with undoped TiO_2 , 0.5 % Zn doped TiO_2 , 1 % Zn doped TiO_2 , 1.5 % Zn doped TiO_2 were radiated for 10, 15 and 20 hours respectively.

Between undoped, 0.5 % Zn doped, 1 % Zn doped and 1.5 % Zn doped TiO_2 films, undoped TiO_2 film seems to be the best that causes Rhodamine B to discolorate. While doping TiO_2 with Zn does not seem to fasten the discoloration of Rhodamine B, comparing the three concentrations of Zn dopant, it is possible to say that 1 % is the optimum concentration that nearly catches the discoloration effect of undoped TiO_2 .

Figure 3.87 shows absorption of unirradiated Rhodamine B solution and Rhodamine B solutions in which SLS glasses coated with undoped TiO_2 , 0.5 % Zn doped TiO_2 , 1 % Zn doped TiO_2 , 1.5 % Zn doped TiO_2 were radiated for 15 hours. Maximum absorption of unirradiated Rhodamine B solution was measured 0.443 at 554 nm. Absorbance values of Rhodamine B solutions in which SLS glasses coated with undoped TiO_2 , 0.5 % Zn doped TiO_2 , 1 % Zn doped TiO_2 , 1.5 % Zn doped TiO_2 were radiated for 15 hours are 0.079 at 533 nm, 0.240 at 541 nm, 0.104 at 541 nm and 0.130 at 539 nm respectively.

Blue shift in maximum absorption peak that occurs due to N-deethylation of Rhodamine B [149] can be seen at undoped, 0.5 % Zn doped TiO_2 , 1 % Zn doped TiO_2 and 1.5 % Zn doped TiO_2 .



Figure 3.84. After 10 hours radiation (left to right: unradiated Rhodamine B, Rhodamine B belongs to undoped TiO_2 , 0.5 % Zn- TiO_2 , 1 % Zn- TiO_2 , 1.5 % Zn- TiO_2)



Figure 3.85. After 15 hours radiation (left to right: unradiated Rhodamine B, Rhodamine B belongs to undoped TiO_2 , 0.5 % Zn- TiO_2 , 1 % Zn- TiO_2 , 1.5 % Zn- TiO_2)



Figure 3.86. After 20 hours radiation (left to right: unradiated Rhodamine B, Rhodamine B belongs to undoped TiO_2 , 0.5 % Zn- TiO_2 , 1 % Zn- TiO_2 , 1.5 % Zn- TiO_2)

Results of XRD and BET analysis discussed in Sections 3.1.3.5 and 3.1.5 showed that anatase crystallite size of TiO_2 (12 nm) decreased when TiO_2 is doped with 1 % Zn (10.63 nm) and 1.5 % Zn (10.21 nm) and slightly increased when doped with 0.5 % Zn (12.29 nm). Crystallite size and specific surface area are known to be two important parameters that affect photocatalytic activity. Especially crystallite size is believed to have a great influence on recombination rate of electron hole pairs [126]. With regard to these ideas and XRD and BET results of undoped and Zn doped TiO_2 powders it was expected that Zn dopant would slightly increase the photocatalytic activity [73,77] instead of decreasing it.

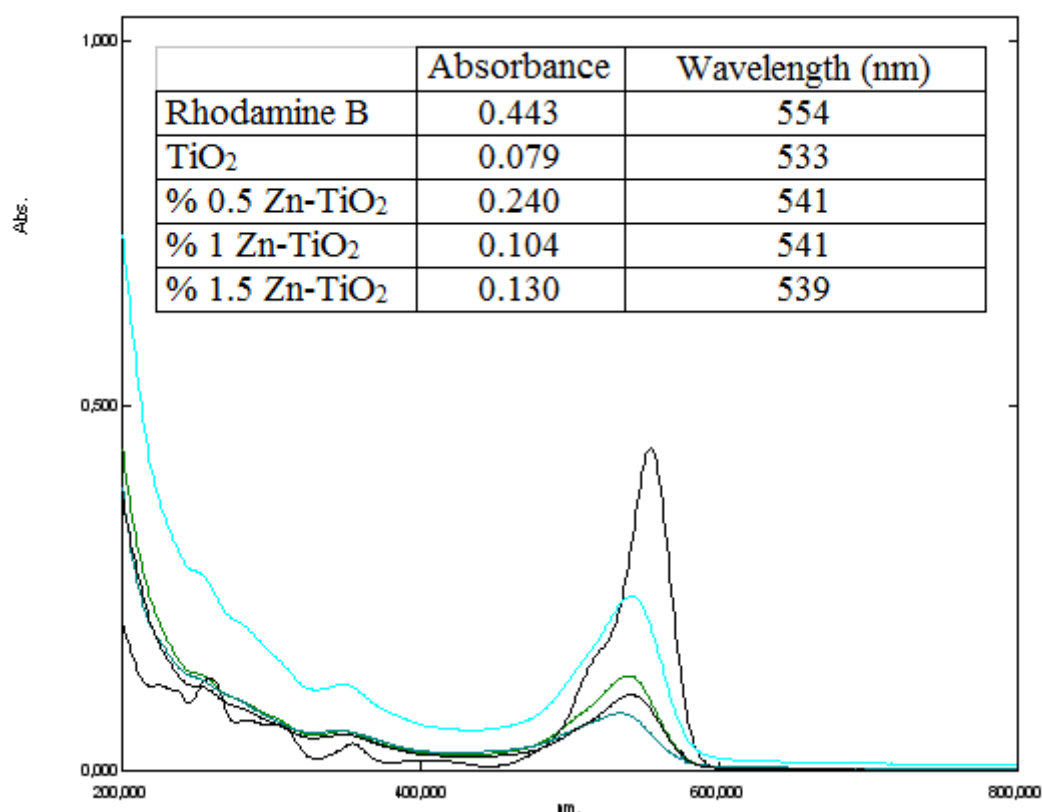


Figure 3.87. Absorbance measurement after 15 hours radiation (Zn dopant)

3.4.2.3. Effect of Cr dopant

Figure 3.88, Figure 3.89 and Figure 3.90 show unirradiated Rhodamine B solution and Rhodamine B solutions in which SLS glasses coated with undoped TiO₂, 0.5 % Cr doped TiO₂, 1 % Cr doped TiO₂, 1.5 % Cr doped TiO₂ were radiated for 10, 15 and 20 hours respectively.

When SLS glasses coated with 0.5 % Cr doped TiO₂, 1 % Cr doped TiO₂, 1.5 % Cr doped TiO₂ are radiated within Rhodamine B for 10 hours, the color of Rhodamine B solution seems to be darkened. After 15 hours radiation discoloration starts at Rhodamine B solutions which belong to SLS glasses coated with 0.5 % Cr and 1 % Cr doped TiO₂.

At the end of 20 hours radiation, colors of Rhodamine B solutions in which SLS glasses coated with 0.5 % Cr doped TiO₂, 1 % Cr doped TiO₂, 1.5 % Cr doped TiO₂ radiated are darkened considerably and also colors of Rhodamine B solutions in which SLS

glasses coated with 0.5 % Cr doped TiO₂, 1 % Cr doped TiO₂ radiated changed from pink to pinkish orange.



Figure 3.88. After 10 hours radiation (left to right: unradiated Rhodamine B, Rhodamine B belongs to undoped TiO₂, 0.5 % Cr-TiO₂, 1 % Cr-TiO₂, 1.5 % Cr-TiO₂)

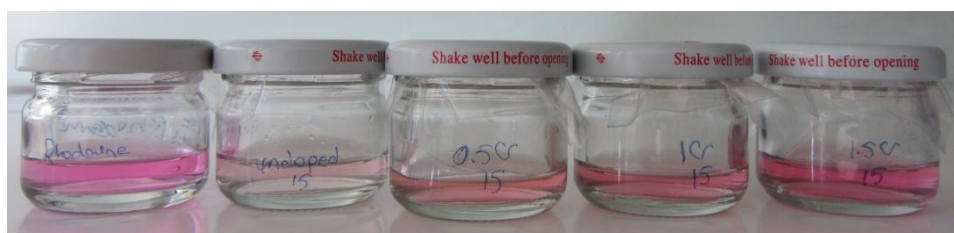


Figure 3.89. After 15 hours radiation (left to right: unradiated Rhodamine B, Rhodamine B belongs to undoped TiO₂, 0.5 % Cr-TiO₂, 1 % Cr-TiO₂, 1.5 % Cr-TiO₂)



Figure 3.90. After 20 hours radiation (left to right: unradiated Rhodamine B, Rhodamine B belongs to undoped TiO₂, 0.5 % Cr-TiO₂, 1 % Cr-TiO₂, 1.5 % Cr-TiO₂)

Figure 3.91 shows absorption of unradiated Rhodamine B solution and Rhodamine B solutions in which SLS glasses coated with undoped TiO₂, 0.5 % Cr doped TiO₂, 1 % Cr doped TiO₂, 1.5 % Cr doped TiO₂ were radiated for 15 hours. Maximum absorption of unradiated Rhodamine B solution was measured 0.443 at 554 nm. Absorbance values of Rhodamine B solutions in which SLS glasses coated with undoped TiO₂, 0.5 % Cr doped TiO₂, 1 % Cr doped TiO₂, 1.5 % Cr doped TiO₂ were radiated for 15 hours are 0.079 at 533 nm, 0.344 at 526 nm, 0.374 at 530 nm and 0.396 at 535 nm respectively.

Although absorbance values of Rhodamine B solutions in which SLS glasses coated with TiO₂, 0.5 % Cr doped TiO₂, 1 % Cr doped TiO₂, 1.5 % Cr doped TiO₂ were

radiated for 15 hours are not as low as the absorbance value of Rhodamine B solution in which SLS glass coated with undoped TiO_2 was radiated for 15 hours, still a blue shift can be seen at maximum absorption peak that occurs due to N-deethylation of Rhodamine B [149].

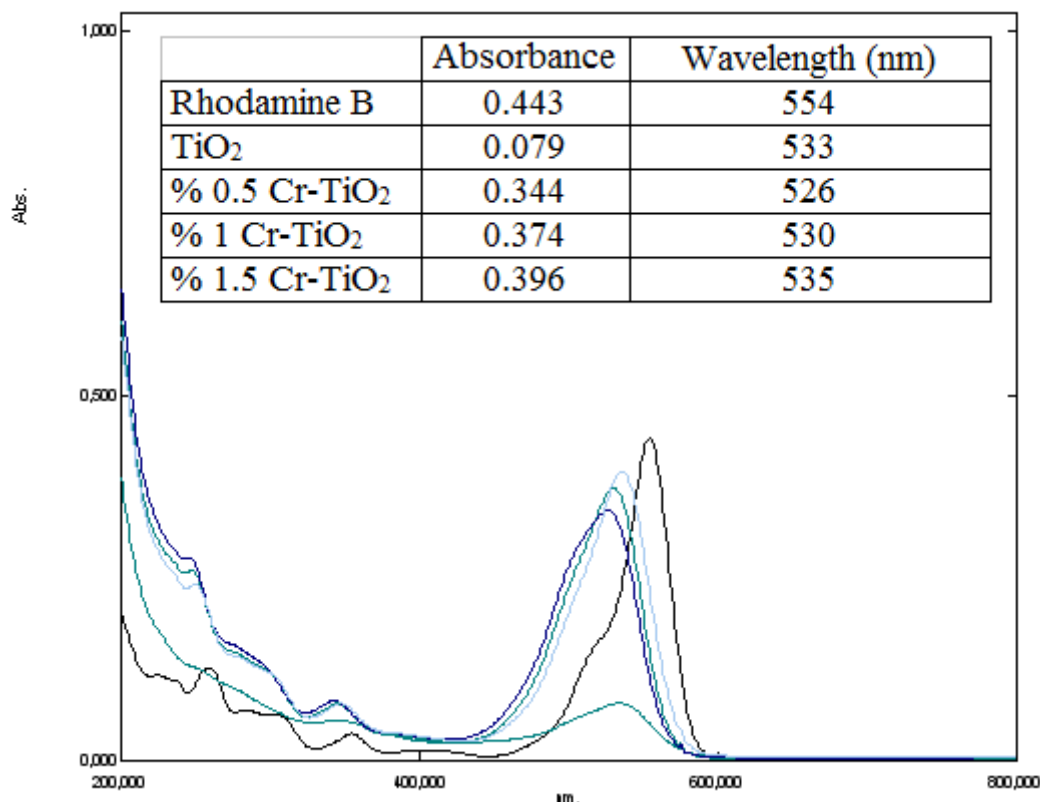


Figure 3.91. Absorbance measurement after 15 hours radiation (Cr dopant)

In literature different ideas can be found about the effect of Cr dopant on photocatalytic activity of TiO_2 [72, 77, 122, 125, 127, 138]. Pawar and his friends mentioned that because of its ionic radius Cr^{3+} ions can penetrate into the lattice of TiO_2 and produce defects in the crystal which inhibits electron-hole recombination and so promotes photocatalytic activity [122].

Lopez and his friends said that this mechanism was only valid when concentration of Cr dopant was low (0.1 %) [127]. Chen and his friends supported this idea and reported that Cr doping caused the photocatalytic activity to decrease when added at higher concentrations and they noted that this concentration according to their study was 0.002 % and above.

Jaimy and friends reported that when the concentration of Cr^{3+} was smaller than or equal to 1 mol % it acted as electron hole trapping center and promotes photocatalytic activity however when concentration of Cr^{3+} was higher than 1 % mol, Cr^{3+} ions acted as electron-hole recombination center and inhibit photocatalytic activity [77,125].

Tian and friends reported the optimum concentration of Cr dopant as 1 % and they told that concentration of Cr caused the existence form of Cr in TiO_2 to be changed. When concentration was higher than the optimum concentration, Cr_2O_3 clusters form and due to these clusters photocatalytic activity was inhibited on the other hand when dopant concentration was low, Cr^{3+} easily could enter into the lattice of TiO_2 [138].

Akpan and his friends listed Cr with the dopants that have a detrimental effect on photocatalytic activity of TiO_2 and they explained the reason by high electron density around the nucleus which repuls and prevents the other electron from entering into lattice [72].

At Section 3.4.5.1 photocatalytic activity of undoped and 0.5 % Ag, 1 % Ag, 1.5 % Ag, 0.5 % Zn, 1 % Zn, 1.5 % Zn, 0.5 % Cr, 1 % Cr, 1.5 % Cr doped TiO_2 films after salt spray test can be seen. Results of Section 3.4.5.1 show that after salt spray test while photocatalytic activity of undoped and all other doped TiO_2 films decrease only the photocatalytic activity of 0.5 % and 1 % Cr doped TiO_2 films increase. This result can be a proof for the ideas that are listed above reported that Cr had a promotive effect on photocatalytic activity only at lower concentrations.

3.4.3. Examination the effects of concentration of dopants

3.4.3.1. Dopant concentration (0.5 %)

Figure 3.92, Figure 3.93 and Figure 3.94 show unirradiated Rhodamine B solution and Rhodamine B solutions in which SLS glasses coated with undoped TiO_2 , 0.5 % Ag doped TiO_2 , 0.5 % Zn doped TiO_2 , 0.5 % Cr doped TiO_2 were radiated for 10, 15 and 20 hours respectively.

When dopant concentration is chosen 0.5 %, Ag seems to be the only dopant that promotes discoloration effect of TiO_2 . At this concentration while both Zn and Cr dopants cause the color of Rhodamine B to be darkened, Cr dopant also changes the color of Rhodamine B from pink to pinkish orange.



Figure 3.92. After 10 hours radiation (left to right: unradiated Rhodamine B, Rhodamine B belongs to undoped TiO_2 , 0.5 % Ag- TiO_2 , 0.5 % Zn- TiO_2 , 0.5 % Cr- TiO_2)



Figure 3.93. After 15 hours radiation (left to right: unradiated Rhodamine B, Rhodamine B belongs to undoped TiO_2 , 0.5 % Ag- TiO_2 , 0.5 % Zn- TiO_2 , 0.5 % Cr- TiO_2)

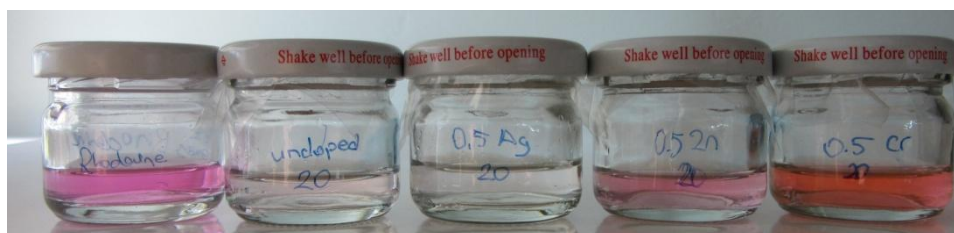


Figure 3.94. After 20 hours radiation (left to right: unradiated Rhodamine B, Rhodamine B belongs to undoped TiO_2 , 0.5 % Ag- TiO_2 , 0.5 % Zn- TiO_2 , 0.5 % Cr- TiO_2)

Figure 3.95 shows absorption of unradiated Rhodamine B solution and Rhodamine B solutions in which SLS glasses coated with undoped TiO_2 , 0.5 % Ag doped TiO_2 , 0.5 % Zn doped TiO_2 , 0.5 % Cr doped TiO_2 were radiated for 15 hours.

Maximum absorption of unradiated Rhodamine B solution was measured 0.443 at 554 nm. Absorbance values of Rhodamine B solutions in which SLS glasses coated with undoped TiO_2 , 0.5 % Ag doped TiO_2 , 0.5 % Zn doped TiO_2 , 0.5 % Cr doped TiO_2 were radiated for 15 hours are 0.079 at 533 nm, 0.057 at 533 nm, 0.240 at 541 nm and 0.344 at 526 nm respectively.

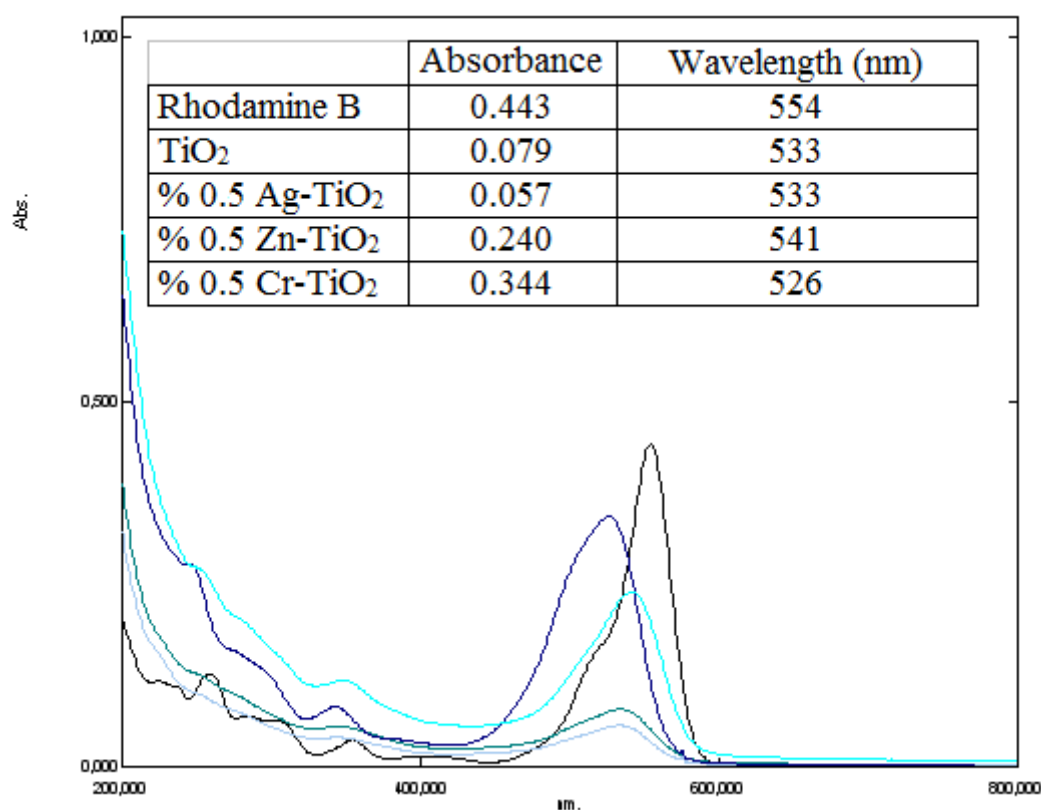


Figure 3.95. Absorbance measurement after 15 hours radiation (0.5 %)

3.4.3.2. Dopant concentration (1 %)

Figure 3.96, Figure 3.97 and Figure 3.98 show unirradiated Rhodamine B solution and Rhodamine B solutions in which SLS glasses coated with undoped TiO₂, 1 % Ag doped TiO₂, 1 % Zn doped TiO₂, 1 % Cr doped TiO₂ were radiated for 10, 15 and 20 hours respectively.

When dopant concentration is chosen 1 %, Ag seems to be the only dopant that promotes discoloration effect of TiO₂. At this concentration while Zn dopant slightly reduces the discoloration effect of TiO₂, Cr dopant almost does not help discoloration at all and causes the color of Rhodamine B to change from pink to pinkish orange.

Figure 3.99 shows absorption of unirradiated Rhodamine B solution and Rhodamine B solutions in which SLS glasses coated with undoped TiO₂, 1 % Ag doped TiO₂, 1 % Zn doped TiO₂, 1 % Cr doped TiO₂ were radiated for 15 hours. Maximum absorption of unirradiated Rhodamine B solution was measured 0.443 at 554 nm. Absorbance values of Rhodamine B solutions in which SLS glasses coated with undoped TiO₂, 1 % Ag doped

TiO₂, 1 % Zn doped TiO₂, 1 % Cr doped TiO₂ were radiated for 15 hours are 0.079 at 533 nm, 0.054 at 533 nm, 0.104 at 541 nm and 0.374 at 530 nm respectively.



Figure 3.96. After 10 hours radiation (left to right: unradiated Rhodamine B, Rhodamine B belongs to undoped TiO₂, 1 % Ag-TiO₂, 1 % Zn-TiO₂, 1 % Cr-TiO₂)



Figure 3.97. After 15 hours radiation (left to right: unradiated Rhodamine B, Rhodamine B belongs to undoped TiO₂, 1 % Ag-TiO₂, 1 % Zn-TiO₂, 1 % Cr-TiO₂)



Figure 3.98. After 20 hours radiation (left to right: unradiated Rhodamine B, Rhodamine B belongs to undoped TiO₂, 1 % Ag-TiO₂, 1 % Zn-TiO₂, 1 % Cr-TiO₂)

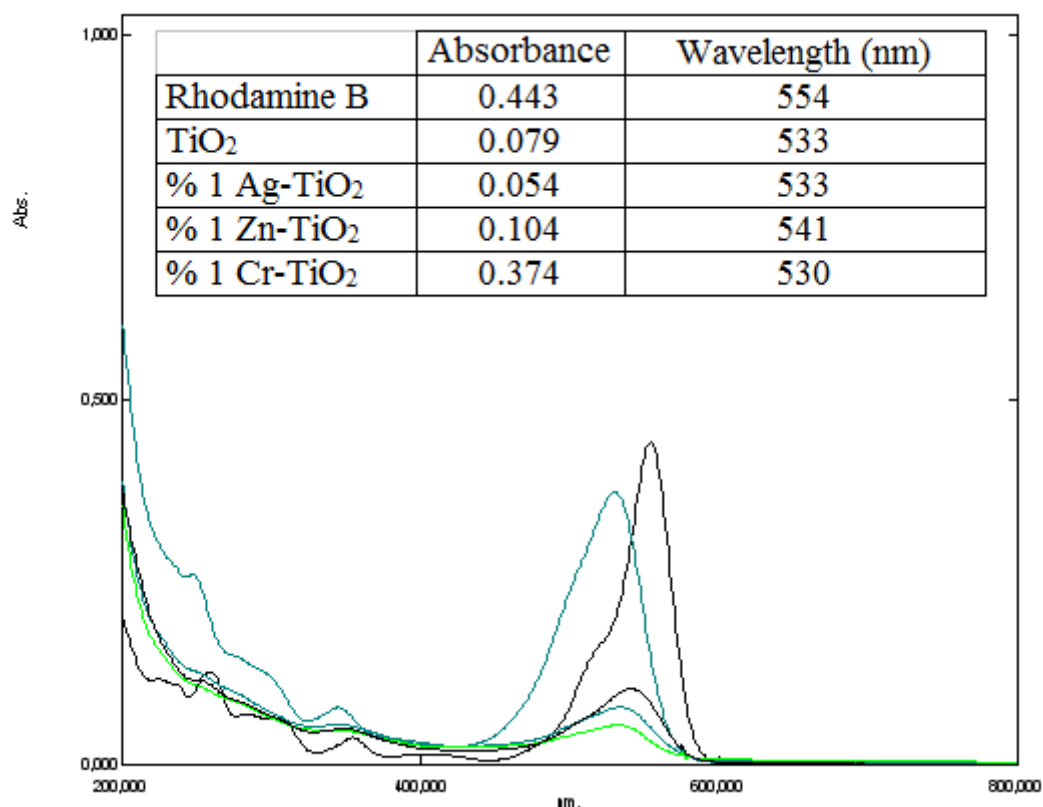


Figure 3.99. Absorbance measurement after 15 hours radiation (1 %)

3.4.3.3. Dopant concentration (1.5 %)

Figure 3.100, Figure 3.101 and Figure 3.102 show unirradiated Rhodamine B solution and Rhodamine B solutions in which SLS glasses coated with undoped TiO₂, 1.5 % Ag doped TiO₂, 1.5 % Zn doped TiO₂, 1.5 % Cr doped TiO₂ were radiated for 10, 15 and 20 hours respectively.

When dopant concentration is chosen 1.5 %, Ag seems to be the only dopant that promotes discoloration effect of TiO₂. At this concentration, while Zn dopant slightly reduces the discoloration effect of TiO₂, Cr dopant almost does not help discoloration at all and causes the color of Rhodamine B to be darkened.



Figure 3.100. After 10 hours radiation (left to right: unradiated Rhodamine B, Rhodamine B belongs to undoped TiO_2 , 1.5 % Ag- TiO_2 , 1.5 % Zn- TiO_2 , 1.5 % Cr- TiO_2)

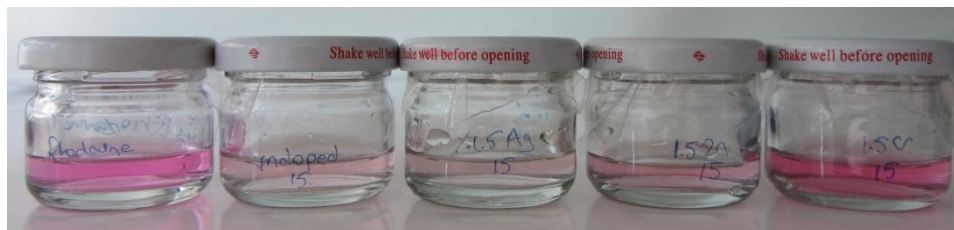


Figure 3.101. After 15 hours radiation (left to right: unradiated Rhodamine B, Rhodamine B belongs to undoped TiO_2 , 1.5 % Ag- TiO_2 , 1.5 % Zn- TiO_2 , 1.5 % Cr- TiO_2)



Figure 3.102. After 20 hours radiation (left to right: unradiated Rhodamine B, Rhodamine B belongs to undoped TiO_2 , 1.5 % Ag- TiO_2 , 1.5 % Zn- TiO_2 , 1.5 % Cr- TiO_2)

Figure 3.103 shows absorption of unradiated Rhodamine B solution and Rhodamine B solutions in which SLS glasses coated with undoped TiO_2 , 1.5 % Ag doped TiO_2 , 1.5 % Zn doped TiO_2 , 1.5 % Cr doped TiO_2 were radiated for 15 hours.

Maximum absorption of unradiated Rhodamine B solution was measured 0.443 at 554 nm. Absorbance values of Rhodamine B solutions in which SLS glasses coated with undoped TiO_2 , 1.5 % Ag doped TiO_2 , 1.5 % Zn doped TiO_2 , 1.5 % Cr doped TiO_2 were radiated for 15 hours are 0.079 at 533 nm, 0.065 at 534 nm, 0.130 at 539 nm and 0.396 at 535 nm respectively.

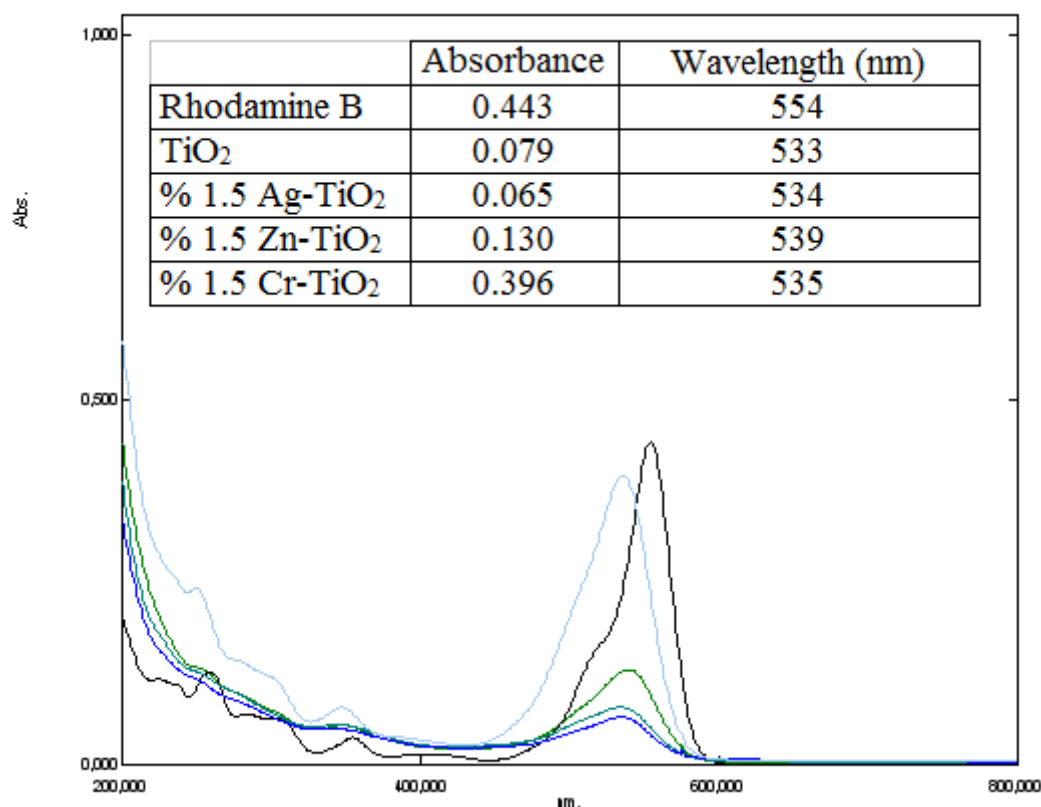


Figure 3.103. Absorbance measurement after 15 hours radiation (1.5 %)

3.5. Physical Testing Of TiO₂ Films

3.5.1. Adhesion test

Adhesion between SLS glasses and the films of undoped and 0.5 % Ag, 1 % Ag, 1.5 % Ag, 0.5 % Zn, 1 % Zn, 1.5 % Zn, 0.5 % Cr, 1 % Cr, 1.5 % Cr doped TiO₂ that were coated on SLS glasses and sintered at 400 °C for 1 hour were tested according to ASTM D 3359 Method B.

A crosscut pattern was made through the films to SLS glasses by using multiple blade with 1 mm spacing. After removing the detached flakes of the coatings by a brush, an adhesive tape was applied over the crosscut patterns and smoothed by rubbing the films with a pencil eraser. Finally the tape was removed quickly by pulling it rapidly back over itself as close to an angle of 180°. Results were examined according to the classification given in Table 3.21 and it was found out that for all TiO₂ films, the edges of the cuts were completely smooth; none of the coating on the grid squares was detached and percent area removed was zero.

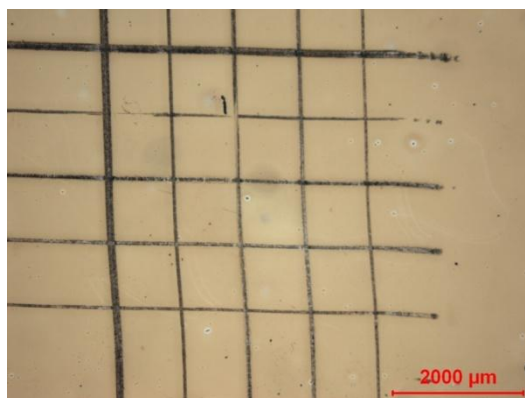
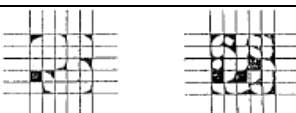
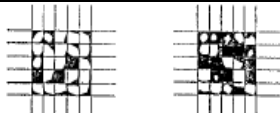
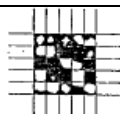


Figure 3.104. Microscope image of undoped TiO₂ coated SLS glass after adhesion test

It can be said that whether undoped or doped, all TiO₂ coatings showed a perfect adhesion to the SLS glass which can be classified as 5B. Microscope image of undoped TiO₂ coated SLS glass after adhesion test can be seen in Figure 3.104.

Table 3.21. Classification of cross-cut test results

Classification	Surface of crosscut area from which flaking has occurred for six parallel cuts	Percent area removed
5B		0 %
4B		Less than 5 %
3B		5-15 %
2B		15-35 %
1B		35-65 %
0B		Greater than 65 %

3.5.2. Taber abrasion test

3.5.2.1. Effect of tin side and air side of float glass

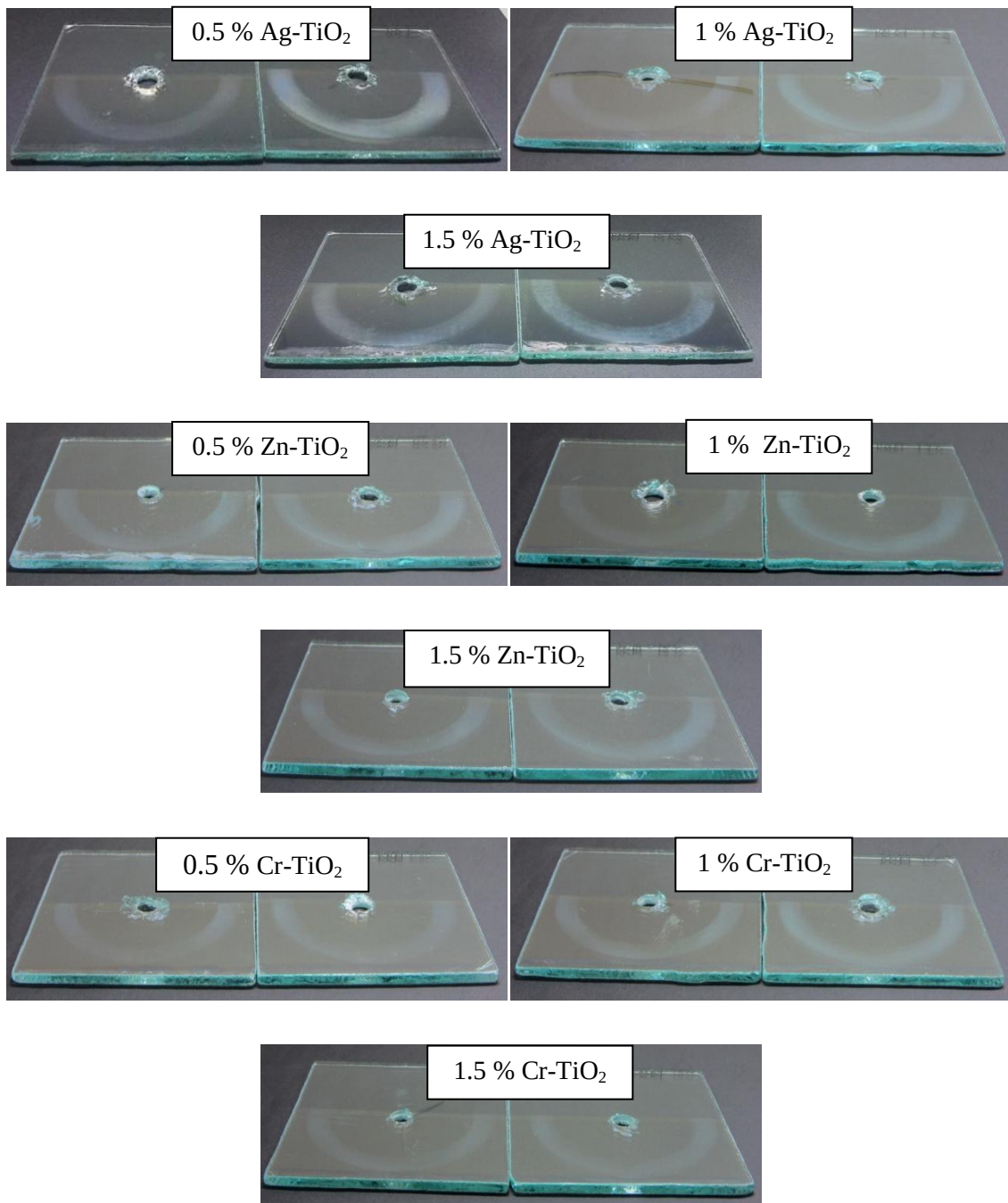


Figure 3.105. Taber abrasion of tin sides (right ones) and air sides (left ones) of coated SLS glasses

As explained in Section 1.3.2, it is known that flat glasses that are produced by float process have two sides; air and tin. Taber abrasion test was applied to both sides of SLS glasses whose one halves were coated with undoped and 0.5 % Ag, 1 % Ag, 1.5 % Ag, 0.5 % Zn, 1 % Zn, 1.5 % Zn, 0.5 % Cr, 1 % Cr, 1.5 % Cr doped TiO_2 and the other halves were remained uncoated.

From Figure 3.105 which shows the appearance of both tin and air sides of SLS glasses after taber abrasion test, it can be seen that no matter what they were coated with, air sides of SLS glasses are more resistive to taber abrasion than the tin sides of SLS glasses.

The most obvious resistivity difference of two sides can be seen at SLS glass coated with 0.5 % Ag- TiO_2 . When other nine pairs of SLS glasses are compared, it can be said that the resistivity differences between two sides are more obvious at SLS glasses that were coated with % 1-Ag- TiO_2 , 1 % Zn- TiO_2 , 1 % Cr- TiO_2 and a slight difference can be noticed at SLS glasses that were coated with % 1.5-Ag- TiO_2 , 1.5 % Zn- TiO_2 , 0.5 % Zn- TiO_2 , 0.5 % Cr- TiO_2 and 1.5 % Cr- TiO_2 .

Kırtay in his PhD Thesis, compared the tin and air side of coated float glass according ROR and BOR resistance test and he found that tin side had lower mechanical strength compared to air side. He had also used Taber 5151 Abraser with CS-10F discs for testing abrasion resistance however he did not mention at which side of the float glass he tested [68].

Taking into consideration the abrasion resistance comparison of tin and air side of SLS glasses that is discussed in this section, in the following sections effect of dopants and dopant amounts on taber abrasion resistance will be discussed only by using the air sides of SLS glasses.

3.5.2.2. Effect of Ag dopant

Appearance of taber abraded SLS glasses that were coated with undoped, 0.5 % Ag, 1 % Ag and 1.5 % Ag doped TiO_2 can be seen at Figure 3.106. Abrasion resistance of SLS glass coated with 1 % Ag doped TiO_2 seems slightly better than the other ones however it can be said that doping TiO_2 with Ag did not make a remarkable difference at its abrasion resistance.

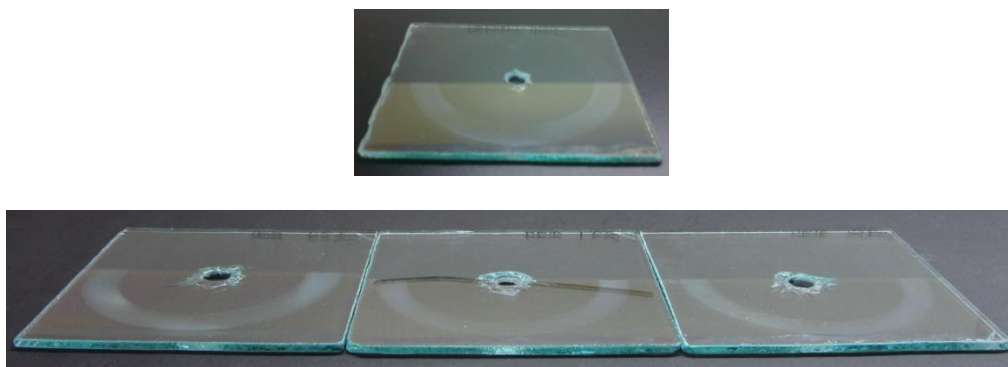


Figure 3.106. Taber abrasion results of SLS glasses coated with; Undoped TiO_2 , Bottom (from left to right): 0.5 % Ag- TiO_2 , 1 % Ag- TiO_2 , 1.5 % Ag- TiO_2

3.5.2.3. Effect of Zn dopant

Appearance of taber abraded SLS glasses that were coated with undoped, 0.5 % Zn, 1 % Zn, 1.5 % Zn doped TiO_2 can be seen at Figure 3.107. It is possible to say that by increasing Zn dopant concentration abrasion resistance of SLS glasses decreases.

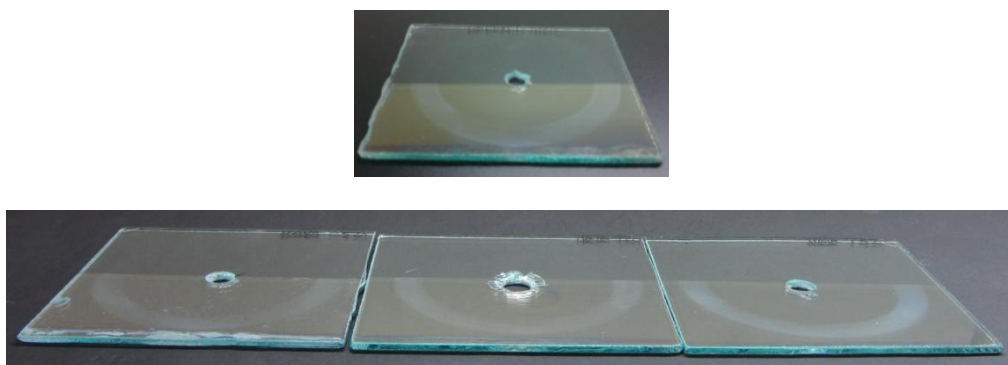


Figure 3.107. Taber abrasion results of SLS glasses coated with; Undoped TiO_2 , Bottom (from left to right): 0.5 % Zn- TiO_2 , 1 % Zn- TiO_2 , 1.5 % Zn- TiO_2

Appearance of SLS glass coated with 0.5 % Zn doped TiO_2 is better than the appearance of SLS glass coated with 1 % Zn doped TiO_2 and appearance of SLS glass coated with 1 % Zn doped TiO_2 is better than the appearance of SLS glass coated with 1.5 % Zn doped TiO_2 . It can be said that appearance of SLS glass coated with undoped TiO_2 is similar to the appearance of SLS glass coated with 1 % Zn doped TiO_2 .

3.5.2.4. Effect of Cr dopant

Appearance of taber abraded SLS glasses that were coated with undoped, 0.5 % Cr, 1 % Cr doped and 1.5 % Cr doped TiO_2 can be seen At Figure 3.108. Doping with 0.5 % Cr seems to promote abrasion resistance of TiO_2 film. However it is not possible to say same thing for the other two concentrations of Cr dopant. It can be seen that appearances of SLS glasses coated with 1 % Cr and 1.5 % Cr doped TiO_2 are slightly worse than the appearance of SLS glass coated with undoped TiO_2 .

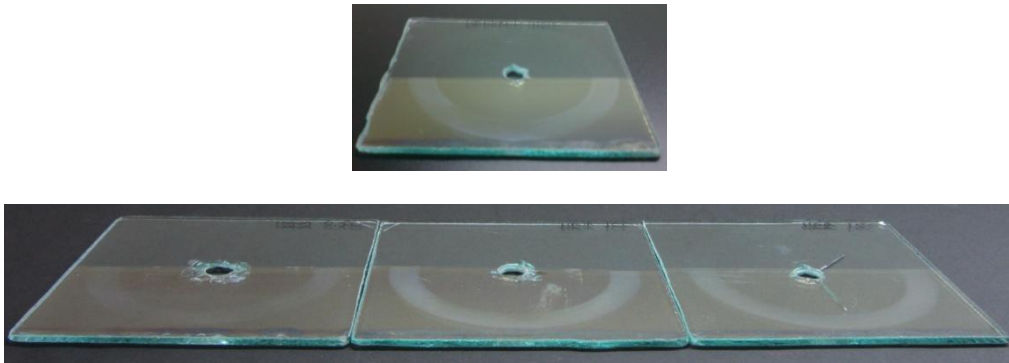


Figure 3.108. Taber abrasion results of SLS glasses coated with; Undoped TiO_2 , Bottom (from left to right): 0.5 % Cr- TiO_2 , 1 % Cr- TiO_2 , 1.5 % Cr- TiO_2

3.5.2.5. Effect of dopant concentration (0.5 %)

Appearance of taber abraded SLS glasses that were coated with undoped, 0.5 % Ag, 0.5 % Zn and 0.5 % Cr doped TiO_2 can be seen at Figure 3.109. It is possible to say that there is not a remarkable difference between the abrasion resistivity of the SLS glasses that were coated with 0.5 % Ag, 0.5 % Zn and 0.5 % Cr doped TiO_2 .

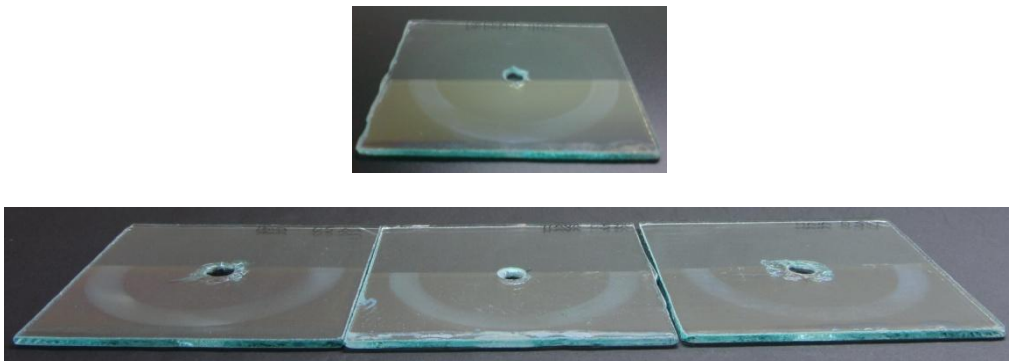


Figure 3.109. Taber abrasion results of SLS glasses coated with; Undoped TiO_2 , Bottom (from left to right): 0.5 % Ag- TiO_2 , 0.5 % Zn- TiO_2 , 0.5 % Cr- TiO_2

3.5.2.6. Effect of dopant concentration (1 %)

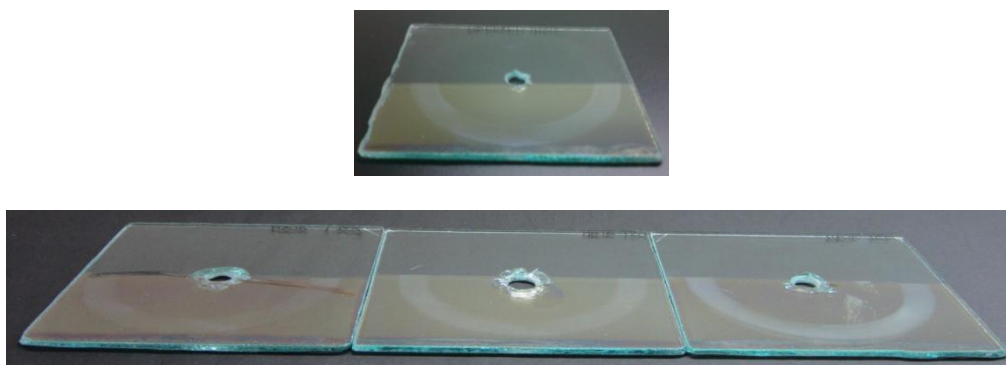


Figure 3.110. Taber abrasion results of SLS glasses coated with; Undoped TiO_2 , Bottom (from left to right): 1 % Ag- TiO_2 , 1 % Zn- TiO_2 , 1 % Cr- TiO_2

Appearance of taber abraded SLS glasses that were coated with undoped, 1 % Ag, 1 % Zn doped and 1 % Cr doped TiO_2 can be seen at Figure 3.110. SLS glass that was coated with 1 % Ag doped TiO_2 seems more resistive to taber abrasion than SLS glass coated with 1 % Zn doped TiO_2 and SLS glass coated with 1 % Zn doped TiO_2 seems more resistive to taber abrasion than SLS glass coated with 1 % Cr doped TiO_2 .

3.5.2.7. Effect of dopant concentration (1.5 %)

Appearance of taber abraded SLS glasses that were coated with undoped, 1.5 % Ag, 1.5 % Zn doped and 1.5 % Cr doped TiO_2 can be seen at Figure 3.111. SLS glass that was coated with 1.5 % Ag doped TiO_2 shows the best resistivity to taber abrasion. There is not a remarkable difference between the resistivity of SLS glasses that were coated with 1.5 % Zn doped and 1.5 % Cr doped TiO_2 .

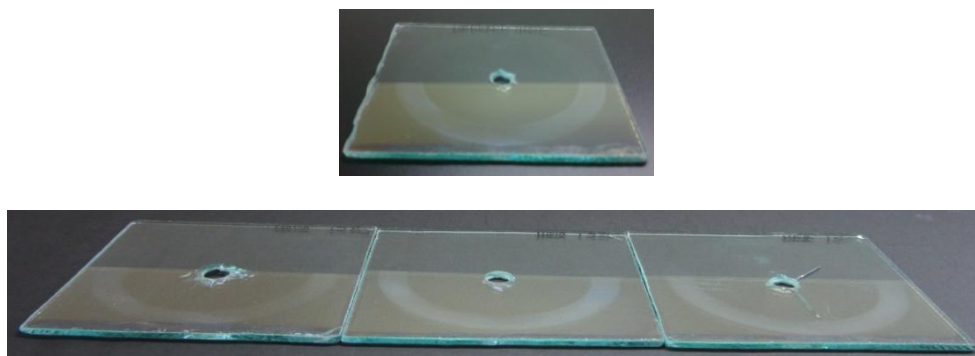


Figure 3.111. Taber abrasion results of SLS glasses coated with; Undoped TiO_2 , Bottom (from left to right): 1.5 % Ag- TiO_2 , 1.5 % Zn- TiO_2 , 1.5 % Cr- TiO_2

3.5.2.8. Effect of sintering temperature

Appearance of taber abraded SLS glasses that were coated with undoped TiO_2 and sintered at 550 °C, 500 °C, 400 °C for 1 hour can be seen at Figure 3.112. It is so obvious that abrasion resistivity increases by increasing sintering temperature.

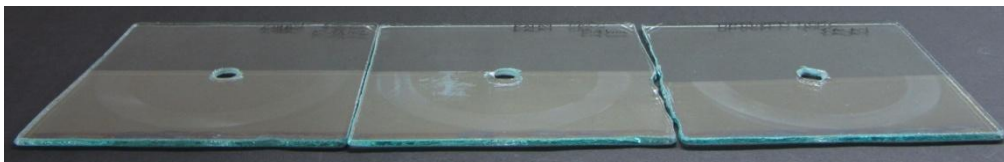


Figure 3.112. Taber abrasion results of SLS glasses coated with undoped TiO_2 ; Sintering temperatures from left to right: 550 °C, 500 °C, 400 °C

SLS glass that was coated with undoped TiO_2 and sintered at 600 °C for 1 hour could not be tested by taber abrader since at 600 °C, glass started to bend as can be seen at Figure 3.113.

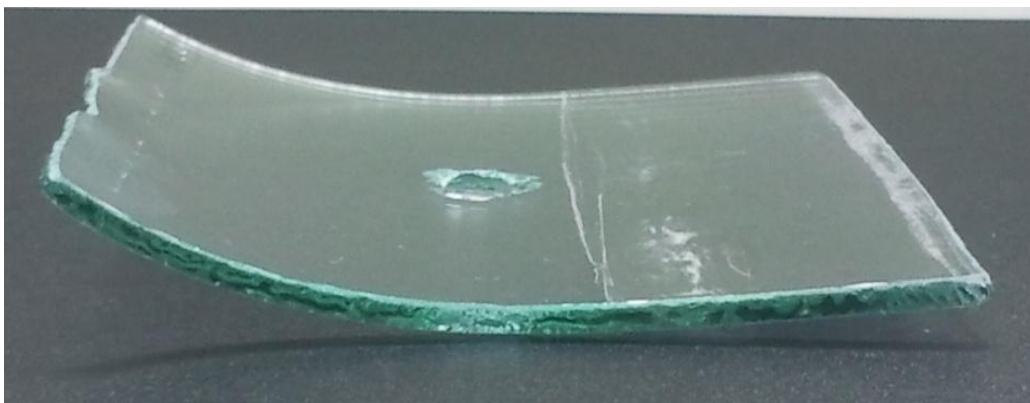


Figure 3.113. SLS glass coated with undoped TiO_2 and sintered at 600 °C

3.5.3. Scratch test

A load from 10 N to 0.1 N was applied on SLS glasses that were coated with undoped TiO_2 , 0.5 % Ag, 1 % Ag, 1.5 % Ag, 0.5 % Zn, 1 % Zn, 1.5 % Zn, 0.5 % Cr, 1 % Cr, 1.5 % Cr doped TiO_2 like a practice target as given in Figure 3.114.

The minimum load that was necessary to cause a track on coated SLS glasses was given as the scratch hardness of the coated SLS glasses.

Scratch test result of SLS glass coated with 1 % Zn doped TiO_2 is given in Figure 3.115 as an example.

Both air and tin sides of coated glasses were tested and it was found that scratch test results of both sides of the SLS glasses were approximately same.

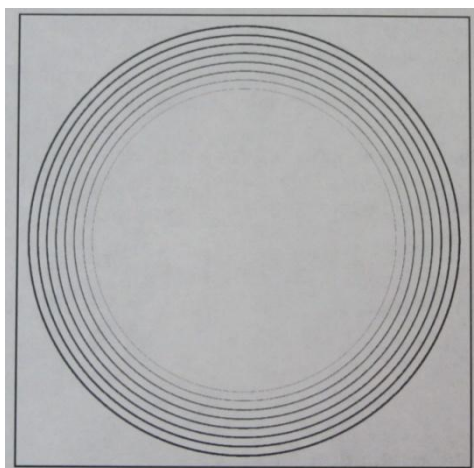


Figure 3.114. Sample result graphic of scratch test

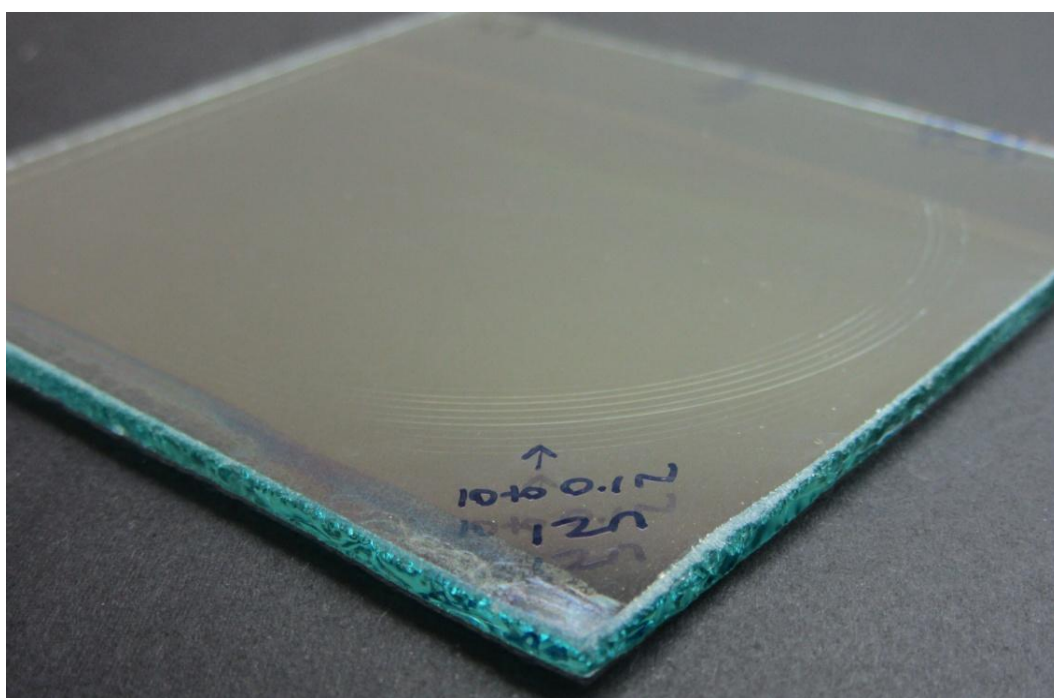


Figure 3.115. Scratch test result of SLS glass coated with 1 % Zn- TiO_2

Table 3.22. Scratch test results of SLS glasses coated with undoped TiO₂, 0.5 % Ag-TiO₂, 1 % Ag-TiO₂, 1.5 % Ag-TiO₂, 0.5 % Zn-TiO₂, 1 % Zn-TiO₂, 1.5 % Zn-TiO₂, 0.5 % Cr-TiO₂, 1 % Cr-TiO₂, 1.5 % Cr-TiO₂

SLS glass coated with	Scratch hardness result (N)
Undoped TiO ₂	2
0.5 % Ag-TiO ₂	3
1 % Ag-TiO ₂	3
1.5 % Ag-TiO ₂	3
0.5 % Zn-TiO ₂	2
1 % Zn-TiO ₂	3
1.5 % Zn-TiO ₂	3
0.5 % Cr-TiO ₂	2
1 % Cr-TiO ₂	3
1.5 % Cr-TiO ₂	3

3.5.4. Salt spray test

3.5.4.1. Appearance evaluation after salt spray test

Although at the end of the salt spray test, when visually inspected no cracks, no blistering and no corrosion sign were seen at the uncoated SLS glass and the SLS glasses that were coated with undoped TiO₂, 0.5 % Ag-TiO₂, 1 % Ag-TiO₂, 1.5 % Ag-TiO₂, 0.5 % Zn-TiO₂, 1 % Zn-TiO₂, 1.5 % Zn-TiO₂, 0.5 % Cr-TiO₂, 1 % Cr-TiO₂, 1.5 % Cr-TiO₂, when examined later after photocatalytic activity test very slight removals from the film surfaces were observed.

3.5.4.2. Transmittance measurement after salt spray test

Figure 3.116 shows transmittance spectras of SLS glasses that were coated first with SiO₂ then with undoped TiO₂, 0.5 % Ag-TiO₂, 1 % Ag-TiO₂, 1.5 % Ag-TiO₂ before and after salt spray test.

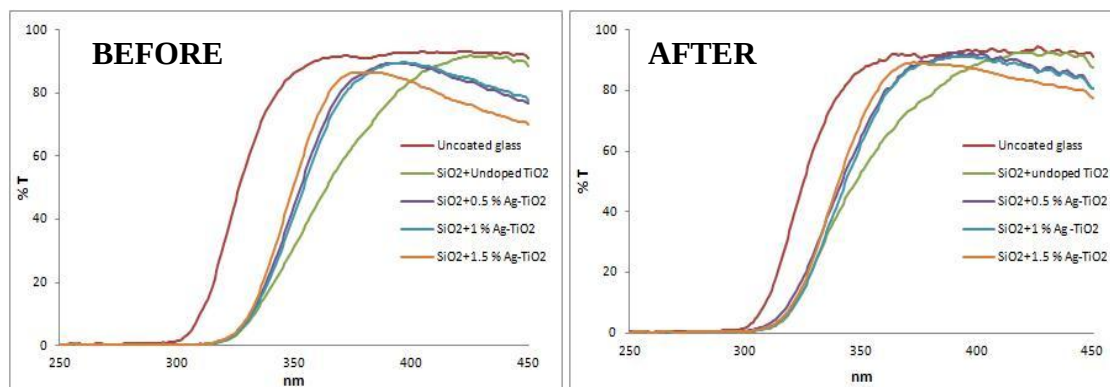


Figure 3.116. Comparison of transmittance spectras of SLS glasses coated first with SiO_2 then with undoped TiO_2 , 0.5 % Ag- TiO_2 , 1 % Ag- TiO_2 , 1.5 % Ag- TiO_2 before and after salt spray test.

Transmittances of uncoated SLS glass and SLS glasses that have been first coated with SiO_2 then coated with undoped TiO_2 , 0.5 % Ag doped, 1 % Ag doped, 1.5 % Ag doped TiO_2 measured before salt spray test at 400 nm and at 450 nm are 93 %, 84 %, 89 %, 89 %, 83 % and 92 %, 88 %, 77 %, 78 %, 70 % respectively.

Transmittances of uncoated SLS glass and SLS glasses that were first coated with SiO_2 then coated with undoped TiO_2 , 0.5 % Ag doped, 1 % Ag doped, 1.5 % Ag doped TiO_2 measured after salt spray test at 400 nm and at 450 nm are 93 %, 88 %, 91 %, 90 %, 87 % and 92 %, 88 %, 80 %, 80 %, 77 % respectively.

After salt spray test TiO_2 film still seems to shift to shorter wavelength ranges when doped with 0.5 % Ag, 1 % Ag and 1.5 % Ag. Besides, an increment can be seen at the transmittance values of SLS glasses coated with undoped TiO_2 , 0.5 % Ag doped, 1 % Ag doped, 1.5 % Ag doped TiO_2 after salt spray test.

Transmittances of uncoated SLS glass and SLS glasses that have been first coated with SiO_2 then coated with undoped TiO_2 , 0.5 % Ag doped, 1 % Ag doped, 1.5 % Ag doped TiO_2 measured before salt spray test and after salt spray test at 350 nm are 86 %, 31 %, 44 %, 41 %, 51 % and 87 %, 53 %, 65 %, 62 %, 70 % respectively. It can be seen from these results that UV blocking property of undoped TiO_2 , 0.5 % Ag doped, 1 % Ag doped and 1.5 % Ag doped TiO_2 films reduces after salt spray test.

Figure 3.117 shows transmittance spectras of SLS glasses that were coated first with SiO_2 then with undoped TiO_2 , 0.5 % Zn-TiO_2 , 1 % Zn-TiO_2 , 1.5 % Zn-TiO_2 before and after salt spray test.

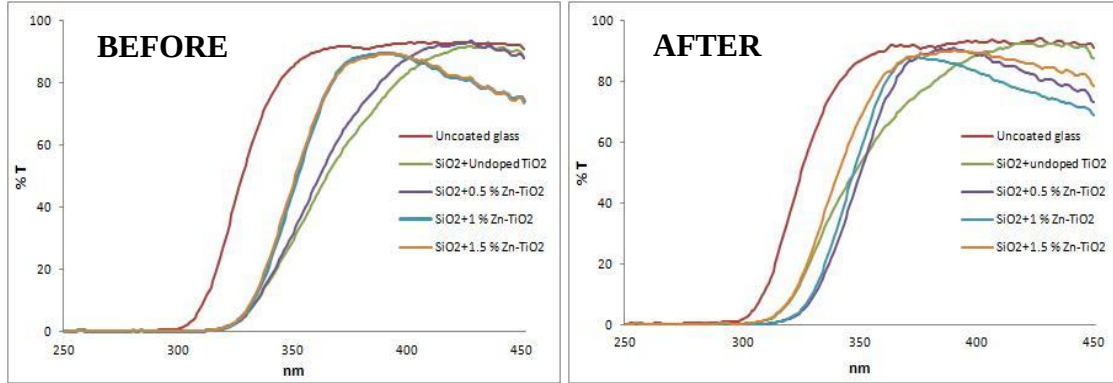


Figure 3.117. Comparison of transmittance spectras of SLS glasses coated first with SiO_2 then with undoped TiO_2 , 0.5 % Zn-TiO_2 , 1 % Zn-TiO_2 , 1.5 % Zn-TiO_2 before and after salt spray test

Transmittances of uncoated SLS glass and SLS glasses that were first coated with SiO_2 then coated with undoped TiO_2 , 0.5 % Zn doped, 1 % Zn doped, 1.5 % Zn doped TiO_2 measured before salt spray test at 400 nm and at 450 nm are 93 %, 84 %, 88 %, 88 %, 88 % and 92 %, 88 %, 88 %, 74 %, 74 % respectively.

Transmittances of uncoated SLS glass and SLS glasses that were first coated with SiO_2 then coated with undoped TiO_2 , 0.5 % Zn doped, 1 % Zn doped, 1.5 % Zn doped TiO_2 measured after salt spray test at 400 nm and at 450 nm are 93 %, 88 %, 89 %, 83 %, 89 % and 92 %, 88 %, 73 %, 69 %, 79 % respectively.

After salt spray test TiO_2 film still seems to shift to shorter wavelength ranges when doped with 0.5 % Zn , 1 % Zn and 1.5 % Zn . Compared to the shift caused by 0.5 % Zn before salt spray test, it is obvious that shift caused by 0.5 % Zn becomes similar with the shifts casues by 0.5 % Zn , 1 % Zn after salt spray test. Besides, transmittance of SLS glasses coated with 0.5 % Zn and 1 % Zn seems to decrease and transmittance of SLS glasses coated with 1.5 % Zn seems to decrease after salt spray test.

Transmittances of uncoated SLS glass and SLS glasses were first coated with SiO_2 then coated with undoped TiO_2 , 0.5 % Zn doped, 1 % Zn doped, 1.5 % Zn doped TiO_2 measured before salt spray test and after salt spray test at 350 nm are 86 %, 31 %, 33 %, 33 %, 33 % and 86 %, 31 %, 33 %, 33 %, 33 % respectively.

48 %, 50 % and 87 %, 53 %, 49 %, 57 %, 68 % respectively. It can be seen from these results that UV blocking property of undoped TiO_2 , 0.5 % Zn doped, 1 % Zn doped and 1.5 % Zn doped TiO_2 films reduces after salt spray test.

Figure 3.118 shows transmittance spectras of SLS glasses that were coated first with SiO_2 than with undoped TiO_2 , 0.5 % Cr- TiO_2 , 1 % Cr- TiO_2 , 1.5 % Cr- TiO_2 before and after salt spray test.

Transmittances of uncoated SLS glass and SLS glasses that were first coated with SiO_2 then coated with undoped TiO_2 , 0.5 % Cr doped, 1 % Cr doped, 1.5 % Cr doped TiO_2 measured before salt spray test at 400 nm and at 450 nm are 93 %, 84 %, 83 %, 85 %, 88 % and 92 %, 88 %, 88 %, 72 %, 72 % respectively.

Transmittances of uncoated SLS glass and SLS glasses that were first coated with SiO_2 then coated with undoped TiO_2 , 0.5 % Cr doped, 1 % Cr doped, 1.5 % Cr doped TiO_2 measured after salt spray test at 400 nm and at 450 nm are 93 %, 88 %, 81 % , 88 %, 82 % and 92 %, 88 %, 87 %, 79 %, 69 % respectively.

After salt spray test TiO_2 film still seems to shift to shorter wavelength ranges when doped with 1 % Cr, 1.5 % Cr and 0.5 % Cr still causes neither blue nor red shift.

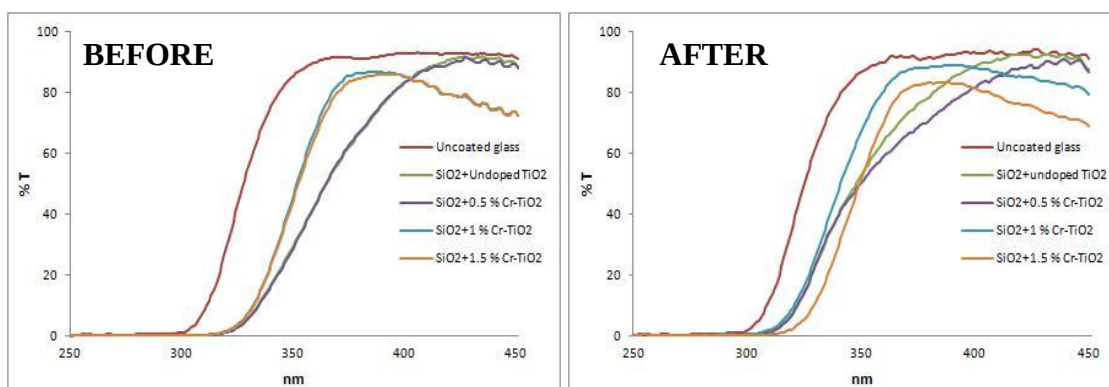


Figure 3.118. Comparison of transmittance spectras of SLS glasses coated first with SiO_2 then with undoped TiO_2 , 0.5 % Cr- TiO_2 , 1 % Cr- TiO_2 , 1.5 % Cr- TiO_2 before and after salt spray test

When transmittance spectras before and after salt spray test are compared it is obvious that transmittance of SLS glass coated with 0.5 % Cr and 1.5 % Cr at 400 nm decreases while transmittance of SLS glass coated with 1 % Cr at 400 nm increases. While at 450

nm transmittance of SLS glass coated with 0.5 % Cr does not change, transmittance of SLS glass coated with 1 % Cr increases and transmittance of SLS glass coated with 1.5 % Cr decreases.

Transmittances of uncoated SLS glass and SLS glasses that were first coated with SiO_2 then coated with undoped TiO_2 , 0.5 % Cr doped, 1 % Cr doped, 1.5 % Cr doped TiO_2 measured before salt spray test and after salt spray test at 350 nm are 86 %, 31 %, 30 %, 49 %, 47 % and 87 %, 53 %, 50 %, 67 %, 52 % respectively. It can be seen from these results that UV blocking property of undoped TiO_2 , 0.5 % Cr doped, 1 % Cr doped and 1.5 % Cr doped TiO_2 films reduces after salt spray test.

3.5.4.3. Photocatalytic activity evaluation after salt spray test

Figure 3.119 shows unirradiated Rhodamine B solution and Rhodamine B solutions in which SLS glasses coated with undoped TiO_2 , 0.5 % Ag doped TiO_2 , 1 % Ag doped TiO_2 , 1.5 % Ag doped TiO_2 were radiated before and after salt spray test for 15 hours.

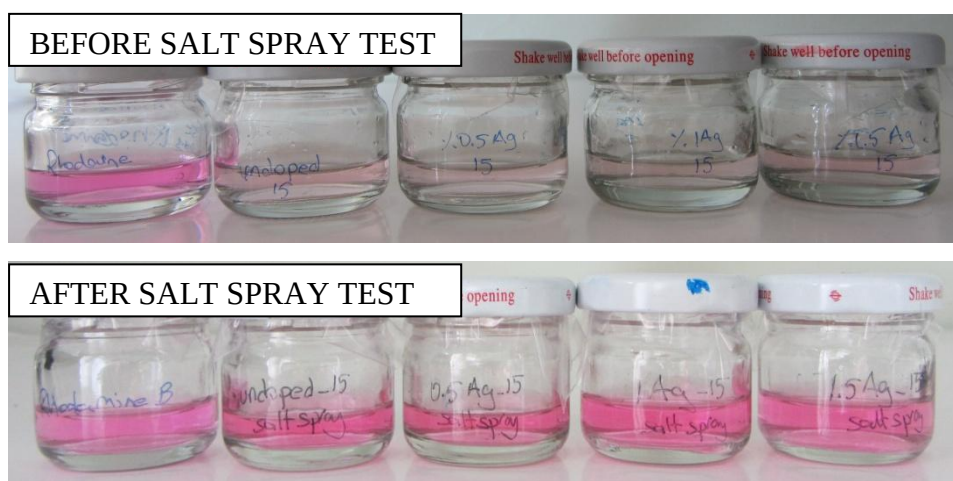


Figure 3.119. Comparison of photocatalytic activity of Ag doped TiO_2 films before and after salt spray test (left to right: unirradiated Rhodamine B, Rhodamine B belongs to undoped TiO_2 , 0.5 % Ag- TiO_2 , 1 % Ag- TiO_2 , 1.5 % Ag- TiO_2)

Looking at Figure 3.119 and Table 3.23 it is possible to say that undoped, 0.5 % Ag, 1 % Ag doped TiO_2 films showed no more a photocatalytic activity and 1.5 % Ag doped TiO_2 film almost lost its photocatalytic activity after salt spray test. Absorbance values of Rhodamine B solutions in which SLS glasses coated with undoped TiO_2 , 0.5 % Ag doped TiO_2 , 1 % Ag doped TiO_2 , 1.5 % Ag doped TiO_2 solutions were radiated for 15

hours before and after salt spray test, increased from 0.079 to 0.575, from 0.057 to 0.481, from 0.054 to 0.505 and from 0.065 to 0.414 respectively. Taking into consideration that absorbance value of unirradiated Rhodamine B is 0.443, it is obvious that after salt spray test undoped, 0.5 % Ag and 1 % Ag doped TiO₂ solutions caused color of Rhodamine B to be darkened. However looking at Table 3.23 it should also be noted that glasses coated with undoped TiO₂, 0.5 % Ag and 1 % Ag doped TiO₂ are still better than the uncoated glass even after salt spray test.

Table 3.23. Absorbance values of unirradiated Rhodamine B solution and Rhodamine B solutions in which uncoated SLS glass and SLS glasses coated with undoped TiO₂, 0.5 % Ag doped TiO₂, 1 % Ag doped TiO₂, 1.5 % Ag doped TiO₂ were radiated before and after salt spray test for 15 hours.

	Before salt spray test		After salt spray test	
	A	Wavelength (nm)	A	Wavelength (nm)
Rhodamine B	0.443	554	0.443	554
Uncoated glass	1.314	549	1.314	549
Undoped TiO ₂	0.079	533	0.575	551
0.5 % Ag-TiO ₂	0.057	533	0.481	545
1 % Ag-TiO ₂	0.054	531	0.505	546
1.5 % Ag-TiO ₂	0.065	534	0.414	545

Figure 3.120 shows unirradiated Rhodamine B solution and Rhodamine B solutions in which SLS glasses coated with undoped TiO₂, 0.5 % Zn doped TiO₂, 1 % Zn doped TiO₂, 1.5 % Zn doped TiO₂ were radiated before and after salt spray test for 15 hours.

Looking at Figure 3.120 it is possible to say that after salt spray test undoped, 0.5 % Zn, 1 % Zn, 1.5 % Zn doped TiO₂ films cause color of Rhodamine B to be darkened.

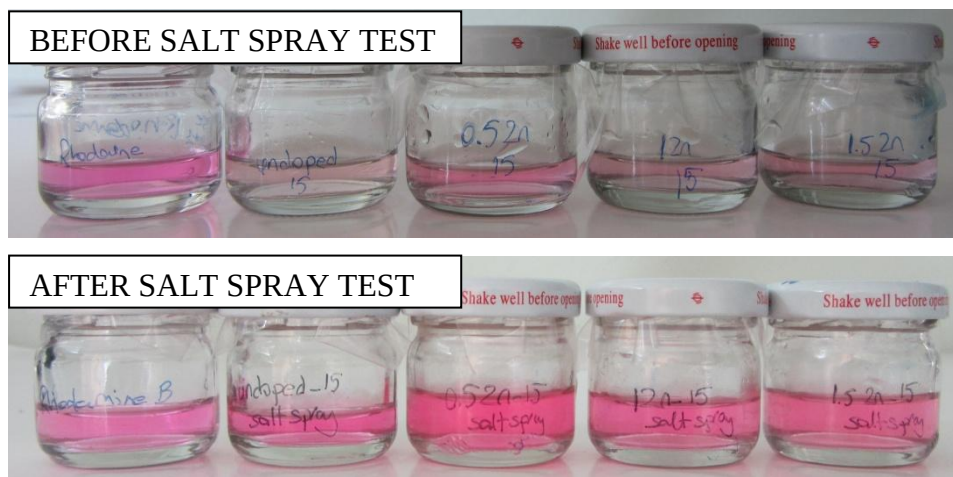


Figure 3.120. Comparison of photocatalytical activity of Zn doped TiO₂ films before and after salt spray test (left to right: unirradiated Rhodamine B, Rhodamine B belongs to undoped TiO₂, 0.5 % Zn-TiO₂, 1 % Zn-TiO₂, 1.5 % Zn-TiO₂)

Table 3.24. Unirradiated Rhodamine B solution and Rhodamine B solutions in which uncoated SLS glass and SLS glasses coated with undoped TiO₂, 0.5 % Zn doped TiO₂, 1 % Zn doped TiO₂, 1.5 % Zn doped TiO₂ were radiated before and after salt spray test for 15 hours.

	Before salt spray test		After salt spray test	
	A	Wavelength (nm)	A	Wavelength (nm)
Rhodamine B	0.443	554	0.443	554
Uncoated glass	1.314	549	1.314	549
Undoped TiO ₂	0.079	533	0.575	551
0.5 % Zn-TiO ₂	0.240	541	0.602	545
1 % Zn-TiO ₂	0.104	541	0.409	545
1.5 % Zn-TiO ₂	0.130	539	0.359	542

Table 3.24 shows that absorbance values of Rhodamine B solutions in which SLS glasses coated with undoped TiO₂, 0.5 % Zn doped TiO₂, 1 % Zn doped TiO₂, 1.5 % Zn doped TiO₂ solutions were radiated for 15 hours before and after salt spray test,

increased from 0.079 to 0.575, from 0.240 to 0.602, from 0.104 to 0.409 and from 0.130 to 0.359 respectively. Taking into consideration that absorbance value of unirradiated Rhodamine B is 0.443 it can be said that undoped, 0.5 % Zn doped TiO_2 films show no and 1 % Zn, 1.5 % Zn doped TiO_2 films show nearly no photocatalytic activity after salt spray test. However looking at Table 3.24 it should also be noted that glasses coated with undoped TiO_2 and 0.5 % Zn doped TiO_2 are still better than the uncoated glass even after salt spray test.

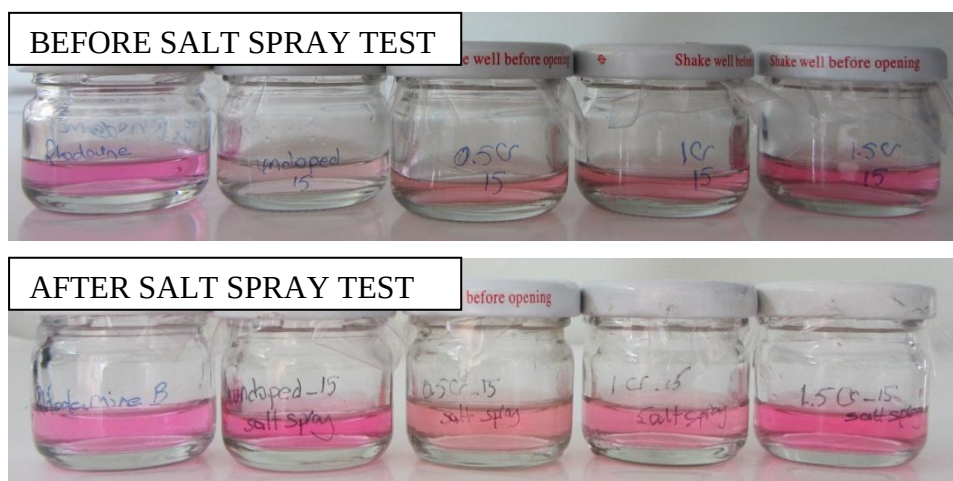


Figure 3.121. Comparison of photocatalytic activity of Cr doped TiO_2 films before and after salt spray test (left to right: unirradiated Rhodamine B, Rhodamine B belongs to undoped TiO_2 , 0.5 % Cr- TiO_2 , 1 % Cr- TiO_2 , 1.5 % Cr- TiO_2)

Figure 3.121 shows unirradiated Rhodamine B solution and Rhodamine B solutions in which SLS glasses coated with undoped TiO_2 , 0.5 % Cr doped TiO_2 , 1 % Cr doped TiO_2 , 1.5 % Cr doped TiO_2 were radiated before and after salt spray test for 15 hours.

Table 3.25 shows that absorbance values of Rhodamine B solutions in which SLS glasses coated with undoped TiO_2 , 0.5 % Cr, 1 % Cr, 1.5 % Cr doped TiO_2 solutions were radiated for 15 hours before and after salt spray test, increased from 0.079 to 0.575, from 0.344 to 0.283, from 0.374 to 0.307 and from 0.396 to 0.524 respectively. Taking these absorbance values and absorbance value of unirradiated Rhodamine B into consideration it is possible to say that while photocatalytic activity of 1.5 % Cr doped TiO_2 decreases, photocatalytic activity of 0.5 % Cr and 1 % Cr doped TiO_2 increases after salt spray test. However looking at Table 3.25 it should also be noted that glasses

coated with undoped TiO₂ and 1.5 % Cr doped TiO₂ are still better than the uncoated glass even after salt spray test.

As discussed in Section 3.4.2.3, Cr dopant is thought to promote photocatalytic activity only at low concentrations [77, 125, 127]. Taking this idea into consideration, it can be thought that photocatalytic activity of 0.5 % Cr and 1 % Cr doped TiO₂ might have increased after salt spray test due to a decrease at Cr dopant concentration caused by salt spray test.

Table 3.25. Unradiated Rhodamine B solution and Rhodamine B solutions in which uncoated SLS glass and SLS glasses coated with undoped TiO₂, 0.5 % Cr doped TiO₂, 1 % Cr doped TiO₂, 1.5 % Cr doped TiO₂ were radiated before and after salt spray test for 15 hours.

	Before salt spray test		After salt spray test	
	A	Wavelength (nm)	A	Wavelength (nm)
Rhodamine B	0.443	554	0.443	554
Uncoated glass	1.314	549	1.314	549
Undoped TiO ₂	0.079	533	0.575	551
0.5 % Cr-TiO ₂	0.344	526	0.283	528
1 % Cr-TiO ₂	0.374	530	0.307	536
1.5 % Cr-TiO ₂	0.396	535	0.524	541

3.6. Determination The Shelf Life Of TiO₂ Solutions

3.6.1. Appearance evaluation

When Figure 3.122 is compared with Figure 2.2, it can be said that there is not a significant difference between the the appearances of undoped TiO₂, 0.5 % Ag-TiO₂, 1 % Ag-TiO₂, 1.5 % Ag-TiO₂, 0.5 % Zn-TiO₂, 1 % Zn-TiO₂, 1.5 % Zn-TiO₂, 0.5 % Cr-TiO₂, 1 % Cr-TiO₂, 1.5 % Cr-TiO₂ solutions at the 0th day and the 60th day of their preparation. The reason why the undoped TiO₂, 0.5 % Ag-TiO₂, 1 % Ag-TiO₂, 1.5 % Ag-TiO₂, 0.5 % Zn-TiO₂, 1 % Zn-TiO₂, 1.5 % Zn-TiO₂, 0.5 % Cr-TiO₂, 1 % Cr-TiO₂,

1.5 % Cr-TiO₂ solutions were still stable after 60 days is the low pH values of the solutions which were given in Section 2.2.2.1.

It can be noted that during this thesis study, these solutions were still stable almost 10 months after their preparation. In literature it was reported that when the pH range of the TiO₂ sol was between 1 and 2 it was possible to get homogenous and stable sols for more than 1 year [113, 151, 152]. Although it was reported in literature that when TiO₂ sol was prepared at low pH it was stable for more than 1 year, there is not a study showing how the photocatalytic activity, photoinduced wettability and transmittance % of the film prepared with this sol change after 1 year.

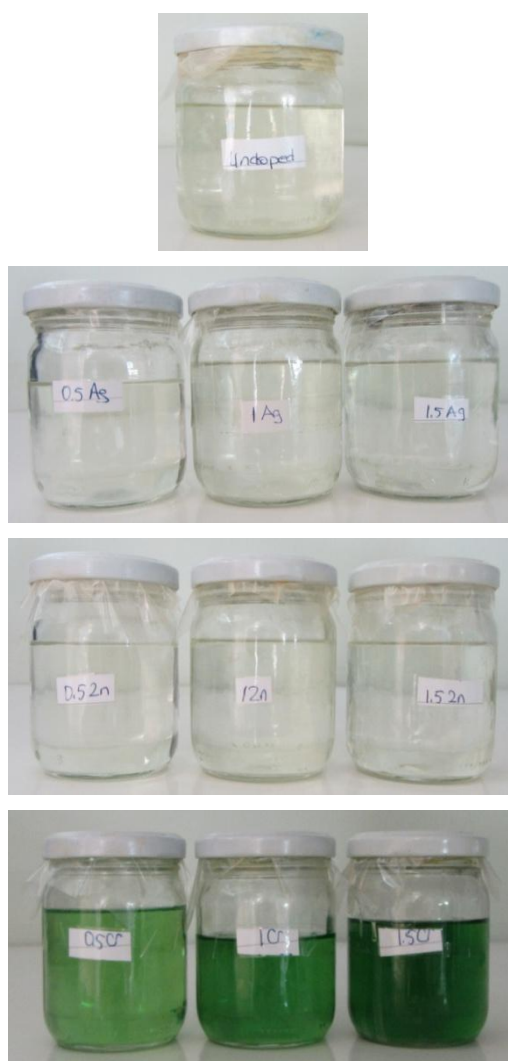


Figure 3.122. Photographs of the undoped TiO₂, 0.5 % Ag-TiO₂, 1 % Ag-TiO₂, 1.5 % Ag-TiO₂, 0.5 % Zn-TiO₂, 1 % Zn-TiO₂, 1.5 % Zn-TiO₂, 0.5 % Cr-TiO₂, 1 % Cr-TiO₂, 1.5 % Cr-TiO₂ solutions at the 60th day of their preparation.

3.6.2. Viscosity measurement

Viscosity of each TiO_2 solution was measured 51 cP at the 60th day of their preparation. When compared with the viscosity measured at the 0th day of preparation, it can be said that no increment occurred at viscosity of the solutions after 60 days.

3.6.3. Transmittance measurement

Figure 3.123 shows transmittance spectras of SLS glasses coated first with SiO_2 then with undoped TiO_2 , 0.5 % Ag- TiO_2 , 1 % Ag- TiO_2 , 1.5 % Ag- TiO_2 at the 0th day and the 60th day of the preparation of the solutions.

Transmittances of uncoated SLS glass and SLS glasses that were first coated with SiO_2 then coated at the 0th day of preparation with undoped TiO_2 , 0.5 % Ag doped, 1 % Ag doped, 1.5 % Ag doped TiO_2 at 400 nm and at 450 nm are 93 %, 84 %, 89 %, 89 %, 83 % and 92 %, 88 %, 77 %, 78 %, 70 % respectively. Transmittances of uncoated SLS glass and SLS glasses that were first coated with SiO_2 then coated at the 60th day of preparation with undoped TiO_2 , 0.5 % Ag doped, 1 % Ag doped, 1.5 % Ag doped TiO_2 at 400 nm and at 450 nm are 93 %, 91 %, 90 %, 90 %, 89 % and 92 %, 80 %, 78 %, 79 %, 78 % respectively.

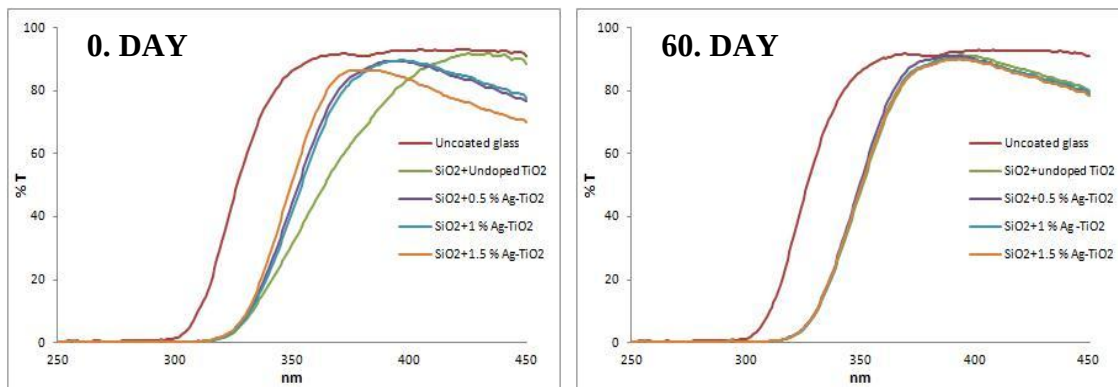


Figure 3.123. Comparison of transmittance spectras of SLS glasses coated first with SiO_2 then with undoped TiO_2 , 0.5 % Ag- TiO_2 , 1 % Ag- TiO_2 , 1.5 % Ag- TiO_2 at the 0th and the 60th day of the preparation of the solutions.

Absorption edge of TiO_2 film no more seems to shift to shorter wavelength ranges when doped with 0.5 % Ag, 1 % Ag, 1.5 % Ag when SLS glasses are coated at the 60th day of preparation of the solutions. At 450 nm, transmittance of SLS glass that was coated with

undoped TiO_2 decreases and all transmittance values of the SLS glasses that were coated at the 60th day of preparation with undoped and 0.5 % Ag, 1 % Ag 1.5 % Ag doped TiO_2 approximately become similar. Ag dopant seems not to affect the transmittance value of TiO_2 film any more.

Transmittances of uncoated SLS glass and SLS glasses that were first coated with SiO_2 then coated at the 0th day and the 60th day of preparation with undoped TiO_2 , 0.5 % Ag doped, 1 % Ag doped, 1.5 % Ag doped TiO_2 at 350 nm are 86 %, 31 %, 44 %, 41 %, 51 % and 86 %, 48 %, 51 %, 49 %, 49 % respectively. It can be seen from these results that while UV blocking property of undoped and 0.5 % Ag, 1 % Ag doped TiO_2 film reduces, UV blocking property of 1.5 % Ag doped TiO_2 film enhances very slightly when TiO_2 solutions were used at the 60th day of their preparation.

Transmittances of uncoated SLS glass and SLS glasses that were first coated with SiO_2 then coated at the 0th day of preparation with undoped TiO_2 , 0.5 % Zn doped, 1 % Zn doped, 1.5 % Zn doped TiO_2 at 400 nm and at 450 nm are 93 %, 84 %, 88 %, 88 %, 88 % and 92 %, 88 %, 88 %, 74 %, 74 % respectively (Figure 3.124). Transmittances of uncoated SLS glass and SLS glasses that were first coated with SiO_2 then coated at the 60th day of preparation with undoped TiO_2 , 0.5 % Zn doped, 1 % Zn doped, 1.5 % Zn doped TiO_2 at 400 nm and at 450 nm are 93 %, 91 %, 89 %, 90 %, 89 % and 92 %, 80 %, 79 %, 81 %, 81 % respectively.

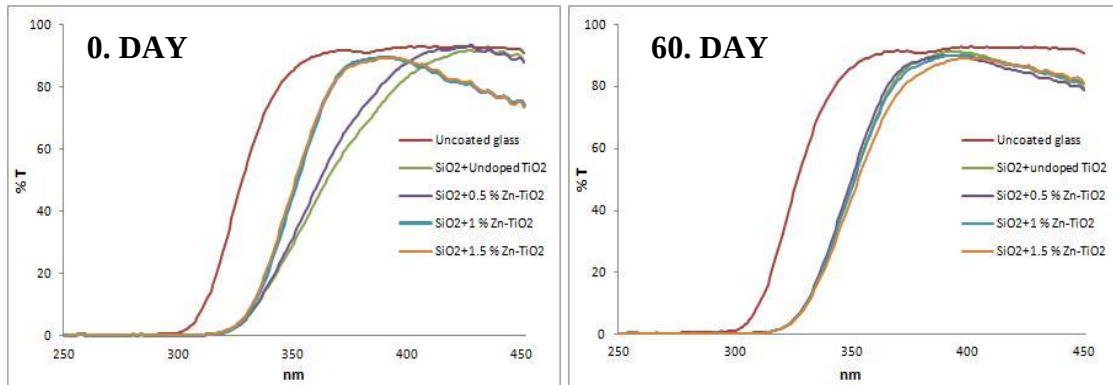


Figure 3.124. Comparison of transmittance spectras of SLS glasses coated first with SiO_2 then with undoped TiO_2 , 0.5 % Zn- TiO_2 , 1 % Zn- TiO_2 , 1.5 % Zn- TiO_2 at the 0th and the 60th day of the preparation of the solutions.

Absorption edge of TiO_2 film no more seems to shift to shorter wavelength ranges when doped with 1 % Zn, 1.5 % Zn when SLS glasses were coated at the 60th day of preparation of solutions. At 450 nm, transmittance of SLS glass coated with undoped TiO_2 decreases and all transmittance values of the SLS glasses coated at the 60th day of preparation with undoped and 0.5 % Zn 1 % Zn, 1.5 % Zn doped TiO_2 approximately become similar. Zn dopant seems not to affect the transmittance value of TiO_2 film any more.

Transmittances of uncoated SLS glass and SLS glasses that were first coated with SiO_2 then coated at the 0th and the 60th day of preparation with undoped TiO_2 , 0.5 % Zn doped, 1 % Zn doped, 1.5 % Zn doped TiO_2 at 350 nm are 86 %, 31 %, 33 %, 48 %, 50 % and 86 %, 48 %, 50 %, 47 %, 44 % respectively. It can be seen from these results that while UV blocking property of undoped and 0.5 % Zn doped TiO_2 film reduces, UV blocking property of 1 % Zn doped TiO_2 film remains nearly same and UV blocking property of 1.5 % Zn doped TiO_2 film enhances when TiO_2 solutions were used at the 60th day of preparation.

Transmittances of uncoated SLS glass and SLS glasses that were first coated with SiO_2 then coated at the 0th day of preparation with undoped TiO_2 , 0.5 % Cr doped, 1 % Cr doped, 1.5 % Cr doped TiO_2 at 400 nm and at 450 nm are 93 %, 84 %, 83 %, 85 %, 88 % and 92 %, 88 %, 88 %, 72 %, 72 % respectively (Figure 3.125).

Transmittances of uncoated SLS glass and SLS glasses that were first coated with SiO_2 then coated at the 60th day of preparation with undoped TiO_2 , 0.5 % Cr doped, 1 % Cr doped, 1.5 % Cr doped TiO_2 at 400 nm and at 450 nm are 93 %, 91 %, 88 %, 87 %, 87 % and 92 %, 80 %, 78 %, 79 %, 79 % respectively.

Absorption edge of TiO_2 film no more seems to shift to shorter wavelength ranges when doped with 1 % Cr and 1.5 % Cr, when SLS glasses were coated at the 60th day of preparation of solutions. At 450 nm, transmittance of SLS glass that was coated with undoped TiO_2 decreases and all transmittance values of the SLS glasses that were coated at the 60th day of preparation with undoped and 0.5 % Cr, 1 % Cr, 1.5 % Cr doped TiO_2 approximately become similar. Cr dopant seems not to affect the transmittance value of TiO_2 film any more.

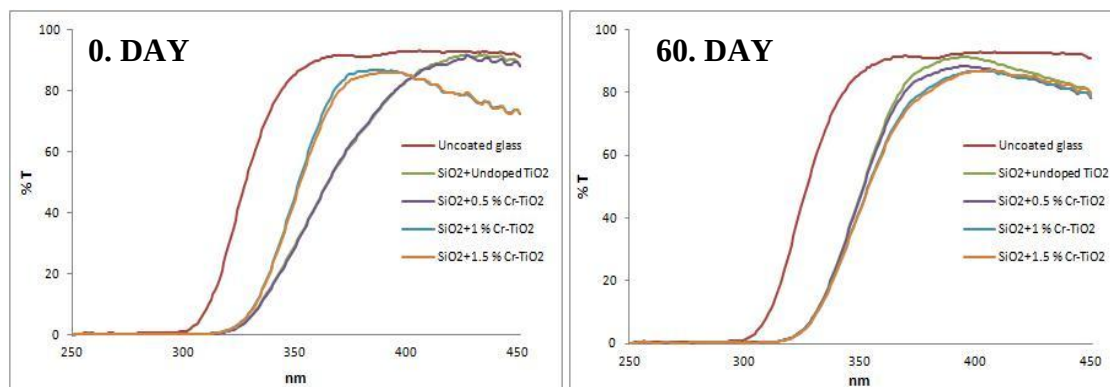


Figure 3.125. Comparison of transmittance spectras of SLS glasses coated first with SiO_2 then with undoped TiO_2 , 0.5 % Cr- TiO_2 , 1 % Cr- TiO_2 , 1.5 % Cr- TiO_2 at the 0th and the 60th day of the preparation of the solutions.

Transmittances of uncoated SLS glass and SLS glasses that were first coated with SiO_2 then coated at the 0th and the 60th day of preparation with undoped TiO_2 , 0.5 % Cr doped, 1 % Cr doped, 1.5 % Cr doped TiO_2 at 350 nm are 86 %, 31 %, 30 %, 49 %, 47 % and 86 %, 48 %, 47 %, 43 %, 43 % respectively.

It can be seen from these results that while UV blocking property of undoped and 0.5 % Cr doped TiO_2 film reduces, UV blocking property of 1 % Cr and 1.5 % Cr doped TiO_2 film enhances when TiO_2 solutions were used at the 60th day of preparation.

3.6.4. Contact angle measurement and photoinduced wettability test

Figure 3.126 shows contact angle of water droplet on SLS glasses that were coated at the 60th day of preparation with undoped, 0.5 % Ag, 1 % Ag and 1.5 % Ag doped TiO_2 solutions.

Results which are arithmetic mean of three measurements showed that when solutions were used at the 60th day of their preparation similar to when they were used at the 0th day of their preparation, 0.5 %, 1 %, 1.5 % Ag doping had almost no effect on initial hydrophilicity of TiO_2 film.

However it should be noted that initial contact angle values of the films formed by using solutions at the 60th day of their preparation are greater than the initial contact angle values of the films formed by using solutions at the 0th day of their preparation.

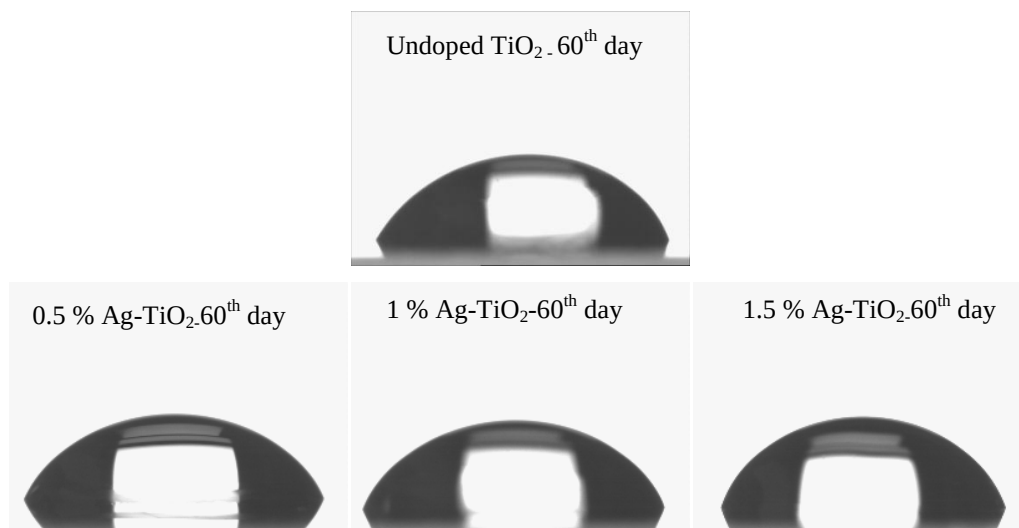


Figure 3.126. Contact angle measurement of SLS glasses coated at the 60th day of preparation with undoped TiO_2 , 0.5 % Ag- TiO_2 , 1 % Ag- TiO_2 , 1.5 % Ag- TiO_2

Table 3.26 shows the changes in contact angles of uncoated SLS glass and SLS glasses that were coated at the 60th day of preparation with undoped, 0.5 % Ag, 1 % Ag, 1.5 % Ag doped TiO_2 solutions during UV irradiation and storage in dark and Figure 3.127 shows the comparison of the photoinduced wettability of SLS glasses that were coated at the 0th and the 60th day of preparation with undoped, 0.5 %, 1 %, 1.5 % Ag doped TiO_2 solutions.

Table 3.26. Changes in contact angles of uncoated SLS glass, SLS glasses coated at the 60th day of preparation with undoped, 0.5 % Ag, 1 % Ag, 1.5 % Ag doped TiO_2 during UV irradiation and storage in dark.

	0 min. UV	15 min. UV	30 min. UV	45 min. UV	60 min. UV	18 hrs. Dark	24 hrs. Dark	48 hrs. Dark
Uncoated glass	45°	63°	57°	58°	65°	52°	63°	56°
Undoped TiO_2	65°	37°	25°	8°	6.5°	29°	42°	44°
0.5 % Ag- TiO_2	65°	40°	26°	15°	5°	30°	32°	35°
1 % Ag- TiO_2	68°	46°	25°	21°	7°	28°	31°	41°
1.5 % Ag- TiO_2	71°	42°	17°	10°	7°	30°	34°	35°

SLS glasses that were coated with undoped and 0.5 % Ag, 1 % Ag, 1.5 % Ag doped TiO₂ solutions at the 60th day of their preparation also showed approximately the same behaviour during UV irradiation and storage in dark as they had showed when were coated with the solutions at the 0th day of their preparation.

Compared to their 0th day usage, it can be said that when the solutions were used to form films on SLS glasses at the 60th day of their preparation, UV irradiation time to get the same hydrophilicity takes longer.

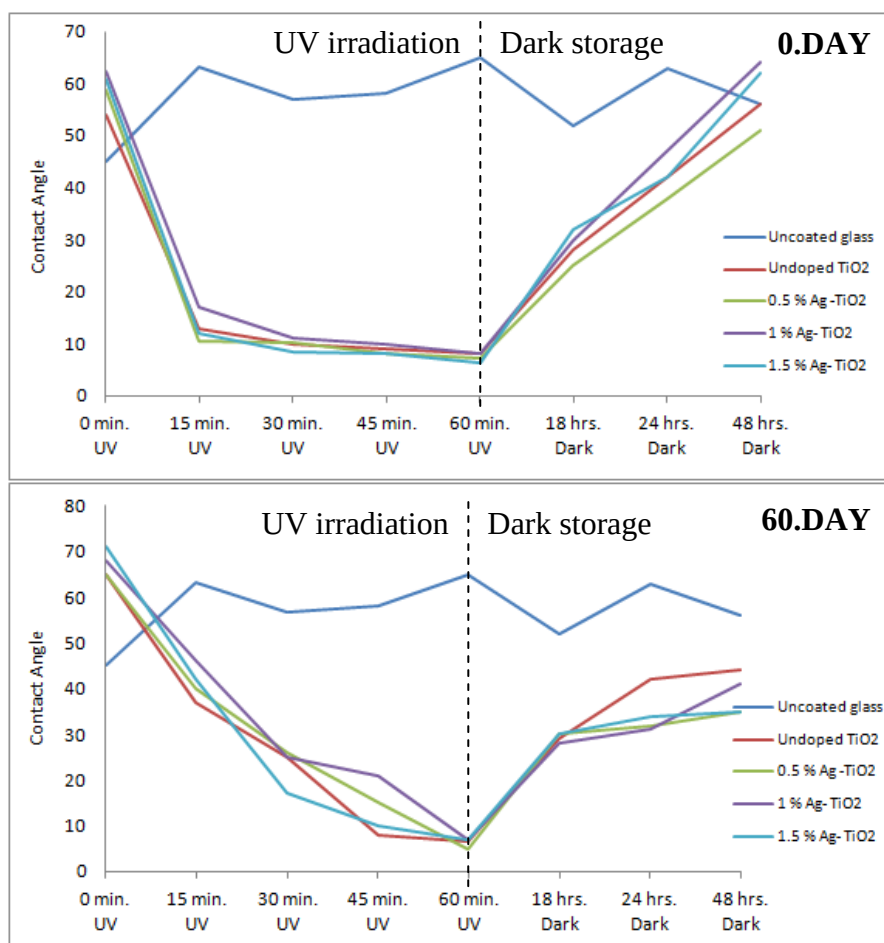


Figure 3.127. Comparison of the photoinduced wettability of uncoated SLS glass, SLS glasses coated at the 0th and the 60th day of preparation with undoped, 0.5 % Ag, 1 % Ag, 1.5 % Ag doped TiO₂ during UV irradiation and storage in dark.

While contact angles of all undoped and 0.5 % Ag, 1 % Ag, 1.5 % Ag doped TiO₂ films formed by the solutions at the 0th day of preparation, decrease from 60 degrees to 15 degrees after 15 minutes irradiation, contact angles of all undoped and 0.5 % Ag, 1 %

Ag, 1.5 % Ag doped TiO_2 films formed by the solutions at the 60th day of preparation, decrease from 60 degrees to only 40 degrees after 15 minutes irradiation.

Another difference between the 0th day and the 60th day usage of undoped and 0.5 %, 1 %, 1.5 % Ag doped TiO_2 solutions is that while undoped and 0.5 %, 1 %, 1.5 % Ag doped TiO_2 films formed by the solutions at the 0th day of preparation gain their initial contact angle values after storage in dark for 48 hours, it takes more than 48 hours for the undoped and 0.5 % Ag, 1 % Ag, 1.5 % Ag doped TiO_2 films formed by the solutions at the 60th day of preparation to get their initial contact angle values.

Figure 3.128 shows contact angle of water droplet on SLS glasses that were coated at the 60th day of preparation with undoped, 0.5 % Zn, 1 % Zn and 1.5 % Zn doped TiO_2 .

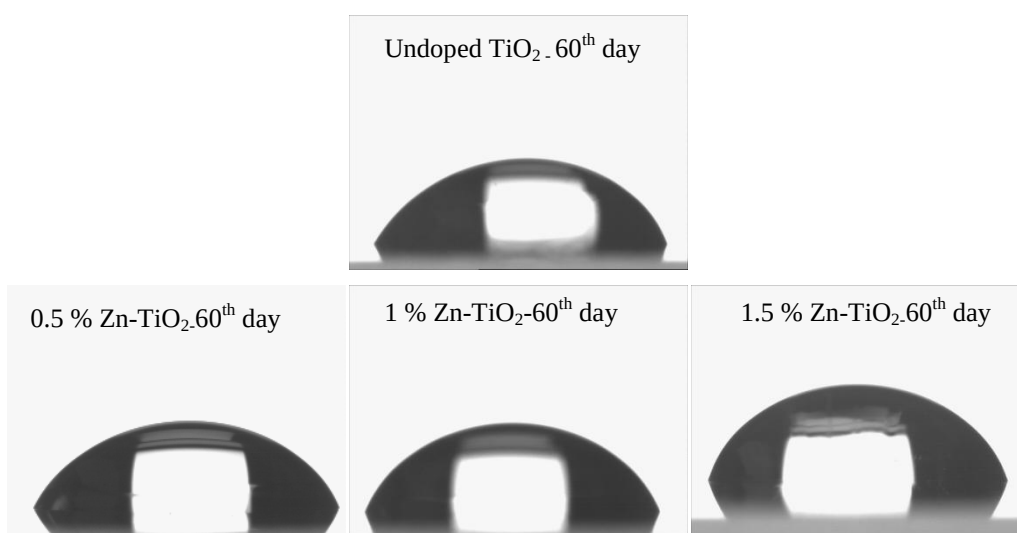


Figure 3.128. Contact angle measurement of SLS glasses coated at the 60th day of preparation with undoped TiO_2 , 0.5 % Zn- TiO_2 , 1 % Zn- TiO_2 , 1.5 % Zn- TiO_2

Results which are arithmetic mean of three measurements show that when solutions are used at the 60th day of preparation like when they are used at the 0th day of preparation, 0.5 %, 1 %, 1.5 % Zn doping has almost no effect on initial hydrophilicity of TiO_2 film.

However it should be noted that initial contact angle values of the films formed by using solutions at the 60th day, are greater than the initial contact angle values of the films formed by using solutions at the 0th day of their preparation.

Table 3.27. Changes in contact angles of uncoated SLS glass, SLS glasses coated at the 60th day of preparation with undoped, 0.5 % Zn, 1 % Zn, 1.5 % Zn doped TiO₂ during UV irradiation and storage in dark.

	0 min. UV	15 min. UV	30 min. UV	45 min. UV	60 min. UV	18 hrs. Dark	24 hrs. Dark	48 hrs. Dark
Uncoated glass	45°	63°	57°	58°	65°	52°	63°	56°
Undoped TiO ₂	65°	37°	25°	8°	6.5°	29°	42°	44°
0.5 % Zn-TiO ₂	64°	47°	19°	11°	7°	34°	38°	40°
1 % Zn-TiO ₂	69°	40°	25°	7°	9,7°	30°	35°	38°
1.5 % Zn-TiO ₂	72°	40°	25°	7°	10°	31°	32°	41°

SLS glasses coated with undoped and 0.5 % Zn, 1 % Zn, 1.5 % Zn doped TiO₂ solutions at the 60th day of their preparation also show approximately the same behaviour during UV irradiation and storage in dark as they had showed when coated with the solutions at the 0th day of their preparation.

While contact angles of all undoped and 0.5 % Zn, 1 % Zn, 1.5 % Zn doped TiO₂ films formed by the solutions at the 0th day of preparation, decreases from 60 degrees to 15 degrees after 15 minutes irradiation, contact angles of all undoped and 0.5 % Zn, 1 % Zn, 1.5 % Zn doped TiO₂ films formed by the solutions at the 60th day of preparation, decreases from 60 degrees to only 40 degrees after 15 minutes irradiation.

Compared to their 0th day usage it can be said that when the solutions are used to form films on SLS glasses at the 60th day of their preparation, UV irradiation time to get the same hydrophilicity takes longer.

Another difference between the 0th day and the 60th day usage of undoped and 0.5 % Zn, 1 % Zn, 1.5 % Zn doped TiO₂ solutions is that while undoped and 0.5 % Zn, 1 % Zn, 1.5 % Zn doped TiO₂ films formed by the solutions at the 0th day of preparation gain their initial contact angle values after storage in dark for 48 hours, it takes more than 48 hours for the undoped and 0.5 % Zn, 1 % Zn, 1.5 % Zn doped TiO₂ films formed by the solutions at the 60th day of preparation to get their initial contact angle values.

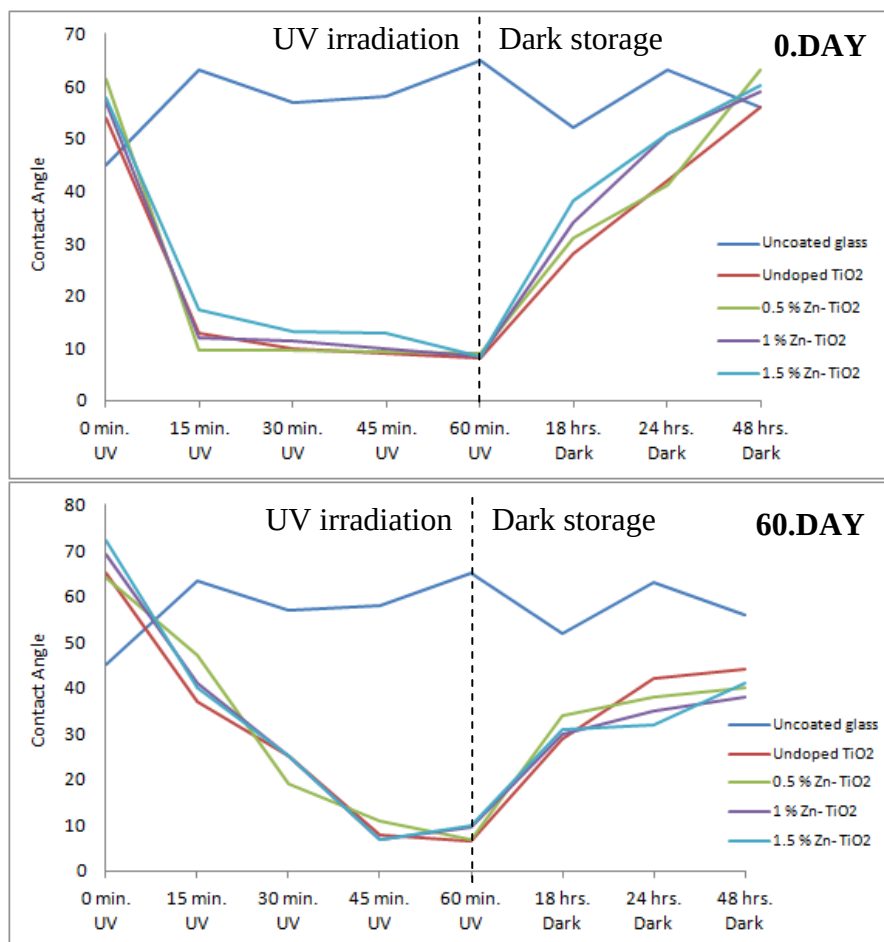


Figure 3.129. Comparison of the photoinduced wettability of uncoated SLS glass, SLS glasses coated at the 0th and the 60th day of preparation with undoped, 0.5 % Zn, 1 % Zn, 1.5 % Zn doped TiO₂ during UV irradiation and storage in dark.

Figure 3.130 shows contact angle of water droplet on SLS glasses coated at the 60th day of preparation with undoped, 0.5 % Cr, 1 % Cr and 1.5 % Cr doped TiO₂ solutions.

Results which are arithmetic mean of three measurements show that when solutions are used at the 60th day of preparation 0.5 %, 1 %, 1.5 % Cr doping has almost no effect on initial contact angle value of TiO₂ film. However it should be noted that initial contact angle values of the films formed by using solutions at the 60th day are greater than the initial contact angle values of the films formed by using solutions at the 0th day of preparation.

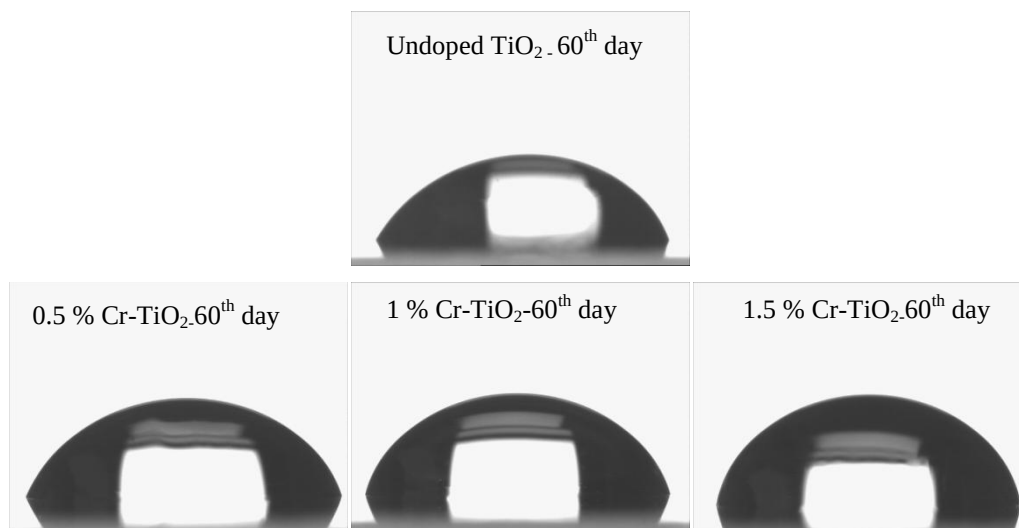


Figure 3.130. Contact angle measurement of SLS glasses coated at the 60th day of preparation with undoped TiO_2 , 0.5 % Cr- TiO_2 , 1 % Cr- TiO_2 , 1.5 % Cr- TiO_2

Table 3.28 shows the changes in contact angles of uncoated SLS glass and SLS glasses that were coated at the 60th day of preparation with undoped, 0.5 %, 1 %, 1.5 % Cr doped TiO_2 solutions during UV irradiation and storage in dark and Figure 3.131 shows the comparison of the photoinduced wettability of SLS glasses coated at the 0th and the 60th day of preparation with undoped, 0.5 %, 1 %, 1.5 % Cr doped TiO_2 solutions.

Table 3.28. Changes in contact angles of uncoated SLS glass, SLS glasses coated at the 60th day of preparation with undoped, 0.5 % Cr, 1 % Cr, 1.5 % Cr doped TiO_2 during UV irradiation and storage in dark.

	0 min. UV	15 min. UV	30 min. UV	45 min. UV	60 min. UV	18 hrs. Dark	24 hrs. Dark	48 hrs. Dark
Uncoated glass	45°	63°	57°	58°	65°	52°	63°	56°
Undoped TiO_2	65°	37°	25°	8°	6.5°	29°	42°	44°
0.5 % Cr- TiO_2	67°	42°	29°	20°	11°	33°	43°	49°
1 % Cr- TiO_2	70°	60°	42°	26°	26°	33°	42°	67°
1.5 % Cr- TiO_2	75°	80°	81°	78°	77°	76°	80°	85°

SLS glasses that were coated with undoped and 0.5 % Cr, 1 % Cr, 1.5 % Cr doped TiO_2 solutions at the 60th day of preparation show different behaviours during UV irradiation and storage in dark.

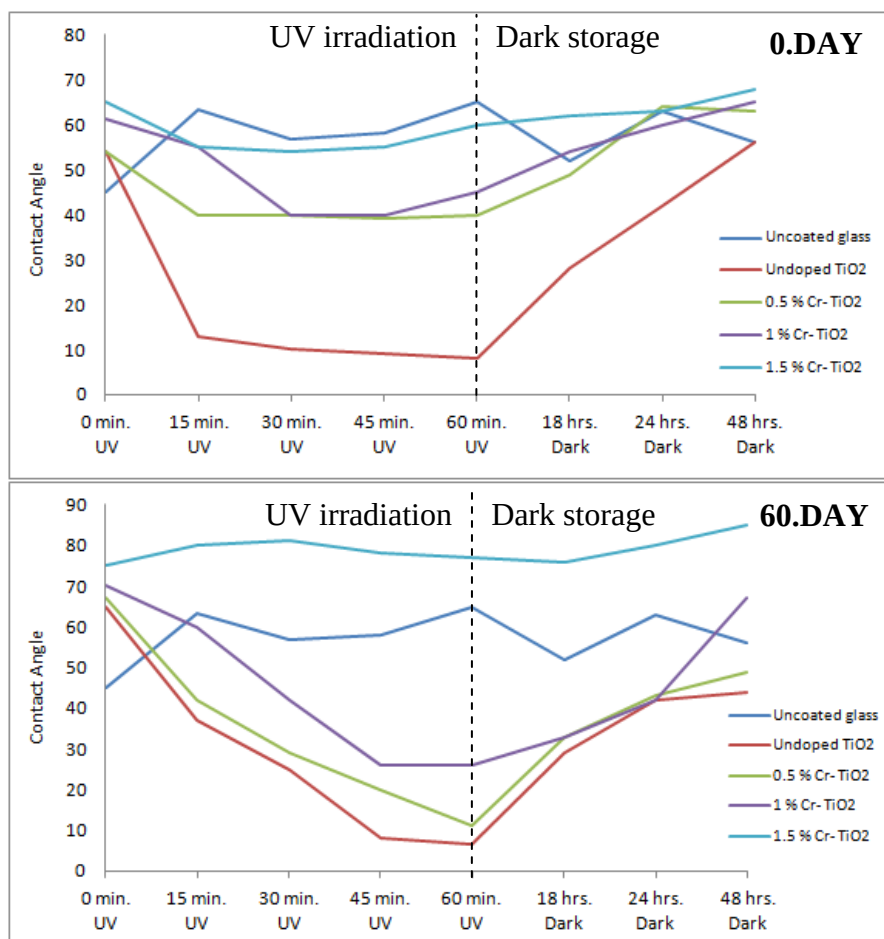


Figure 3.131. Comparison of the photoinduced wettability of uncoated SLS glass, SLS glasses coated at the 0th and the 60th day of preparation with undoped, 0.5 % Cr, 1 % Cr, 1.5 % Cr doped TiO_2 during UV irradiation and storage in dark.

Undoped and 0.5 % Cr doped TiO_2 films behave similar after 15 and 30 minutes UV irradiation. However after 45 minutes and 60 minutes UV irradiation, the contact angle of 0.5 % Cr doped TiO_2 film starts to decrease more slowly compared to undoped TiO_2 film. Looking at 1 % Cr doped TiO_2 film, it can be said that 15 minutes UV irradiation causes almost no decrease at its contact angle. Although a decrease is seen after 30 minutes and 45 minutes UV irradiation, it is very slight compared to the undoped and

0.5 % Cr doped TiO_2 films and the same contact angle values after 45 minutes and 60 minutes UV irradiation shows that UV irradiation starts not to affect the hydrophilicity of the 1 % Cr doped TiO_2 film after 45 minutes.

Totally different from undoped, 0.5 % and 1 % Cr doped TiO_2 films, 1.5 % Cr doped TiO_2 film seems to be not affected from UV irradiation. It has almost the same contact angle values during the photoinduced wettability test.

When these results are compared to photoinduced wettability test results of SLS glasses coated at the 0th day of preparation with 0.5 %, 1 % Cr and 1.5 % Cr doped TiO_2 solutions, it is possible to say that when coated with the solutions at the 60th day of preparation 0.5 % and 1 % Cr doped TiO_2 start to show photoinduced wettability while 1.5 % Cr doped TiO_2 starts to behave even worse than uncoated SLS glass.

Why Cr dopant causes such a change in photoinduced wettability when Cr doped TiO_2 solutions are used at the 60th day of preparation is needed to be further studied to be understood.

3.6.5. Photocatalytic activity evaluation

Figure 3.132 shows unirradiated Rhodamine B solution and Rhodamine B solutions in which SLS glasses coated at the 0th and the 60th day of preparation with undoped TiO_2 , 0.5 % Ag, 1 % Ag, 1.5 % Ag doped TiO_2 solutions were irradiated for 15 hours.

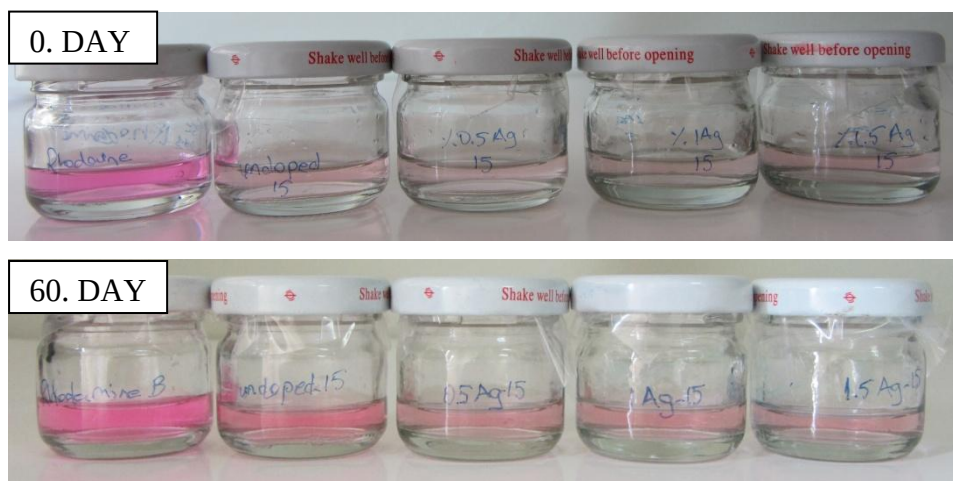


Figure 3.132. Comparison of photocatalytical activity of SLS glasses coated with Ag- TiO_2 at the 0th and the 60th day of preparation (left to right: unirradiated Rhodamine B, Rhodamine B belongs to undoped TiO_2 , 0.5 % Ag- TiO_2 , 1 % Ag- TiO_2 , 1.5 % Ag- TiO_2)

It is possible to see from Figure 3.132 that although as shown in Section 3.6.1 appearances of undoped TiO₂, 0.5 % Ag doped TiO₂, 1 % Ag doped TiO₂, 1.5 % Ag doped TiO₂ solutions did not change 60 days after preparation, films prepared by using these solutions do not show the same photocatalytic activity anymore.

Photoinduced wettability test results discussed in the previous section which showed that it took longer UV irradiation time to have the same hydrophilicity for the SLS glasses coated at the 60th day of preparation with undoped TiO₂, 0.5 % Ag, 1 % Ag, 1.5 % Ag doped TiO₂ compared to the the SLS glasses coated at the 0th day of preparation with undoped TiO₂, 0.5 % Ag, 1 % Ag, 1.5 % Ag doped TiO₂ solutions, also support these photocatalytic test results.

Table 3.29 shows numerically how different are the photocatalytic activity of the undoped TiO₂, 0.5 % Ag doped TiO₂, 1 % Ag doped TiO₂, 1.5 % Ag doped TiO₂ solutions at the 0th and the 60th day of preparation.

Table 3.29. Absorbance values of unirradiated Rhodamine B solution and Rhodamine B solutions in which SLS glasses coated at the 0th and the 60th day of preparation with undoped TiO₂, 0.5 % Ag, 1 % Ag, 1.5 % Ag doped TiO₂ were radiated for 15 hours.

	0 th day		60 th day	
	A	Wavelength (nm)	A	Wavelength (nm)
Rhodamine B	0.443	554	0.443	554
Undoped TiO ₂	0.079	533	0.239	539
0.5 % Ag-TiO ₂	0.057	533	0.139	537
1 % Ag-TiO ₂	0.054	531	0.145	537
1.5 % Ag-TiO ₂	0.065	534	0.113	536

Absorbance values of Rhodamine B solutions in which SLS glasses at the 0th and the 60th day of preparation coated with undoped TiO₂, 0.5 % Ag, 1 % Ag, 1.5 % Ag doped TiO₂ solutions were radiated for 15 hours increase from 0.079 to 0.239, from 0.057 to 0.139, from 0.054 to 0.145 and from 0.065 to 0.113 respectively.

Looking at the absorbance value of unirradiated Rhodamine B it is possible to say that when used at the 60th day of preparation undoped TiO₂, 0.5 % Ag doped TiO₂, 1 % Ag doped TiO₂, 1.5 % Ag doped TiO₂ solutions still show photocatalytic activity however it is not as much as the photocatalytic activity that they showed when they were used immediately after preparation. It should also be noted that when used 60 days after preparation, 0.5 % Ag, 1 % Ag, 1.5 % Ag doped TiO₂ films show higher photocatalytic activity than undoped TiO₂ film.

Figure 3.133 shows unirradiated Rhodamine B solution and Rhodamine B solutions in which SLS glasses coated at the 0th and the 60th day of preparation with undoped TiO₂, 0.5 %, 1 %, 1.5 % Zn doped TiO₂ were radiated for 15 hours. Looking at Figure 3.133 and Table 3.30, it is possible to say that there is a decrease at photocatalytic activity of undoped, 0.5 % Zn, 1 % Zn and 1.5 % Zn doped TiO₂ solutions when used at the 60th day of preparation.

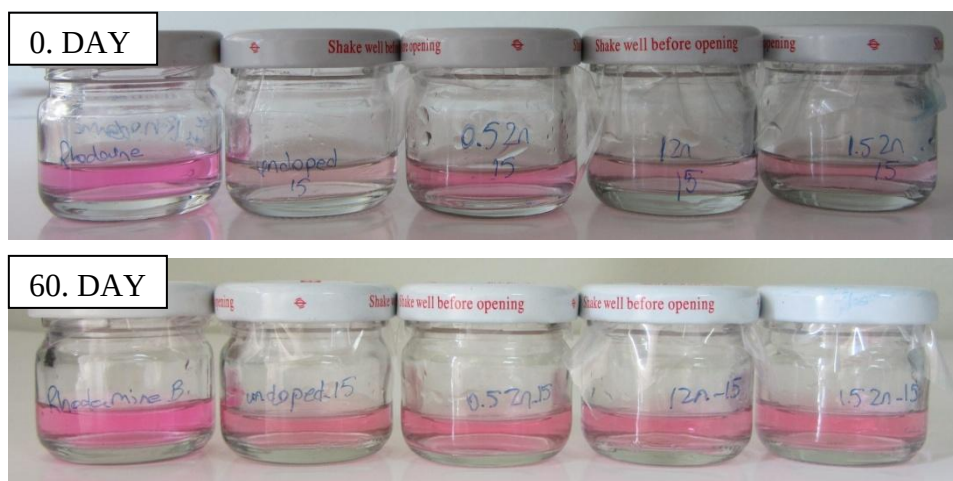


Figure 3.133. Comparison of photocatalytic activity of SLS glasses coated with Zn-TiO₂ at the 0th and the 60th day of preparation (left to right: unirradiated Rhodamine B, Rhodamine B belongs to undoped TiO₂, 0.5 % Zn-TiO₂, 1 % Zn-TiO₂, 1.5 % Zn-TiO₂).

Photoinduced wettability test results discussed in the previous section which showed that it took longer UV irradiation time to have the same hydrophilicity for the SLS glasses coated at the 60th day of preparation with undoped TiO₂, 0.5 % Zn, 1 % Zn, 1.5 % Zn doped TiO₂ solutions compared to the the SLS glasses coated at the 0th day of preparation with undoped TiO₂, 0.5 % Zn, 1 % Zn, 1.5 % Zn doped TiO₂ solutions, also support these photocatalytic activity test results.

Table 3.30. Absorbance values of unirradiated Rhodamine B solution and Rhodamine B solutions in which SLS glasses coated at the 0th and the 60th day of preparation with undoped TiO₂, 0.5 % Zn, 1 % Zn, 1.5 % Zn doped TiO₂ were radiated for 15 hours.

	0 th day		60 th day	
	A	Wavelength (nm)	A	Wavelength (nm)
Rhodamine B	0.443	554	0.443	554
Undoped TiO ₂	0.079	533	0.239	539
0.5 % Zn-TiO ₂	0.240	541	0.268	542
1 % Zn-TiO ₂	0.104	541	0.231	542
1.5 % Zn-TiO ₂	0.130	539	0.266	540

Absorbance values of Rhodamine B solutions in which SLS glasses at the 0th and the 60th day of preparation coated with undoped TiO₂, 0.5 % Zn doped TiO₂, 1 % Zn doped TiO₂, 1.5 % Zn doped TiO₂ solutions were radiated for 15 hours increase from 0.079 to 0.239, from 0.240 to 0.268, from 0.104 to 0.231 and from 0.130 to 0.226 respectively.

From these results it is possible to say that while undoped TiO₂ solution shows the best photocatalytic activity when all undoped and Zn doped TiO₂ solutions are used immediately after preparation, all undoped and Zn doped TiO₂ solutions nearly show the same photocatalytic activity when they are used at the 60th day of preparation.

Figure 3.134 shows unirradiated Rhodamine B solution and Rhodamine B solutions in which SLS glasses coated at the 0th and the 60th day of preparation with undoped TiO₂, 0.5 % Cr doped TiO₂, 1 % Cr doped TiO₂, 1.5 % Cr doped TiO₂ were radiated for 15 hours.

Looking at Figure 3.134 and Table 3.31 it is possible to say that 0.5 % Cr, 1 % Cr and 1.5 % Cr doped TiO₂ solutions no more show photocatalytic activity when used at the 60th day of preparation.



Figure 3.134. Comparison of photocatalytic activity of SLS glasses coated with Cr-TiO₂ at the 0th and the 60th day of preparation (left to right: unirradiated Rhodamine B, Rhodamine B belongs to undoped TiO₂, 0.5 % Cr-TiO₂, 1 % Cr-TiO₂, 1.5 % Cr-TiO₂)

Table 3.31. Absorbance values of unirradiated Rhodamine B solution and Rhodamine B solutions in which uncoated SLS glass and SLS glasses coated at the 0th and the 60th day of preparation with undoped TiO₂, 0.5 % Cr doped TiO₂, 1 % Cr doped TiO₂, 1.5 % Cr doped TiO₂ were radiated for 15 hours.

	0 th day		60 th day	
	A	Wavelength (nm)	A	Wavelength (nm)
Rhodamine B	0.443	554	0.443	554
Uncoated glass	1.314	549	1.314	549
Undoped TiO ₂	0.079	533	0.239	539
0.5 % Cr-TiO ₂	0.344	526	0.498	537
1 % Cr-TiO ₂	0.374	530	0.551	536
1.5 % Cr-TiO ₂	0.396	535	0.526	539

Absorbance values of Rhodamine B solutions in which SLS glasses at the 0th and the 60th day of preparation coated with undoped TiO₂, 0.5 % Cr doped TiO₂, 1 % Cr doped TiO₂, 1.5 % Cr doped TiO₂ solutions were radiated for 15 hours, increase from 0.079 to

0.239, from 0.344 to 0.498, from 0.374 to 0.551 and from 0.396 to 0.526 respectively. Taking the absorbance value of unirradiated Rhodamine B into consideration, it is obvious that when used at the 60th day of preparation, 0.5 % Cr, 1 % Cr and 1.5 % Cr doped TiO₂ solutions cause color of Rhodamine B to be darkened. However looking at Table 3.31 it should also be noted that glasses coated with 0.5 % Cr, 1 % Cr and 1.5 % Cr doped TiO₂ are still better than the uncoated glass even when coating solutions are used at the 60th day of preparation.

Although photoinduced wettability test result discussed in the previous section which showed that SLS glass coated at the 60th day of preparation with 1.5 % Cr-TiO₂ solution behaved worse than uncoated SLS glass supports the photocatalytic activity test result, photoinduced wettability test results which showed that SLS glasses coated at the 60th day of preparation with 0.5 % Cr and 1 % Cr doped TiO₂ solutions started to show photoinduced wettability do not support these photocatalytic activity test results.

Although as discussed in Section 3.3.1, it is believed that there is a correlation between photoinduced wettability and photocatalytic activity [136], it is possible to find opposite ideas in literature which support the result found in this study; For instance Yuan and his friends reported that while wettability of Cr doped TiO₂ films were observed to be improved, photocatalytic activity of the same Cr doped TiO₂ films were found to be similar even lower than that of undoped TiO₂ films [141].

4. CONCLUSIONS

In this study it was aimed to investigate the effects of three different concentrations (0.5 %, 1 %, 1.5 %) of Ag, Zn and Cr dopants on photocatalytic activity, transmittance %, photoinduced wettability and physical properties (adhesion, taber abrasion, scratch resistance, salt spray corrosion resistance) of TiO₂ film formed on SLS glass. Shelf lives of TiO₂ solutions were also determined and the effect of shelf life on photocatalytic activity, transmittance % and photoinduced wettability was investigated. Results that were found at the end of this thesis study are listed below:

1. It was seen that without coating a SiO₂ layer between the SLS glass and TiO₂ film, Na⁺ ions diffused from SLS glass to TiO₂ film prevented the crystallization of TiO₂ film at low sintering temperatures and at high sintering temperatures caused the anatase phase to transform into rutile and brookite phases which are known to have no photocatalytic activity.
2. Photocatalytic activity test results showed that degradation of Rhodamine B was not possible if there was not a SiO₂ film between SLS glass and TiO₂ film.
3. TEM results showed that crystallite sizes of undoped and doped TiO₂ powders changed between 10 nm and 12 nm which was also shown by XRD analysis.
4. It was seen that while surface area of Ag doped TiO₂ powder increased by increasing Ag dopant concentration and surface area of Zn doped TiO₂ powder increased by increasing Zn dopant concentration, surface area of Cr doped TiO₂ powder increased by increasing Cr dopant concentration only up to 1 %.
5. It was found that more or less all three dopants increased surface roughness of TiO₂ film. Besides, initial contact angle values of TiO₂ films indicated that roughness and contact angle values were directly proportional.
6. Coating SLS glass with undoped and 0.5 % Ag, 1 % Ag, 1.5 % Ag, 0.5 % Zn, 1 % Zn, 1.5 % Zn, 0.5 % Cr, 1 % Cr, 1.5 % Cr doped TiO₂ solution did not decrease transmittance value of SLS glass at 450 nm.
7. Transmittance value of SLS glass at 450 nm decreased slightly when first coated with SiO₂ solution than with undoped and 0.5 % Zn, 0.5 % Cr doped TiO₂ solutions and decreased dramatically when first coated with SiO₂ solution then with 0.5 % Ag, 1 %

Ag, 1.5 % Ag, 1 % Zn, 1.5 % Zn, 1 % Cr, 1.5 % Cr doped TiO₂ solutions. The effect of SiO₂ layer on transmittance has been first showed in this study. These results showed that it is necessary to find an optimum thickness for SiO₂ layer for both to prevent Na⁺ diffusion and to prevent the decrease at transmittance of SLS glass.

8. Transmittance measurements showed that all TiO₂ films behaved as UV blockers. The films that had the lowest transmittance value at UV region were 0.5 % Zn doped TiO₂ film and 0.5 % Cr doped TiO₂ film. This UV blocking behaviour became stronger when there was SiO₂ layer between SLS glass and TiO₂ film.

9. Transmittance measurements showed that while in the absence of SiO₂ layer non of the dopants caused blue shift, in the presence of SiO₂ layer absorption edge of undoped TiO₂ film shifted to shorter wavelength ranges when doped with 0.5 % Ag, 1% Ag, 1.5 % Ag, 1% Zn, 1.5% Zn, % 1 Cr, % 1.5 Cr.

10. Photoinduced wettability test results showed that undoped, 0.5 % Ag, 1 % Ag, 1.5 % Ag, 0.5 % Zn, 1 % Zn 1.5 % Zn doped TiO₂ films became nearly supehyrophilic (contact angles <10°) after 45-60 minutes UV irradiation.

11. It was shown that Cr dopant has a serious detrimental effect on photoinduced wettability property of TiO₂ film.

12. The optimum withdrawal rate for dip-coating of SLS glasses with TiO₂ solutions was determined as 15 cm/min.

13. Optimum pH of Rhodamine B solution for optimum photocatalytic degradation was found to be 9.

14. Optimum sintering temperature for optimum photocatalytic degradation of Rhodamine B was found to be 400 °C.

15. Ag dopant was found to be the only dopant that promoted photocatalytic activity of TiO₂ film slightly. Optimum Ag dopant concentration was determined as 1 %. Changing the concentration of Ag dopant between 0.5 % and 1.5 % was found to cause a slight difference at photocatalytic activity. These results were found to be in good agreement with photoinduced wettability test results.

16. Zn doping was found to inhibit photocatalytic activity of TiO₂ film slightly. It was seen that between Zn doped TiO₂ films, 1 % Zn doped TiO₂ film showed the highest

photocatalytic activity. These results were found to be partly in agreement with photoinduced wettability test results.

17. It was shown that when its concentration was 0.5 %, 1 % and 1.5 %, Cr dopant had a serious detrimental effect on photocatalytic activity of TiO₂ film.

18. Adhesion test showed that doping with Ag, Zn, Cr did not change adherence of TiO₂ to the SLS glass.

19. It was seen that Ag, Zn and Cr dopants had a slight effect on scratch hardness of TiO₂ film. While 0.5 % Ag, 1 % Ag, 1.5 % Ag, 1 % Zn, 1.5 % Zn, 1 % Cr, 1.5 % Cr doping slightly increased, 0.5 % Zn and 0.5 % Cr doping slightly decreased scratch hardness of TiO₂ film.

20. It was seen that 0.5 % Ag, 1 % Ag 1.5 % Ag, 0.5 % Zn 1 % Zn, 0.5 % Cr doping did not change while 1.5 % Zn, 1 % Cr, 1.5 % Cr doping slightly decreased taber abrasion resistance of TiO₂ film.

21. No matter coated with undoped or Ag, Zn, Cr doped TiO₂ solutions, taber abrasion resistance of air sides of all coated SLS glasses were higher than that of tin sides.

22. Salt spray test was found to cause undoped, 0.5 % Ag, 1 % Ag, 1.5 % Ag, 0.5 % Zn, 1 % Zn, 1.5 % Zn, 1.5 % Cr doped TiO₂ films to loose their photocatalytic properties while it was determined that photocatalytic activity of 0.5 % Cr, 1 % Cr doped TiO₂ increased after salt spray test.

23. At 450 nm transmittance values of undoped film and 0.5 Cr doped TiO₂ film did not change, transmittance values of 0.5 % Ag, 1 % Ag 1.5 % Ag, 1.5 % Zn doped TiO₂ films increased, transmittance values of 0.5 % Zn, 1 % Zn, 1.5 % Cr doped TiO₂ films decreased after salt spray test.

24. It was seen that undoped, 0.5 % Ag, 1 % Ag, 1.5 % Ag, 0.5 % Zn, 1 % Zn, 1.5 % Zn, 0.5 % Cr, 1 % Cr, 1.5 % Cr doped TiO₂ solutions were stable nearly for 1 year. However it was determined that films formed on glass surface by using these solutions at the 60th day of their preparation did not show the same photocatalytic activity, photoinduced wettability and transmittance values any more. It was determined that photocatalytic activity of undoped, 0.5 % Ag, 1 % Ag, 1.5 % Ag, 0.5 % Zn, 1 % Zn, 1.5 % Zn, 0.5 % Cr, 1 % Cr, 1.5 % Cr doped TiO₂ films decreased. It was seen that it

took longer time for undoped, 0.5 % Ag, 1 % Ag, 1.5 % Ag, 0.5 % Zn, 1 % Zn, 1.5 % Zn doped TiO₂ films to gain the same hydrophilicity under UV light and it took longer time for all TiO₂ films to gain their initial contact angle values. After salt spray test 0.5 % Cr and 1 % Cr doped TiO₂ films started to show photo induced wettability property while 1.5 % Cr doped TiO₂ film had worse contact angle values than that of uncoated SLS glass at photoinduced wettability test. It was determined that transmittance values of undoped, 0.5 % Cr and 0.5 % Zn doped TiO₂ films decreased while transmittance values of 0.5 % Ag, 1 % Ag, 1.5 % Ag, 1 % Zn, 1.5 % Zn, 1 % Cr, 1.5 % Cr doped TiO₂ films increased.

How the photocatalytic activity, photoinduced wettability and transmittance values of TiO₂ films have changed when these films are formed with 0.5 % Ag, 1 % Ag, 1.5 % Ag, 0.5 % Zn, 1 % Zn, 1.5 % Zn, 0.5 % Cr, 1 % Cr, 1.5 % Cr doped TiO₂ solutions at the 60th day of their preparation has been first investigated in this study.

Taking the results exhibited here into consideration following subjects can be studied in the future:

- Effect of Cr dopant on photocatalytic activity of TiO₂ can be further studied with concentrations less than 0.5 %.
- Optimization of SiO₂ intermediate layer can be done to minimize its negative effect on transmittance at visible region and to maximize its UV blocking property at UV region.
- Storage life time at which first day photocatalytic activity of TiO₂ solutions able to be preserved can be determined.
- Studies to reduce photocatalytic degradation time can be done by optimizing pH and storage life.

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ÖZGEÇMİŞ

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Lise	-	Bursa Milli Piyango Anadolu Lisesi	1998
Üniversite	Kimya Mühendisliği	İstanbul Teknik Üniversitesi	2002
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İş Deneyimi

Yıl	Firma/Kurum	Görevi
2006-	TÜBİTAK MAM ME	Araştırmacı
2003-2005	COGNİS	Ar-ge Mühendisi

Bilimsel Eserler:

Davydenko, L.O., Nazarchuk, M.O., Plyuto, Y.V., Koyuncu, C.Z., Avcı, G.G., Duygulu, Ö. (2012) Synthesis of Mesoporous Silica Films by Low-Temperature Template Removal. The 13th Ukrainian-Polish Symposium, 11-14 September, Kyiv, Ukraine.

Avcı, G.G., Koyuncu, C.Z., Günay, V. (2010) İşlevsel Nano-Yapılı Kaplama Teknolojileri, Nanoteknoloji ve Nano-Malzeme Süreçleri. Editörler.; Baykara, T., Günay, V., Musluoğlu, E. TÜBİTAK MAM Malzeme Enstitüsü, Kocaeli, Türkiye.

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Avcı, G.G., Koyuncu, C.Z., Günay, V. (2009) Synthesis of ZnO Flowers by Hydrothermal Method. The 4th International Conference on Surfaces, Coatings and Nanostructured Materials (NanoSmat), 19-22 October, Rome, Italy.

Avcı, G.G., Koyuncu, C.Z., Günay, V. (2009) Alkali and Scratch Resistant, Hydrophobic Nanocomposite Coating on Polycarbonate Substrate. The 4th International Conference on Surfaces, Coatings and Nanostructured Materials (NanoSmat), 19-22 October, Rome, Italy.

Avcı, G.G., Koyuncu, C.Z., Günay, V. (2009) Nano Gümüş Sentezi. 5.Ulusal Nanobilim ve Nanoteknoloji Konferansı, 08-12 Haziran, Eskişehir, Türkiye.

Projelerde Yaptığı Görevler:

1. Araştırmacı - Alüminyum ve Alaşımları için Korozyon Önleyici, Çevreye Duyarlı Nanokaplamalar 2010-2013
2. Araştırmacı - Mam-Nano Kaplamalı İşlevsel Malzemelerin Geliştirilmesi 2010-2011
3. Araştırmacı - Mam-Nano Kaplamalı İşlevsel Tekstillerin Geliştirilmesi 2007-2009
4. Araştırmacı - TCP Kalite Tekstil Malzemenin Buruşmazlık Özelliğinin Geliştirilmesi 2006-2008
5. Araştırmacı - Development Of Antibacterial Nanostructured Material Active To Indoor Light 2006-2007
6. Araştırmacı - Denim ve Gabardin Tekstil Malzeme Yüzeylerinin Özellikli Kaplanması 2004-2007

7. Arařtırmacı - Sol-Jel Yöntemi İle İşlevsel Kaplamaların Geliştirilmesi 2006-2012
8. Arařtırmacı - Malzeme Enstitüsü Teknolojik Destekler Projesi (Kaplama ve Korozyon Laboratuvarları’nda yapılan endüstriyel hizmet testleri) 2006-

Ödüller:

1. 2009 TÜBİTAK-MAM Teşvik Ödülü
“TCP Kalite Tekstil Malzemenin Buruşmazlık Özelliğinin Geliştirilmesi”
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