

Nanostructure Thin Films of Titanium Dioxide Coated on Glass and Its Anti UV Effect for Living Organisms

Mohammad Hossein Habibi^{1,*}, Mojtaba Nasr-Esfahani², Giti Emtiazi³ and Baharak Hosseinkhani³

¹Nanotechnology Laboratory, Department of Chemistry, University of Isfahan, Isfahan, 81746-73441, Iran

²Department of Materials Science and Engineering, Islamic Azad University, Najafabad Branch, Iran

³Department of Biology, University of Isfahan, Isfahan, 81746-73441, Iran

Abstract: The increasing use of ultraviolet (UV) light in medicine, industrial environments, for cosmetic use, and even in consumer products necessitates that greater attention be paid to the potential hazards of this type of electromagnetic radiation. To avoid any adverse effects of exposure to this type of radiation, suitable protection filters were produced to block UV bands. Nanostructure composite and thin film of titanium dioxide coatings on glass have been prepared by the sol-gel method. TiO₂ sol suspension was prepared by first adding titanium tetra isopropoxide (Ti(OPr)₄ or TTP) to a mixture of ethanol and HCl (molar ratio TTP:HCl:EtOH:H₂O = 1:1.1:10:10) and then adding a 2 wt.% solution of hydroxyl ethyl cellulose (HEC) as dispersant followed by stirring. Precalcined TiO₂ nanopowder was mixed with a sol and heat treated. Thin and composite films were deposited on the glass substrate (microscope glass slide) by spin-coating them at ambient conditions. After drying, samples were heated to 500 °C. The resulting films were characterized by UV-Vis spectroscopy, X-ray diffraction (XRD) and Atomic Force Microscopy (AFM). The purpose of our study was to determine if thin and composite TiO₂ films with ultraviolet light have any effect on the growth of *Escherichia coli* (*E. coli*), *Staphylococcus aureus* (*S. aureus*) and *Bacillus species* (*Bacillus sp.*) We have seen unusual results in which TiO₂ thin and composite films protect *E. coli*, *S. aureus* and *Bacillus sp* from UV light. The survival of *E. coli* with UV alone was 3.2 % while with UV and TiO₂ composite film was 91%. The UV-absorbing coatings are transparent, colorless, and exhibit high optical quality. The UV-protective coatings offer an easy method to protect the living organisms against UV.

Keywords: UV-absorbing, nanostructure, composite thin film, coatings on glass UV-protection, living organisms.

1. INTRODUCTION

The Ultraviolet (UV) field is a fast growing area and many processes work best at the 200–400 nm range. UV light sources are used in conjunction with UV filters and reflectors to produce products such as fiber optics, printed circuit boards, paints, graphic arts, printing and curing adhesives. The UV spectrum is often divided into three areas: UVA (315–400 nm) which is typically used for UV curing and photochemical reactions such as printed circuit board production, UVB (280–315 nm) which is used for scientific applications such as genetic visualizations, and UVC (100–280 nm) which is used in areas such as mineral fluorescence. UVA is the most commonly encountered type of UV light. Initially UVA exposure has a pigment-darkening effect where the skin produces melanin to protect itself against exposure. This is followed by erythema (sun burn of the skin) if the exposure is excessive. The atmosphere absorbs very little UVA. UVB is typically the most destructive form of UV and is not completely absorbed in the atmosphere. It has enough energy to cause photochemical damage to cellular DNA. UVB effects include erythema, cataracts and exposure can also result in the development of skin cancer. Individuals working outdoors are at greatest risk from the effects of UVB. Germicidal lamps have been specifically developed to emit UVC because of its ability to kill bacteria [1-4]. Clearly there are risks to humans associated with exposure to various wavelengths of UV radiation.

Titanium dioxide (TiO₂) has many interesting physical properties, which makes it suitable for various thin film applications. Since the pioneering work of Fujishima and Honda [5] researchers paid special attention to TiO₂ thin films, which had many applications in photocatalysis, solar energy cells, gas sensors [6-17]. But most of the researchers investigated their photocatalytic activity and mechanism, while to the best of our knowledge, there is no report

on the UV-protecting nanostructure composite thin film of titanium dioxide coated on glass for living organisms.

In continuation of our efforts to prepare and characterize different nano thin films coated on glass [18-20], in this paper we describe the preparation of transparent TiO₂ thin film and a composite film of nanopowder TiO₂ with titania sol, using sol-gel and spin coating methods. These films were characterized by AFM, XRD and UV-Vis spectrophotometry. The purpose of our study was to determine if thin and composite TiO₂ films with ultraviolet light had any effect on the growth of *E. coli*, *S. aureus* and *Bacillus sp.* We have seen unusual results in which TiO₂ thin and composite films protect the *E. coli*, *S. aureus* and *Bacillus sp* from UV light. The biological activities of the films were evaluated and compared by the inactivation of three strains of bacteria based on the decrease in the colony formed on agar plates.

2. EXPERIMENTAL

2.1. Catalyst Fabrication

2.1.1. Materials

Standard ethanol solution (M= 46.07 g/mol, purity ≈ 99.8%) was purchased from Fluka Chemical. Hydrochloric acid (M= 36.5 g/mol, purity ≈ 35.5%) was supplied from Merck. Titanium tetra isopropoxide (Ti(OPr)₄ or TTIP) (Aldrich, 97%), the precursor, was used without further purification. TiO₂ nanopowder was anatase in crystalline form and it has a surface area about 190-290 m²/g and particle size of 15nm was obtained from Aldrich. Hydroxy ethyl cellulose was obtained from Harris Chemical. All chemicals were used as received. Millipore water was used in all experiments.

2.1.2. Preparation of TiO₂ Sol

Different compositions of TiO₂ sol were prepared by altering the molar ratio of TTP:H₂O:EtOH:HCl. The typical sol, reported here, with a the TTP:H₂O:EtOH:HCl molar ratio of 1:10:10:1.1, was found to be most suitable for dissolving HEC and dispersing TiO₂. Increasing the water content and dilution of the sol system may retard the gelation process. The process was exothermic and the pH of the solution about 2 to 3.

*Address correspondence to this author at the Nanotechnology Laboratory, Department of Chemistry, University of Isfahan, Isfahan, 81746-73441, Iran; Tel: +98-311-7932707; Fax: +98-311-6689732; E-mail: habibi@chem.ui.ac.ir or mhhabibi@yahoo.com

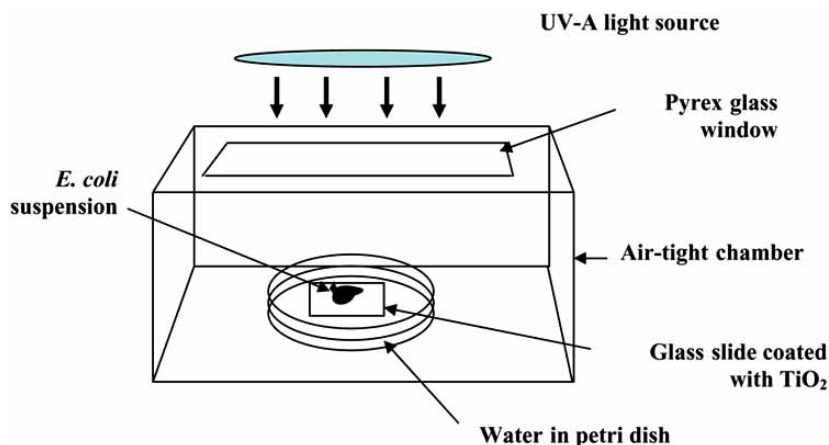


Fig. (1). Schematic illustration of the illumination system.

2.1.3. Stability of Suspensions of Anatase Nanopowder in the Sol

The sedimentation rates of TiO₂ nanopowder dispersed in the alkoxide sol were taken as an indication of their degree of dispersion [21]. HEC addition increased the sedimentation time of 5% powder dispersions from 1 to 70 h and of the 10% powder from 0.5 to 10 h. The added HEC decreased sedimentation rate which is believed to be associated with the better dispersion of the nanopowder.

2.1.4. Preparation of TiO₂ Thin Film

The reagents were used as received. Anhydrous ethyl alcohol (EtOH) was used as the solvent. Water content of the sol had a critical role in the hydrolysis and polycondensation reactions. Titania solution containing HEC was made using the following procedure. First, 5 ml TTP was dissolved in a mixture of 10 ml ethanol and 1.8 ml HCl 35.5 wt% and the solution was agitated for homogenization. In a separated container, HEC solution (2 wt% in water) was prepared by dissolving 28.74 mg HEC in 1.4 ml double distilled water. Then these two solutions (titanium precursor and HEC solution) were added dropwise and stirred overnight at room temperature. The mole ratio of TTP:HCl:EtOH:H₂O was 1:1.1:10:10. Spin-coating technique was used to deposit the sol onto the substrate surface (microscope glass slide). Drops of the mixture were deposited on the surface of the glass slide with spinning. After drying at room temperature in the air, films were heated for 1 hour at 500 °C. For comparison, similar sol without HEC was prepared and deposited onto microscope glass slide.

2.1.5. Preparation of TiO₂ Composite Film

An anatase nanopowder TiO₂ was used in this study as the precalcined photocatalyst powder. It exhibits high photoefficiency due to its high surface area (~190-290 m²/g), with a particle size of ~15 nm. The stabilized suspension of precalcined TiO₂, dispersed in the TiO₂ sol, was prepared by addition of the titania sol followed by 30min of stirring. The amount of nanopowder TiO₂ was adjusted to 70 wt%. The composite films were deposited on the glass substrate (microscope glass slide) by spin-coating at ambient conditions. Samples were heated in static air at a rate of 5 °Cmin⁻¹ up to 700 °C for 1 hour and allowed cooling to room temperature on the bench.

2.2. Catalyst Characterization

The structure and crystallite size were determined by powder X-ray diffraction (Bruker D8 Advanced X-ray diffractometer: Cu K α radiation (1.542 Å); scan rate 0.03 2 θ .s⁻¹). The strongest peaks of TiO₂ corresponding to anatase (101) were selected to evaluate the crystallinity of the samples. The mean crystallite size L was determined from the broadening β of the most intense line, for each

polymorph, in the X-ray diffraction pattern, based on the Scherrer equation:

$$L = \frac{k\lambda}{\beta \cos \theta}$$

where λ is the radiation wavelength, $k = 0.90$ and θ the Bragg angle [22]. The mechanical integrity of coatings (deposited by spin coating method with the same controlled thickness) was measured using a Motorized Clemens scratch tester (equipped with a tungsten carbide ball tool 1mm). Scratches were made under an applied load increasing from 0 to 1000g for the maximum length of 50 mm. The point of coating adhesive failure was determined by visual observation. The load at which the indenter started to scratch the substrate surface was considered as indicative of the coating resistance to scratch failure.

The stability of TiO₂ suspensions was investigated by sedimentation in 50ml, ~20 mm diameter, measuring cylinders. The suspensions were poured into cylinders to the exact height of 20 cm and the sedimentation distance was measured with time. Microstructure of the films was observed by Atomic Force Microscopy.

2.3. Photochemical Reactor

The experiments were carried out in a custom made photocatalytic oxidation reactor measured by 40 cm × 15 cm × 15 cm (Fig. 1). One TiO₂/glass with one time spin coating (75 mm × 25 mm × 1 mm) was used as photocatalyst and irradiated with two 8 W UVA ($\lambda = 365$ nm) at a distance of 5 cm from the top of the model solution.

2.4. Disinfection Experiments

2.4.1. Bacterial Preparation

Three strains of bacteria such as *E. coli*, *S. aureus* and *Bacillus sp* were grown overnight at 37 °C in nutrient broth for 18 to 24 h on a rotary shaker at 150 rpm. Five ml aliquots were centrifuged for 10 min at 3000 rpm and the supernatant broth was decanted. The culture was washed with 5 ml sterile demonized water. The process of centrifuging and washing was repeated three times then the bacteria were resuspended in 5 ml of sterile water.

2.4.2. Bacteria Analysis

The number of bacteria was determined by diluting the suspension to suitable concentration with Ringer's solution and then spread uniformly onto a nutrient agar plate. After overnight incubation at 37 °C the colonies were counted and the initial number of bacteria was calculated. Four replicated were used. The most reproducible results were obtained for plates containing between 30-300 colonies.

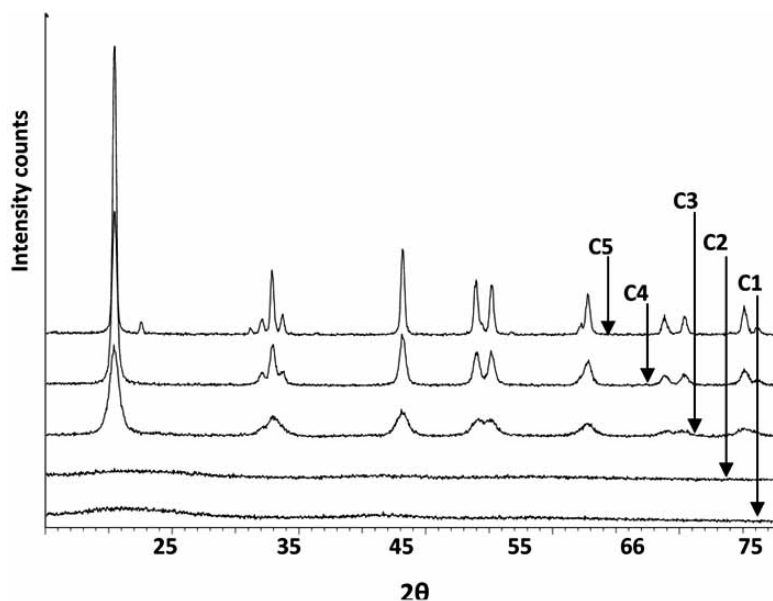


Fig. (2). X-ray diffraction patterns of the samples listed in Table 1 (heat treated at different conditions). Sol-gel-derived TiO₂ powder with HEC, as-prepared (C-1) and heat treated for 1 h at: 125 °C (C-2), 300 °C (C-3), 500 °C (C-4) and 700 °C (C-5).

2.5. Anti UV Effect of TiO₂ Thin and Composite Films

The suspension of bacteria was exposed to TiO₂ thin and composite films coated on glass and irradiated with UV for 5 min and then the number of survival bacteria was investigated.

2.6. The Effect of Nano and Composite TiO₂ Powders on Bacterial Growth

The strain of *E. coli* was grown on Eosin Methylene Blue agar (EMB) medium, *S. aureus* and *Bacillus sp* were grown on Nutrient agar (NA) and nano and composite TiO₂ powders were embedded over the culture. The plate was incubated at 37 °C for 24 h. The zone of inhibition for growth was investigated around the nano and composite TiO₂ powders. Antibacterial effect was studied on different liquid cultures include 109 bacteria during 30 min. The numbers of survival were estimated by plate count method.

3. RESULTS AND DISCUSSION

3.1. Characterization of TiO₂ Photocatalyst

3.1.1. XRD Characterization of Annealed Sol

The XRD results of the sol-gel derived powders of sample A (the sol without HEC), heat treated for 1 hour at different temperatures in air, are shown in Table 1. The as-prepared gel have amorphous structure, showing a very broad peak at about $2\theta=25.2^\circ$ (which is identified as the most intensive peak (101) for the anatase TiO₂). In general, the hydrolysis products in the sol-gel processing do not show crystallinity on XRD spectrum. By increasing the calcinations temperature, the (101) peak of anatase has become sharper, which indicates the dependence of crystallinity to the applied temperature. This happens at temperature lower than 300 °C. The corresponding crystallite size of the anatase in the heated powder is presented in Table 1. This is in accordance with the results of the calcination of the sol-gel-derived TiO₂, at different thermal conditions. As shown in Table 1, the crystallite size of anatase phase, used as a measure of TiO₂ crystallinity, increased markedly with calcination temperature, up to 15.5 nm at 500 °C. It is suggested that the growth process of nanocrystalline anatase is mainly because of the sintering of the single crystals within the agglomerates, and finally the original agglomerate transforms to a larger single crystal [23].

The same observations were carried out for the gels prepared from samples B (the sol with HEC). It can be observed that the crystal formation and the polymorphs evolution in the sol with HEC, upon heat treatment, are approximately the same as the sol without HEC (Fig. 2). As shown in Table 1, the crystal size of anatase TiO₂ was decreased to 13.4 nm at 500 °C by introducing HEC. In other words, for the sol system in this study, organic binder material HEC was found to be very suitable and prevent particle aggregation. Therefore, HEC have been introduced into the sol-gel precursors to prevent film crack formation in composite film. Another advantage, as shown, is that HEC belongs to non-ionic cellulose ether material and substantially free of substances that can induce crystallization of titania.

3.1.2. XRD Characterization of Nanopowder

Nanopowder TiO₂ as-received powder contains ~100% anatase form of titania. Heat treatment of this powder up to 900 °C did not result in the formation of rutile and the maximum detected rutile content remains at about 3%, perhaps due to fewer nucleation sites for rutile. Nanopowder TiO₂ anatase crystallites grew 20-30% compare to its original size when heated to 500 °C. The diffractograms were measured at higher sensitivity to show all peaks ($2\theta=25.28, 37.02, 37.80, 38.82, 48.05, 53.9, \text{ and } 55.06$) correspond to known diffraction maxima of anatase. The peak intensities increased as the heating temperature increased from 100 to 500 °C. These changes are consistent with the conversion of an amorphous titania thin film into anatase by treatment at 500 °C. As shown in Table 1, the size of the anatase crystallites in the composite film follows the size range of the crystallites in the filler powder (TiO₂ nanopowder). Therefore, the size of the TiO₂ crystallites, derived from the sol, does not affect the size of final crystallites.

3.1.3. Surface Characterization of TiO₂ Composite Films

The AFM image of the surface of nanocomposite TiO₂ film heat treated at 500 °C for 60 min (Fig. 3) demonstrates the nanostructure of composite film and shows particle size of TiO₂ in AFM image is correspond with XRD results.

3.1.4. Scratch Adhesive Test of TiO₂ Thin and Composite Films

The normal loads which caused the complete coating removal, for TiO₂ thin and composite films, within the scratch track (observed by optical microscope) are shown in Table 1. For TiO₂ coat-

Table 1. Physical Characteristics (the Crystallite Size and Adhesion Strength) of Different TiO₂ Photocatalysts Heat Treated for 1 h at Different Temperatures

Material	Code	Heat Treatment Condition (°C)	Crystallite Size (nm)	Scratch Adhesion (g/mm ²) ^a
Sample A	A-1	-	0.7	150
	A-2	125	0.7	-
	A-3	300	5.1	-
	A-4	500	15.5	1500
Sample B	B-1	-	0.6	160
	B-2	125	0.6	-
	B-3	300	5.0	-
	B-4	500	13.4	1500
Nanopowder TiO ₂	C-1	-	15	~0
	C-2	500	19.5	~0
Composite TiO ₂ film ^b	D-1	-	15.0	9
	D-2	500	19.3	200

^a Critical linearly increasing loads.

^b Prepared from 70 wt. % P-25 powder in TiO₂ sol

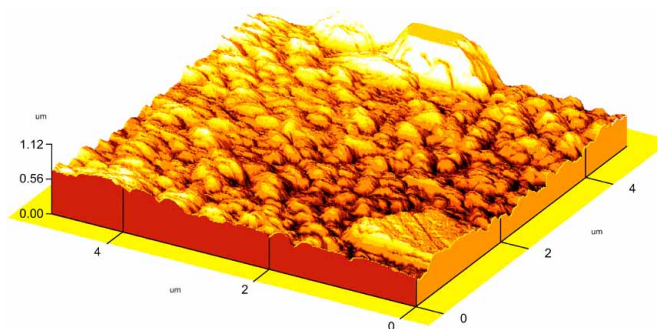


Fig. (3). AFM image of TiO₂ nano thin film heat treated at 500 °C.

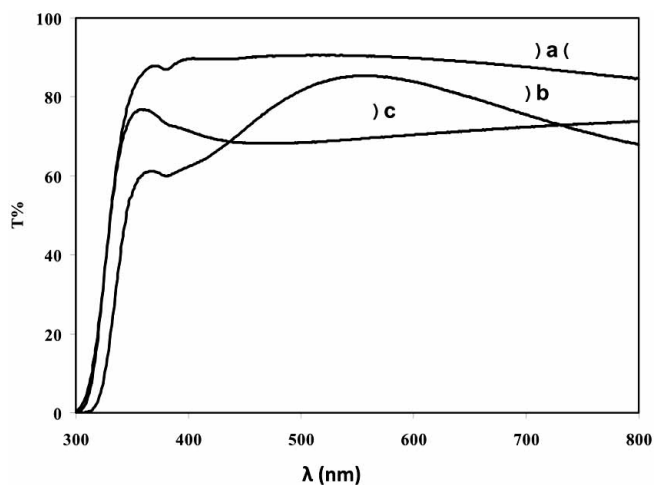


Fig. (4). UV-Vis transmittance spectra of (a) clean microscope slides (b) nano TiO₂ thin films without hydroxyl ethyl cellulose (HEC) coated on glass and (c) nano TiO₂ thin films with HEC heat treated at 500 °C.

ing deposited from a slurry (i.e. without the sol binder), the normal load needed to remove the coatings from the substrate was in the range of 1-10 g. The adhesion strength of the coatings did not change after firing up to 500 °C for 1 h.

3.1.5. UV-Visible Characterization of TiO₂ Thin and Composite Films

Fig. (4) shows the UV-Vis transmittance (T %) spectra of TiO₂ thin films on the microscope slides in the wavelength range of 300-

800 nm. In the visible region, and specifically at 475 nm, transmittance for the TiO₂ thin film without HEC was 75%, while the transmittance of TiO₂ thin film with HEC was 80%. It is clear that the use of HEC did not affect the transmittance of TiO₂ thin film. At about 350 nm the transmittance decreases quickly for all films and approaches zero at around 320 nm. This fast decrease in transmittance is due to absorption of light caused by the excitation and migration of electrons from the valence band to the conduction band of TiO₂. The absorption edge of TiO₂ thin film without HEC is observed at a longer wavelength (Fig. 4) compared to TiO₂ thin

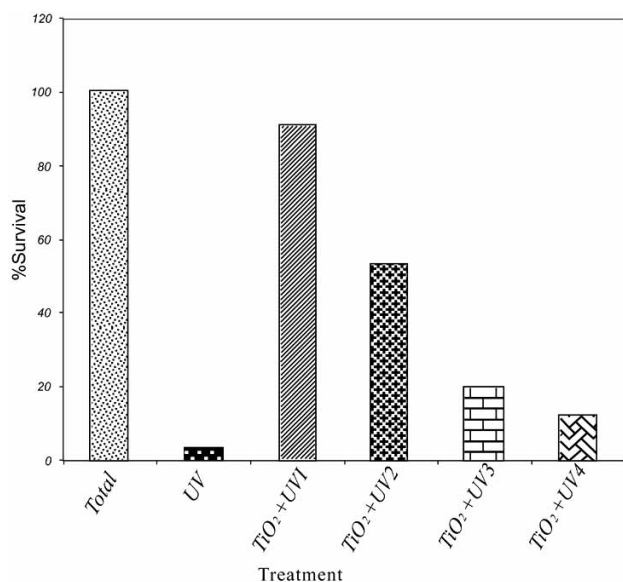


Fig. (5). Survival percent of *E. coli* using TiO₂ thin and composite films in 5 min. UV irradiation (UV: UV alone without TiO₂; TiO₂ + UV1: UV and TiO₂ composite films; TiO₂ + UV2: UV and TiO₂ thin films; TiO₂ + UV3: UV and nano TiO₂; TiO₂ + UV4: UV and nano composite TiO₂).

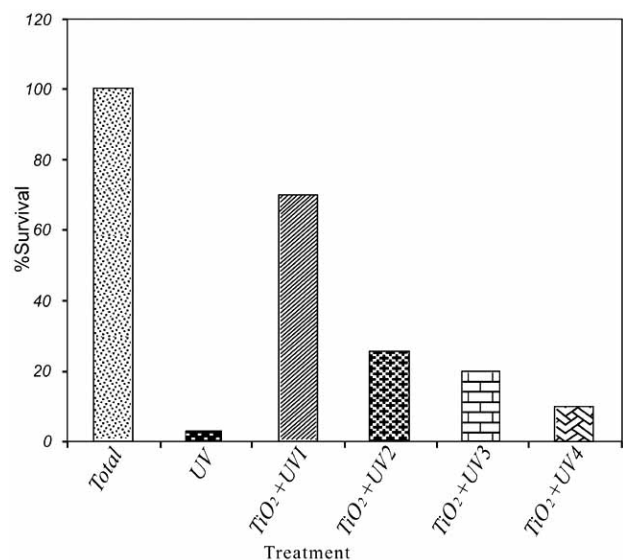


Fig. (6). Survival percent of *S. aureus* using TiO₂ thin and composite films in 5 min. UV irradiation (UV: UV alone without TiO₂; TiO₂ + UV1: UV and TiO₂ composite films; TiO₂ + UV2: UV and TiO₂ thin films; TiO₂ + UV3: UV and nano TiO₂; TiO₂ + UV4: UV and nano composite TiO₂).

film with HEC. The shift is considered to occur due to the difference in size crystallites within the films [24-26].

3.2. Disinfection Experiments

The aim of this research was to determine if TiO₂ thin and composite films and UV light had any effects on the growth and disinfection of *E. coli*, *S. aureus* and *Bacillus sp.* The results showed that TiO₂ thin and composite film protect the *E. coli*, *S. aureus* and *Bacillus sp.* from UV light. The anti UV effects of TiO₂ on bacterial survival are shown in Figs. (5-8). In Figs. (5-7), UV alone without TiO₂, UV and TiO₂ composite films, UV and TiO₂ thin films, UV and TiO₂ nanopowder, UV and TiO₂ composite powder were denoted as UV, TiO₂ + UV1, TiO₂ + UV2, TiO₂ + UV3 and TiO₂ + UV4 respectively and all samples were irradiated with UV light for 5 min. As it is shown UV alone kill most bacteria in 5 min and

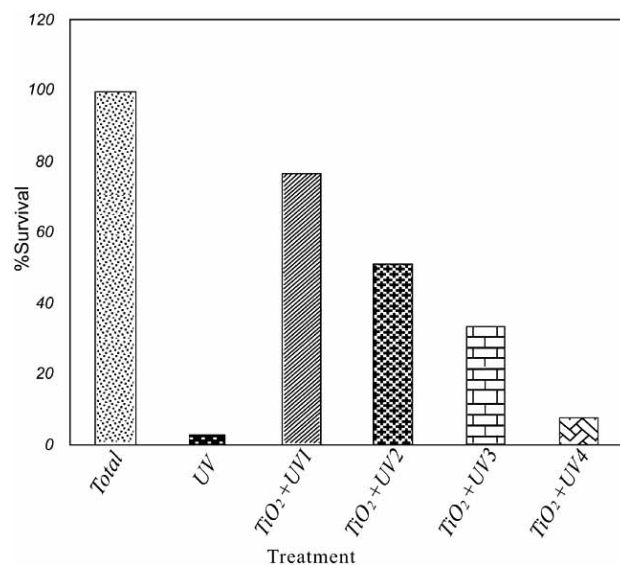


Fig. (7). Survival percent of *Bacillus sp.* Using TiO₂ thin and composite films in 5 min. UV irradiation (UV: UV alone without TiO₂; TiO₂ + UV1: UV and TiO₂ composite films; TiO₂ + UV2: UV and TiO₂ thin films; TiO₂ + UV3: UV and nano TiO₂; TiO₂ + UV4: UV and nano composite TiO₂).

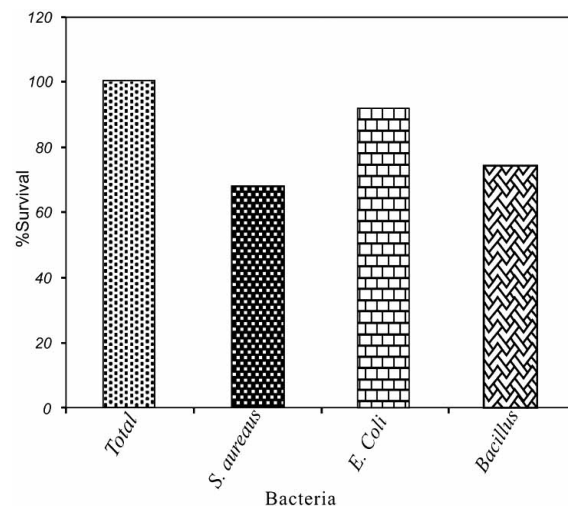


Fig. (8). Comparing the survival percent of *E. coli*, *S. aureus* and *Bacillus sp.* using TiO₂ composite films in 5 min. of UV irradiation.

survival of *E. coli* with UV alone without TiO₂ was 3.2 % while with UV and composite film was 91%. The survival with UV and thin film was %51 (Fig. 5). As shown in Fig. (6), the survival of *S. aureus* with UV alone without TiO₂ was 1.5% while with UV and composite film was 68% (the survival with UV and thin film was only 43%). The survival of *Bacillus sp.* with UV alone without TiO₂ was 2% while with UV and composite film was 75% (Fig. 7). The results showed that the most anti UV effect of TiO₂ composite film are on *E. coli* which is a gram negative bacterium (Fig. 8). However the results of antibacterial effects of this layer showed all three bacteria were survived within 30 min treatment of these bacteria with only thin film of TiO₂ without UV light, while *E. coli* showed clear zone of inhibition on EMB agar around this layer which mean this layer has static effect on *E. coli* but dose not kill any of three studied strains. So, thin film has anti UV and anti bacterial effect but it dose not kill them. The comparison of thin and composite films showed that the thin film has less anti UV effect than composite film on *E. coli* and *S. aureus*. The effect of composite and thin film on survival of *E. coli* showed that the composite film has 40% more effect on the strain survival and protect it more from UV. But it is surprising that the thin film has more anti bacterial effect and

the zone of inhibition on *E. coli* and *S. aureus* is much bigger and clear. Neither of the layer has the effect of bactericide and 30 min treatment of all three strains with composite or thin film did not killed the strains and the number of these strains were the same as the blank (untreated one). While the zone of inhibition has seen when the layers were embedded on solid media which means that the layers are bacteriostatic, which are able to inhibit the growth and reproduction of bacteria but dose not kill them.

The antibacterial activity of photocatalytic TiO₂ thin films with photodeposited silver on the surfaces was studied by Machida, *et al.* [27]. They used bacterial suspension of *E. coli* (150 μL of 5×10⁵ Colony-forming units (CFU) ml) and the sample was irradiated for 30min under a white fluorescent light with luminance of 5200Lux. However in our work we show the zone of inhibition of growth by thin film without any irradiation which is shown the anti bacterial activities of TiO₂. Also Egerton *et al.* [28] were shown that photoelectrocatalytic disinfection of *E. coli* by an iron doped TiO₂ sol-gel electrode was more efficient than undoped electrode and iron doping increases the number of holes available for hydroxyl radical formation by UV irradiation. However some metals (Fe, Ag, Al) have anti bacterial effect on *E. coli* without any irradiation. In our study we have used laminar air flow which kills most bacteria in 20 min, but using TiO₂ thin and composite films, the anti UV effect have increased.

4. CONCLUSION

Transparent thin and composite film of nanopowder TiO₂ on glass substrate using hydroxyl ethyl cellulose (HEC), a non-ionic water-soluble long chain polymer as dispersant were prepared by the sol-gel method, resulting in highly efficient UV-absorbing films. These films were characterized by AFM, X-ray diffraction (XRD), and UV-Vis spectrophotometry. Ultraviolet light has been known to have an effect on various life forms, from complex humans to microscopic bacteria. The central purpose of our study was to determine if ultraviolet light had an effect on the growth of *E. coli*, *S. aureus* and *Bacillus sp.* UV light exposure has deadly effect to the population, leaving only the resistant to survive. UV light has ability to inhibit conjugation or causes mutation, but in this work only we study the survival cells. However we have seen an unusual results in which TiO₂ thin film protects the *E. coli* from UV light but it is possible to have mutation too. The bactericidal activities of the samples were evaluated and compared by the inactivation of three strains of bacteria such as *E. coli*, *S. aureus* and *Bacillus sp.*, based on the decrease in the colony of *E. coli* formed on agar plates. A substantial decrease in the destructive effects of UV radiation on living organisms, i.e. strains of bacteria such as *E. coli*, *S. aureus*, *Bacillus sp* upon irradiation with UV-light was observed with the protective layer. The UV-absorbing coatings can be used in a wide range of applications, especially for the protection of living organisms.

ACKNOWLEDGEMENT

The authors wish to thank the University of Isfahan for financially supporting this work.

REFERENCES

[1] International Radiation Protection Association; International Non-Ionizing Radiation Committee; Guidelines on Limits of Exposure to ultraviolet radiation

tion of wavelengths between 180nm and 400nm (incoherent optical radiation). *Health Phys.*, **1985**, *49*, 331-340.

[2] International Commission on Non-Ionizing Radiation Protection; Guidelines on Limits of Exposure to laser radiation of wavelengths between 180nm and 1000μm. *Health Phys.*, **1996**, *71*, 804-819.

[3] Schott Optical Glass Co.; Main Properties of Optical Glasses, Catalogue, **2000**, pp. 3111-3118.

[4] Heraeus Optics Co.; Main Properties of Infrasil, Catalogue 1999-2003.

[5] Fujishima, A.; Honda, K. Electrochemical photolysis of water at a semiconductor electrode. *Nature*, **1972**, *238*, 37-38.

[6] Wang, R.; Hashimoto, K.; Fujishima, A.; Chikuni, M.; Kitamura, A.; Shimohigoshi, M.; Watanabe, T. Light-induced amphiphilic surfaces. *Nature*, **1997**, *388*, 431-432.

[7] Wang, X.P.; Yu, Y.; Hu, X.F.; Gao, L. Hydrophilicity of TiO₂ films prepared by liquid phase deposition. *Thin Solid Films*, **2000**, *371*, 148-152.

[8] Wang, R.; Hashimoto, K.; Fujishima, A.; Chikuni, M.; Kitamura, A.; Shimohigoshi, M.; Watanabe, T. Photogeneration of highly amphiphilic TiO₂ surfaces. *Adv. Mater.*, **1998**, *10*, 135-138.

[9] Sakai, N.; Wang, R.; Fujishima, A.; Wantanbe, T.; Hashimoto, K. Effect of ultrasonic treatment on highly hydrophilic TiO₂ surfaces. *Langmuir*, **1998**, *14*, 5918-5920.

[10] Ricard, D.; Roussignol, Ph. Surface-mediated enhancement of optical phase conjugation in metal colloids. *Opt. Lett.*, **1985**, *10*, 511-513.

[11] Papp, J.; Shen, H.S.; Kershaw, R.; Dwight, K.; Wold, A. Titanium (IV) oxide photocatalysts with palladium. *Chem. Mater.*, **1993**, *5*, 284-288.

[12] Kozuka, H.; Zhao, G.; Yokoi, T. Sol-gel preparation and photoelectrochemical properties of TiO₂ films containing Au and Ag metal particles. *Thin Solid Films*, **1996**, *277*, 147-154.

[13] Goren, Z.; Willner, I.; Nelson, A.J.; Frank, A.J. Selective photoreduction of CO₂/HCO₃ to formate by aqueous suspensions and colloids of Pd-TiO₂. *J. Phys. Chem.*, **1990**, *94*, 3784-3790.

[14] Hoffmann, M.R.; Martin, S.T.; Choi, W.; Bahnemann, D.W. Environmental applications of semiconductor photocatalysis. *Chem. Rev.*, **1995**, *95*, 69-96.

[15] Ismail, A. A.; Bahnemann, D. W.; Bannat, I.; Wark, M. Gold nanoparticles on mesoporous interparticle networks of titanium dioxide nanocrystals for enhanced photonic efficiencies. *J. Phys. Chem. C*, **2009**, *113*(17), 7429-7435.

[16] Rahimnejad, J. S.; Rahman Setayesh, S.; Gholami, M.R. A credible role of copper oxide on structure of nanocrystalline mesoporous titanium dioxide. *J. Iran. Chem. Soc.*, **2008**, *5*(3), 367-374.

[17] Habibi, M.H.; Khaledi Sardashti, M. Structure and morphology of nanostructured zinc oxide thin films prepared by dip vs. spin-coating methods. *J. Iran. Chem. Soc.*, **2008**, *5*(4), 603-609.

[18] Habibi, M.H.; Nasr-Esfahani M.; Egerton T. A. Preparation, characterization and photocatalytic activity of TiO₂/Methylcellulose nanocomposite films derived from nanopowder TiO₂ and modified sol-gel titania. *J. Mater. Sci.*, **2007**, *42*, 6027-6035.

[19] Habibi, M.H.; Nasr-Esfahani M. Preparation, characterization and photocatalytic activity of a novel nanostructure composite film derived from nanopowder TiO₂ and sol-gel process using organic dispersant. *Dyes Pigm.*, **2007**, *75*, 714-722.

[20] Habibi, M.H.; Nasr-Esfahani M. Photochemical characterization and photocatalytic properties of a nanostructure composite TiO₂ film. *Int. J. Photoenergy*, **2008**, ID628713.

[21] Caruso, R.A.; Schattka, J. H. Cellulose acetate templates for porous inorganic network fabrication. *Adv. Mater.*, **2000**, *24*, 1921-1923.

[22] Spurr, R.A.; Myers, H. Quantitative analysis of anatase-rutile mixtures with an X-ray diffractometer. *Anal. Chem.*, **1957**, *29*, 760-762.

[23] Okada, K.; Yamamoto, N.; Kameshima, Y.; Yasumori, A. Effect of SiO₂ addition on the anatase-to-rutile phase transition. *J. Am. Ceram. Soc.*, **2001**, *84*(7), 1591-1596.

[24] Harizanov, O.; Harizanova, A. Development and investigation of sol-gel solutions for the formation of TiO₂ coatings. *Solar Energ. Mater. Solar Cells* **2000**, *63*, 185-195.

[25] Harizanov, O. Sol-gel BaTiO₃ from a peptized solution. *Mater. Lett.*, **1998**, *34*, 232-239.

[26] Yu, J.; Zaho, X.; Zaho, Q. Effect of film thickness on the grain size and photocatalytic activity of the sol-gel derived nanometer TiO₂ thin films. *J. Mater. Sci. Lett.*, **2000**, *19*, 1015-1017.

[27] Machida, M.; Norimoto, K.; Kimura, T. Antibacterial activity of photocatalytic titanium dioxide thin films with photodeposited silver on the surface of sanitary ware. *J. Am. Ceram. Soc.*, **2005**, *88*(1), 95-100.

[28] Egerton, T.A.; Kosa, S. A. M.; Christensen, P. A. Photoelectrocatalytic disinfection of *E. coli* suspensions by iron doped TiO₂. *Phys. Chem. Chem. Phys.*, **2006**, *8*, 398-406.