Antibacterial Behavior of TiO2 and TiO2/Ag Coated Plexiglas

[1]Yasin R. Eker, [2]Yasin Arslan, [3]Birgul Kacmaz, [4]Nedim Sultan and *[5]Hasan Okuyucu
[1]Necmettin Erbakan Üniversitesi Ahmet Keleşoğlu Eğitim Fakültesi, A Blok, Yeni Yol Caddesi, Meram, Konya, Turkey
[2]Gazi University, Faculty of Technical Education, Besevler-Ankara, Turkey
[3]Gazi University, Faculty of Medicine, Central Microbiology Lab., Besevler-Ankara, Turkey
[4]Gazi University, Faculty of Medicine, Medical Microbiology, Besevler- Ankara, Turkey
*[5]Yildirim Beyazit University, Faculty of Engineering and Natural Sciences, Cankiri Cd. Cicek sk. No:3 Ulus Ankara, Turkey

Abstract

The nosocomial infections are an important problem in hospital environment especially inside the newborn unit incubators mainly made with Plexiglas (Polymethyl Methacrylate (PMMA)). The microbicide effect of titanium dioxide (TiO2) by the photocatalytic decomposition of the organic compounds has been first reported in 1985 [1], afterwards researches have been intensified to develop antibacterial surfaces with TiO2 thin film coated glasses, tiles… [2-4]. Their efficiency is increasing with the addition of heavy metal ions (Ag+ [5-7], Cu2+[8], Fe2+[9]…). In this work, the first study concerning the antibacterial effect against the E. Coli of TiO2 and TiO2 with 10% Ag thin film covered Plexiglas via sol-gel dip coating has been done. TiO2 coated, Ag-TiO2 coated and uncoated surface have been characterized via the antibacterial drop test. On each surface solution containing 106 cfu/ml bacteria is added. The first half of the samples had been tested after 1h illumination under Mercury Light (125W) at room temperature, while the second half had been after 2h illumination. On the TiO2 coated surface, the amount of bacteria is 25% reduced after 1h illumination and 48% after 2h. This reduction is more important with the Ag-TiO2 coated Plexiglas, showing the improved antibacterial effect due to the Ag additive (68%). This results show the interest of the incubators made with Ag-TiO2 thin film coated plexiglas that can reduce or prevent the bacterial contamination.

Key words: Heavy Metals, Antibacterial Effect, Thin Film, Sol-Gel Method, Titanium Dioxide.

1. Introduction

Sources of numerous infectious diseases, bacteria are on the focus of several researches and especially concerning the antibacterial material development [10-12]. In 1985 it has been firstly reported, the elimination of microbial cell in water via the photocatalytic activity of titanium dioxide-platinum particles UV-illuminated during 1 and 2 hours [1]. Afterwards, TiO_2 has been widely used as an inorganic antibacterial agent in many applications [13-15]. The microbicide effect on Escherichia coli (E. coli) due to photocatalytic reactions have been largely studied [16-21]. Generated on the surface of TiO2 under illumination, the hydroxyl radicals (·OH) and the reactive oxygen species (ROS) are sources of microorganisms inactivation via the oxidation of the polyunsaturated phospholipid component of the cell membrane of microbes [13], [19], [22-23]. The permeability of the membrane involved the endotoxin secretions which are also collapsed by the TiO2 photocatalysis [24-25]. The ·OH radicals are approximately thousands time more effective for E. coli inactivation than common disinfectants such as chlorine, ozone

*Corresponding author: Address: Yildirim Beyazit University, Faculty of Engineering and Natural Sciences, Cankiri Cd. Cicek sk. No:3 Ulus Ankara, Turkey. E-mail address: okuyucuh@gmail.com.

and chlorine dioxide [19], [22].

Several methods are known for the preparation of thin films, among them Chemical Vapor Deposition (CVD) [2], [26-27], Physical Vapor Deposition (PVD) [3], [27-28] or sol-gel techniques are the most common [4], [29-31]. Due to the use of sophisticated reactors and/or vacuum systems, and relative difficulty to scale-up for large-scale and large-area production, the sol-gel synthesis is the most rentable technique. The sol-gel spray pyrolysis [29], spin [30] or dip [4], [31] coating are commonly used for films preparation. Following the deposition, the heat treatment temperature of the film induces the crystallization in three different pure or mixed TiO_2 phases: Rutile (tetragonal), anatase (tetragonal) and/or brookite (orthorhombic). The anatase phase has the highest photocatalytic activity [32], [9]. The antimicrobial test of monocristal and polycristal anatase/rutile thin film synthesized with RF Magnetron Sputtering on E.coli shows that rutile and anatase do not present the same behavior. Probably electrons issued from anatase which have highest band gap (3.39 eV for anatase film, 3.20 eV for anatase bulk [33]) have enough energy for the reduction of O_2 in O_2- and the oxidation of H_2O in OH- involving the oxidation of organic membranes [34]. Moreover with more concentrate TiO_2 film the bacteria elimination is increasing, this effect is also observed by the addition of metallic particles during the film preparation [35].

The insertion of several additives has been reported in the literature, according to their properties different benefit on the photocatalytic and antibactericial activity of TiO_2 film has been observed. Commonly improvements due to the doping by transition metals or their components have been observed. Thus with Cu based sensitizers adsorbed on TiO_2, the absorbance of film is increasing and then inducing a faster bacteria elimination [8]. Another effect is to reduce the thickness of the TiO_2 film via the addition of Au or V [35], similar observation has done when TiO_2 film is doped by Fe^{3+} [9]. On the other hand, the photocatalyst activity in dark was developed by the addition of WO_3 or MoO_3 [36-37]. However one of the most studied metals is silver which easily reacts with Oxygen, Sulfur, Phosphor and Nitrogen components of cell membrane [38-40]. The combination of Ag with TiO2 against E.coli has already been studied in particles suspension [11], [41-43] or in film [5-7].

The TiO_2 particles have been usually doped with Ag content from 0.72% to 5%. In addition to the predominant bactericidal effect of Ag, the main influences are the TiO_2 phase and the particle diameters. In fact with similar particle size (~400nm), Chen et al prevents the growth of E. coli with 10µg/ml Ag doped rutile particles [41], while Keleher et al reach the Minimum Inhibitory Concentration with 6.4µg/ml of anatase based particles [11]. This observation is confirmed by Thiel et al showing that 0.72% Ag doped anatase particle with 26 nm diameter is more efficient than 1.01% Ag doped rutile particles with 47 nm. The development of the rutile phase is due to the presence of Ag nanoparticles as well the antibacterial activity [42]. Films can be prepared from particles; however they are usually thick (few µm) eliminating then the transparency of the support [44].

Ag-TiO_2 thin films are currently used to create antibacterial surfaces on different supports (Ceramic [5], Glass [6] [44-45], Stainless Steel [46]…). Different deposition processes are presented in the previous works (Spray Coating [5], PVD [6], CVD [46], Sol-Gel [7], [44], Coating [45]…), Ag is added to TiO_2 film either during the deposition or via a further operation. Whatever the method, a heat treatment between 450°C to 900°C during 30min to 2h is requested involving that the substrate should resist to these temperatures. Furthermore for the degradation of substances or bacteria, Ag/TiO_2 ratios are varying from 0.5% to 10%. The films with highest content around 10% are used for the elimination of E.coli [5-7]. Two important results are deduced from these works; firstly higher is the Ag ratio faster is the bacteria elimination [7], secondly Ag enhance the formation of anatase phase after annealing [6].

This study consists on the preparation of thin TiO_2 and Ag-TiO_2 film on plexiglass used for incubator walls. The main difficulty is to keep the polymer support intact during the film preparation heating. Film formation on the support is characterized by XPS and its activity against E.coli is tested via antibacterial drop test.

2. Experiments

24 Plexiglas supports with 20x20x8 mm dimension were divided in three groups: TiO_2 deposited, TiO_2-Ag deposited and without deposition. All have been cleaned with isopropanol and dried. The first groups were dipped in the film solution which consists of Titanium Nitrate, Methanol and Acetylacetone. The solution pH is kept between 4.5 and 5.5. Afterwards support was annealed 20 seconds at 500°C in Argon atmosphere. The same process is used to prepare the TiO_2-Ag thin film with addition of $AgNO_3$ in the dipping solution containing 10% Ag.

The formation of TiO_2 thin film was checked by Thermo Scientific fully integrated Al Kα (E = 1486.6 eV) monochromated small-spot (spot size 400µm) with 150.0eV set analyzer pass energy X-ray Photoelectron Spectrometer (XPS) system. The composition of the surface layer was automatically determined from the peak areas taking account the sensitivity factors of the corresponding elements. The spectra were fitted without placing constraints using multiple Voigt profiles. The full width at half maximum (FWHM) varied between 1.6 and 2.0 eV and the accuracy of the peak positions was about 0.1 eV.

For the anti-bacterial test, samples were placed in 90 mm sterile petri box and 100µl of solution containing 106 cfu/ml (colony forming unit per milliliter) E.coli ATCC 25922 bacteria was added. They are illuminated during 2 hours under 125W mercury light. At the end of the first hour, four samples of each group were washed with 5ml phosphate tampon solution. Afterwards 10 µl of washing solution sampling was spread in agar plate and incubated at 37 °C for 24 hours. Bacteria colonies were then calculated. The same process was used for the last four samples at the end of the second illumination hour.

3. Results and Discussion

3.1. XPS analysis

On the XPS spectra of the analyzed TiO_2 coated PMMA support three elements are present: Ti, O and C (Figure 1). The deconvolution of the peaks gives more information about the ratio and the bonding of these atoms:

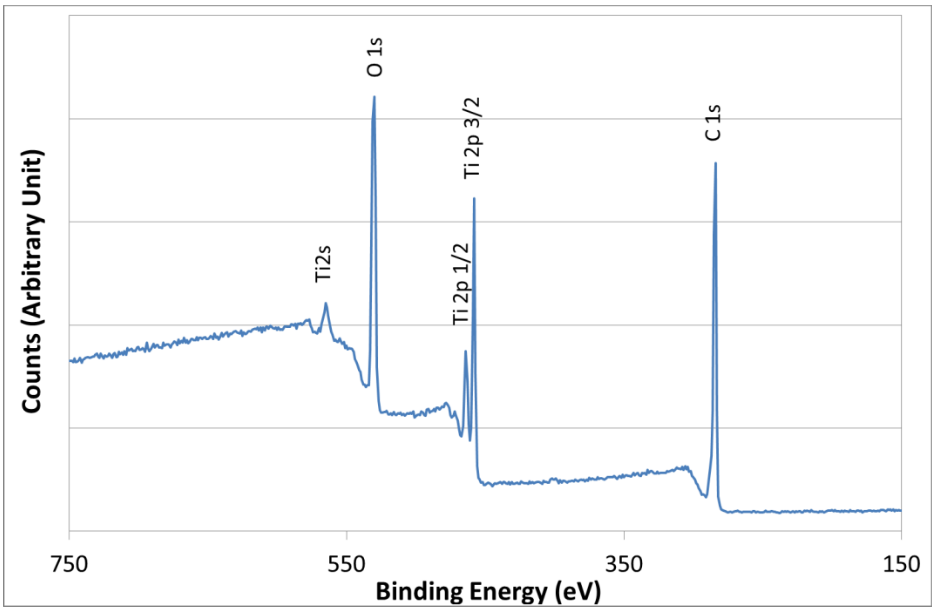

Figure 1. XPS Spectra of TiO_2 coated PMMA.

3.1.1. Ti 2p

The presence of two peaks Ti $2p_{1/2}$ at 463.9 eV and Ti $2p_{3/2}$ at 458.2 eV with an energy bonding difference of 5.7 eV is typical to the formation of TiO_2 (Figure 2a) [44], [47]. Moreover FWHM of Ti $2p_{1/2}$ is 1.26 eV while the one of Ti $2p_{3/2}$ is 2.19 eV, the ratio is 1.74. However in the literature, this ratio is 2 for TiO_2 (rutile or anatase) [48]. This difference can be explained either by a probably additional effect on the Ti 2p peaks, contributions of Ti-O-C bonds are reported in the literature [47], [49], or by the fact that the TiO_2 film is mainly amorphous due to the short annealing, or maybe both.

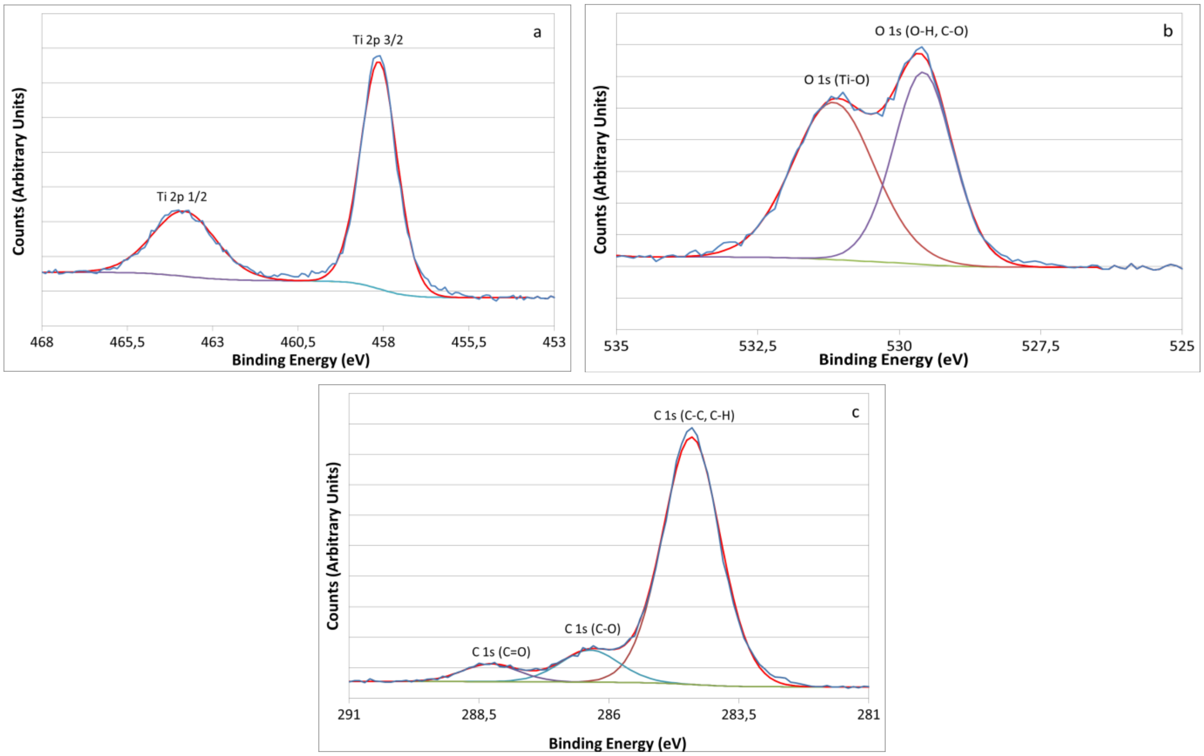

Figure 2. XPS Spectra of Ti2p (a), O1s (b), C1s (c).

3.1.2. O 1s

The O 1s peaks can be fitted with two peaks at 529.7 eV & 531.2 eV (Figure 2b). The first one is attributed to the presence of Ti-O bond while the second to O-H and/or C-O bonds [50-52]. The Ti/O ratio is ½ in TiO_2, but this elemental ratio is 8.4/14.5 = 0.58 from the XPS data (Table 1). Therefore a part of Ti is not used for TiO_2 formation, but for the formation of Ti-O-H [45] or Ti-O-C [47], [49].

3.1.3. C 1s

The C 1s peaks can be fitted with three peaks at 284.4 eV, 286.3 eV and 288.3 eV (Figure 2c). They are attributed to the presence of C-H, C-C for the first peak, C-O for the second one and C=O for the last one [51], [53]. These peaks and the atomic ratios (Table 1) are corresponded to the PMMA support structure consisting of 8xC-H, 3xC-C, 2xC-O and 1xC=O bonds (Figure 3). We can conclude that the thickness of the thin film formed at the surface of the PMMA is less than 10 nm which is the limit thickness of the XPS measurement. This thickness is less than the 40 nm film obtained on glass via the same route. A possibly explanation is the more hydrophilic behavior of glass comparing to the one of PMMA, which can induce the presence of more solution on the glass after dipping.

Figure 1. XPS measurements of element ratio.

Ti $2p_{1/2}$	2.8
Ti $2p_{3/2}$	5.6
O 1s (Ti-O)	14.5
O 1s (O-H, C-O)	16.4
C 1s (C-H, C-C)	50.5
C 1s (C-O)	6.7
C 1s (C=O)	3.5

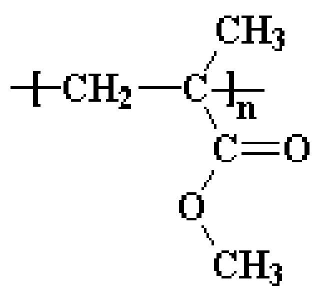

Figure 3. Monomer of PMMA.

3.2. Antimicrobial Test

The E.coli colonies quantities are reducing during the antibacterial drop test of the uncoated PMMA, PMMA coated with TiO_2 film and the one with Ag-TiO_2 film (Figure 4). 25% bacteria are eliminated after 1 hour and 48% after 2 hours for the TiO_2 thin film coated as well as for the uncoated Plexiglas. There is no sign of the well-known photocatalytic activity of TiO_2 anatase and the annealing conditions are insufficient for the formation of the rutile phase. This result confirms that the TiO_2 thin film is amorphous. Even if TiO_2 thin has not a big impact on the elimination of E.coli, it is a good matrix. In fact 68% bacteria elimination was observed after 2 hours of Ag-TiO_2 film illumination.

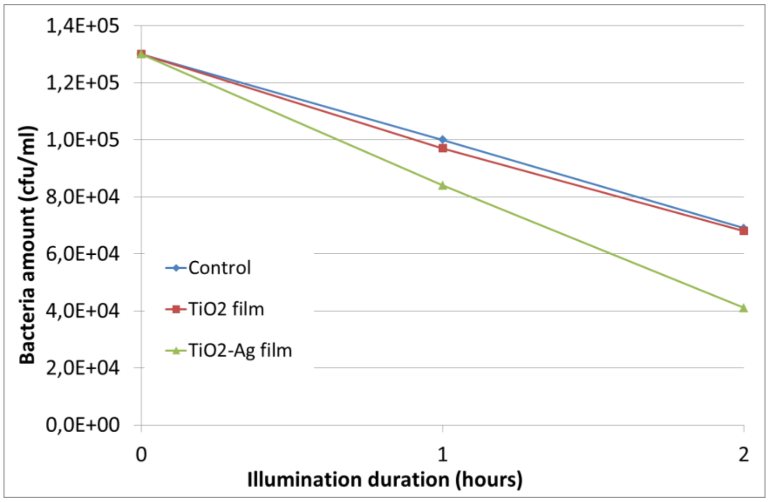

Figure 4. Evolution of the bacteria amount during the antimicrobial test under mercury light.

Conclusions

Due its mechanical properties and its transparency, PMMA is a chosen material for the fabrication of baby incubators. But its low melting point at 160°C does not allow photocatalytic TiO_2 antibacterial surface coatings requiring 1 to 2h high temperature treatment. In this work, amorphous TiO_2 thin film has been coated on Plexiglas via sol-gel dipping method. Homogenous and the surface quality of coated TiO_2 film is very good and transparency of the PMMA is still good after coating. This is an important step for the thin film covering on polymer supports. It is a good matrix for Ag, since bacteria are efficiently eliminated from the surface with Ag-TiO_2 thin film. In the future deeper characterization of Ag-TiO_2 thin film can allow to improve the method and to optimize the film composition. We can hope that this efficient and economical coating method could be widely used in the future.

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