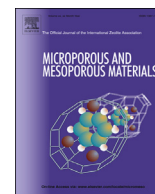




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Optically transparent silver-loaded mesoporous thin film coating with long-lasting antibacterial activity



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ABSTRACT

Infectious diseases caused by microorganisms affect millions of people worldwide. In an effort to prevent infections induced by bacteria, a variety of antibacterial coatings have been designed. In this sense, the possibility to combine broad-range bactericidal agents such as silver and chemically and mechanically stable matrices such as mesoporous oxide thin films has been encouraging. In this study, titania–silica bilayer mesoporous thin film (MTF) coatings have been produced and loaded with silver species, and their bactericidal efficiency against *Pseudomonas aeruginosa* and *Staphylococcus aureus* was assessed over time. In this sense, coatings loaded with silver ions (MTF + Ag⁺) were analyzed in comparison with coatings confining silver nanoparticles (MTF + AgNP). EDS analysis revealed that both types of MTF coatings were loaded with high amounts of silver (MTF + Ag⁺ = 25%; MTF + AgNP = 34%). MTF + Ag⁺ showed extremely high bactericidal efficiency (percent reduction of 99.5 to >99.999) against both strains along 10 cycles of use, comparable to that observed with MTF + AgNP. Interestingly, silver release from both types of coatings was similar over the same testing period. However, contrary to MTF + AgNP, MTF + Ag⁺ have shown absolute optical transparency. This is relevant for any type of coating, as conservation of optical properties of the material surface where they are intended to be applied, is highly desirable. Moreover, the maximum silver ion sorption capacity of film coatings was 3 μg cm⁻² and MTF + Ag⁺ were still loaded with silver after 10 cycles of use which indicates that the bactericidal effect could be extended beyond. These results spotlight the potentiality of MTF + Ag⁺ as antibacterial coatings for any ceramic and/or metallic surface with no alteration of optical and mechanical properties.

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1. Introduction

Infectious diseases induced by microorganisms like bacteria, fungi and viruses are still one of the greatest health problems worldwide. Intensive research has been devoted to drug development for combating those infections. Other efforts were directed to

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strengthen prevention, particularly by designing antibacterial coatings with natural and synthetic organic compounds and/or inorganic substances. Among these, antibacterial properties of silver are well known [1,2], and are still largely exploited in many consumer products and medical devices. Silver is nowadays applied in antimicrobial packaging films [3,4], textiles and sprays to protect from odor-generating microorganisms [5,6], in cosmetics [7], in wound dressing [8,9] and in medical implants and instruments [10,11].

The broad-range bactericidal effect of metallic silver is ascribed to the release of silver ions (Ag⁺) from its surface [12]. The antibacterial effect of this ion is due to interactions with thiol and

amino groups of proteins and with nucleic acids [2,13–15] leading to inactivation and loss of replication ability, respectively. Silver cations also induce cell membrane damage and production of reactive oxygen species that may alter lipids and DNA [16–18]. Considering the current high level of bacterial resistance against antibiotics, silver is used for disinfection as metal coatings, silver salts and nanoparticles. However, low stability and poor long-term antibacterial efficiency may limit its practical applications. For this reason, different materials with slow silver ions release rate and long-term antibacterial activity are required.

Silver-based coatings are aimed at reducing or even preventing microbial colonization and the formation of so-called biofilms, bacteria self-synthesized shelters which are highly difficult to eradicate [19,20]. Metallic silver coatings have been applied in permanent implants such as megaendoprostheses used in reconstruction after removal of bone tumors [11] and have been incorporated in biocompatible coatings, such as hydroxyapatite [21,22] to reduce surgical site infection in orthopedic and dental implants. However, in order to gain more control over the ion release, focus has recently shift from bulk silver to nanostructured coatings [23]. Nanomaterials offer remarkable advantages in antibacterial applications owing to their high surface area and unique physico-chemical properties, which depend on their size and shape [24–26]. In this sense, silver nanoparticles have found multiple applications and showed higher antibacterial efficiency than bulk silver materials [27–29].

Silver nanoparticles are frequently included in composite coatings offering flexible and tailorable structures, together with diverse methods for nanoparticle immobilization [30–34]. Combination of nanosilver and organic matrices is profitable as it facilitates nanoparticle synthesis, processing and immobilization, and minimizes nanoparticle aggregation and uncontrollable release of silver ions [35,36]. Many of these antibacterial coatings have been based in organic polymers [9,37–39] or proteins [40,41], which present some limitations when chemical and mechanical stability are required. As an alternative, mesoporous oxide thin films (MTFs) offering high surface area and the possibility to be tailored in order to control the pore size, shape and interconnectivity, has been widely used to confine silver nanoparticles within the porous reservoirs, leading to an enhanced stability of the nanoparticles [42–45]. Particularly, bactericidal synergy under UV irradiation between photocatalytic titanium dioxide (TiO_2) MTFs and immobilized silver nanoparticles within this porous matrix was recently reported [43,45].

Although the application of MTFs with confined silver nanoparticles has been extensively investigated, nanosilver exhibits a strong absorption of visible light, significantly altering the optical quality of coatings based on MTFs which are originally transparent [46–48]. This is particularly critical for ceramic and/or metallic surfaces where their optical properties must be conserved owing to functional and/or esthetic reasons. Therefore, there is still a need to develop silver-based transparent antibacterial MTF coatings for surfaces which require conservation of their optical properties. Instead of using silver nanoparticles as reservoirs of silver ions, a solution can be achieved by using mesoporous systems as reservoirs through direct adsorption of silver ions.

In this study, titania-silica bilayer MTF coatings were used as nanostructured reservoirs for silver ions, and their antibacterial activity was assessed. The films were synthesized onto glass slides by combining the sol-gel and evaporation-induced self-assembly methods and subsequently incubated with silver nitrate solution to promote adsorption of silver ions on the mesoporous matrix. Optical properties, estimation of silver content, ion adsorption and release, and long-term antibacterial activity for Gram+ (*Staphylococcus aureus*) and Gram- (*Pseudomonas aeruginosa*) bacteria were

evaluated in comparison with analogue films containing photo-deposited silver nanoparticles within the mesoporous titania layer. Optically transparent MTF coatings loaded with silver ions exhibited long-lasting antibacterial activity comparable to the non-transparent MTF coatings with confined silver nanoparticles, spotlighting its potentiality as antibacterial coatings for any ceramic and/or metallic surface with no alteration of optical and mechanical properties.

2. Experimental

2.1. Synthesis and deposition of mesoporous layers

Standard microscope glass slides were thoroughly washed with neutral detergent (Extran[®], Merck Millipore, Darmstadt, Germany), then sequentially rinsed with miliQ water, acetone and isopropanol, and finally dried under nitrogen flow. Titania-silica bilayer MTFs were prepared by sequential dip-coating (withdrawal rate of 2 mm s^{-1}) on the glass substrates at a relative humidity (RH) of 40–50% [49]. A first layer of mesoporous TiO_2 was deposited on the glass substrates, obtained from a TiCl_4 /ethanol solution to which the organic template Pluronic F127 ($\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{106}(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_{70}(\text{CH}_2\text{CH}_2\text{O})_{106}\text{OH}$) (Sigma-Aldrich) and water were added. The final composition of the precursor solution was TiCl_4 :ethanol: H_2O :F127 equal to 1:40:10:0.005 mol ratios. The substrates were dip-coated at 35°C solution temperature. After deposition, the samples were placed in a 50% RH chamber for 24 h and subjected to a consolidation thermal treatment consisting of two successive stages of 24 h at 60 and 130°C , followed by a final heat treatment at 200°C for 2 h. Next, a second layer of mesoporous SiO_2 was deposited on top of the deposited TiO_2 layer. Tetraethyl orthosilicate (TEOS) (Sigma-Aldrich) was used as the inorganic precursor and Pluronic F127 was selected as the template. TEOS was prehydrolyzed by refluxing for 1 h in a water/ethanol solution; $[\text{H}_2\text{O}]/[\text{Si}] = 1$; $[\text{EtOH}]/[\text{TEOS}] = 5$. Surfactant, ethanol and acidic water were added to this prehydrolyzed solution in order to prepare the precursor solution with final composition TEOS:ethanol: H_2O (0.1 M HCl):F127 equal to 1:40:5:0.005 mol ratios. After this second deposition, the samples were introduced into a 50% RH chamber for 24 h and then thermally stabilized with two successive stages of 24 h at 60°C and 130°C . To stabilize the overall structure and to remove the organic template a final thermal treatment at 350°C for 2 h (temperature ramp of $2^\circ\text{C}/\text{min}$) was performed. Glass slides with deposited mesoporous bilayer were cut into sample pieces of 26 mm long and 20 mm wide (5.2 cm^2).

2.2. Silver ions adsorption and photodeposition of silver nanoparticles

Film samples were immersed in a 0.1 M AgNO_3 water-ethanol solution (1:1 vol ratio) for 10 min in the dark to optimize ion infiltration. Subsequently, samples were individually placed in a 60 mm plastic culture dish and 7 mL of the silver solution previously mentioned was added to each one so the film samples were completely immersed. One group of immersed samples was incubated for 60 min in the dark. Another group was placed 4 cm below a UV tube lamp (Yarlux, 15 W, emission peak at 355 nm) for 60 min. All the samples were then withdrawn from the silver solution and thoroughly rinsed with water and dried under nitrogen flow.

2.3. Film coatings characterization

Transmission electron microscopy (TEM) images of MTF coatings were obtained using a Phillips CM 200 electron microscope (Amsterdam, The Netherlands). Samples were obtained by

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