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Silver-functionalized methyl-silica hybrid materials as antibacterial coatings on surgical-grade stainless steel

R. Procaccini [a], A. Bouchet [b], J.I. Pastore [b], C. Studdert [c], S. Ceré [a], S. Pellice [a,*]

[a] Instituto de Investigación en Ciencia y Tecnología de Materiales (INTEMA), UNMdP-CONICET, Av. Juan B. Justo 4302, 7600 Mar del Plata, Argentina
[b] Grupo de Procesamiento Digital de Imágenes. Universidad Nacional de Mar del Plata, Facultad de Ingeniería. Juan B. Justo 4302, 7600 Mar del Plata, Argentina
[c] Instituto de Investigaciones Biológicas (IIB), UNMdP-CONICET, Funes 3250, 7600 Mar del Plata, Argentina

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ABSTRACT

Development of new materials enriched with noble metal ions, such as silver, cobalt or copper, is of great interest in the field of commercial and medical products due to its action against fungus and bacteria. Although a large number of products are chemically active against microorganisms, they are usually limited to fabrics for medical bandages and sportswear in order to avoid, respectively, infections and odors. On the other hand, sol-gel technology becomes the preparation of hybrid materials possible with introduction of different components, as inorganic salts or organic additives within its structure bringing up the possibility to develop functional materials for different purposes.

In this work, the development of an antibacterial coating for metallic substrates is presented. The coating consists in a hybrid organic-inorganic sol-gel material doped with silver. The relation between the structure of the hybrid matrix, aggregation state of silver ions, and biocide behavior is analyzed as a function of the densifying thermal treatment. Sol-gel materials were synthesized through hydrolytic condensation, in acidic conditions, of tetraethoxysilane (TEOS) and methyl-triethoxysilane (MTES). Silica nanoparticles were added in order to give a mechanical reinforcement and silver nitrate as the supplier of Ag^+ ions. Coatings were deposited on 316L stainless steel and microscope glass slides by the dip-coating process at a constant withdrawal rate and densified at 50, 150 and 450 °C. X-ray photoelectron spectroscopy, small angle X-ray spectroscopy and electrochemical impedance spectroscopy were used as characterization techniques in order to elucidate silver aggregation and its influence on the structural evolution of the hybrid matrix, as a function of the thermal treatment. At the same time, the biocide behavior, as a function of silver state, particles size and thermal treatment, was studied by inhibitory halo identification on *Escherichia-coli* cultures in agar diffusion tests.

1. Introduction

The development of new functional materials capable to provide an effective antibacterial activity has a big demand from the contemporary society. This fact is mainly due to the easy propagation that microorganisms have in this globally connected world with a continuously growing population. The action of viruses and bacteria often presents serious damages that can turn in economic losses or even in loss of human lives. In this field, silver is a well-known biocide component due to the activity of Ag^+ ions [1–5]. Silver ions have an effective action against bacteria life inhibiting their DNA replication process, increasing the permeability of the cytoplasmic membrane and inhibiting the respiratory enzymes, causing asphyxia of the bacteria. Thus, silver is effectively used as the active additive, against fungus and bacteria, both in medical devices and in commercial textile products, like sportswear and burn bandages [6–12]. In the same way, the use of silver as antibacterial additive for thin solid coatings could provide a powerful tool in order to set a major obstacle to the spread of infections; specially, in the environments where people is highly exposed to infectious microorganisms as, e.g., public toilets, public transport and hospitals. Nowadays, also for surgical prosthesis and orthopedic devices, silver based coatings are in focus for the prevention of periprosthetic infections is a scientific topic of strong activ-

* Corresponding author.
E-mail address: spellice@fi.mdp.edu.ar (S. Pellice).

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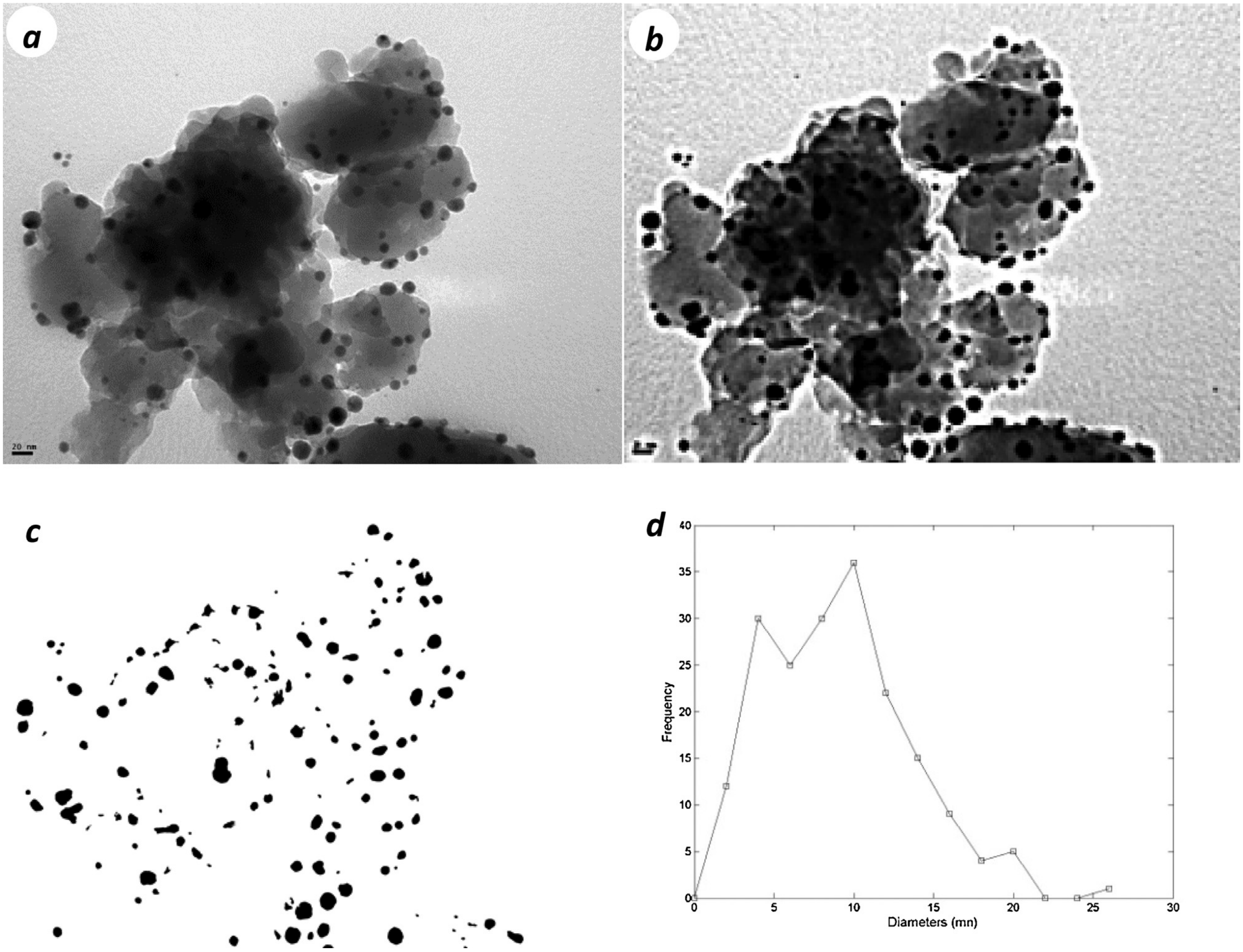

Fig. 1. Algorithm for detection and measurement of size distribution of silver particles. (a) Original image, (b) spectrally filtered image, (c) binary image and (d) size distribution of silver nanoparticles. The size of the bars in figures (a) and (c) represent 20 nm.

ity [13–18]. Certainly, although stainless steel does not present antibacterial properties by itself, it is a material that present optimal conditions in term of sterility and economical suitability as a material for surgical devices [19–21].

A promising method to produce such silver functionalized thin coatings comes from the sol-gel chemistry, which is a worldwide subject of study as a method to produce functional coatings [22,23]. Sol-gel chemistry, as a very versatile method of synthesis, allows the development of hybrid organic-inorganic materials with incorporation of a wide variety of external components, as particles, organic compounds, inorganic salts, etc. Then, through this method, it is possible to combine design a tailored material with both mechanical and functional properties [24]. This feature becomes it in a particularly promising approach to produce efficient antibacterial thin coatings where the biocide functionality derives from silver action. In this kind of materials, silver works by way of the diffusion of Ag^+ ions, or its smallest clusters, through the structure of the containing matrix towards the external surface, where microorganisms are reached. Then, both the development of a sol-gel network with an extremely open structure or the agglomeration process of silver, to form particles that would remain entrapped in the matrix, are features that could strongly limit the resulting antibacterial performance. It was seen that for sol-gel structures without an enough crosslinking density, lixiviation of silver ions may be extremely fast, producing an initial burst release and limiting the long-term antibacterial performance [25–27]. Furthermore, Ag^+ ions present a strong tendency to be reduced in the chemical conditions proper of the sol–gel process, resulting in an agglomeration process that carries to a rise of silver nanoparticles. Certainly, the growth of small silver clusters and nanoparticles is nearly impossible to avoid when the doped sol-gel coating is applied and a thermal treatment is performed [27,28]. So, in order to develop a hybrid organic–inorganic thin coating, providing a controlled silver release rate and avoiding an initial burst release effect and dangerous cytotoxic conditions, both the matrix structure and the agglomeration process of silver should be optimized.

The goal of this work is, in one hand, to deal with the in-situ self-development of silver nanoparticles from is reduction from Ag+ ions added in a hybrid organic-inorganic matrix of a thin coatings; this phenomenon is thermal-dependent and its behavior is of interest both in the fields of optical, electrical and antibacterial materials. On the other hand, the remaining of silver as Ag+ ions, avoiding its self-arrangement in silver nanoparticles, is mainly important for the antibacterial effect. In this sense, the evolution of silver aggregates inside hybrid coatings deposited onto surgical grade stainless steel is analyzed in the present work.

In this work the study of the oxidative state of silver, and the agglomeration phenomena inside of a silica-methyl hybrid matrix reinforced with silica nanoparticles was addressed. The resulting relationship between the aggregation state of silver, the structure of the hybrid matrix and the antibacterial effect in the developed sol–gel coatings was also studied. Through the use of a synchrotron