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Self-assembled monolayers of silver nanoparticles firmly grafted on glass surfaces: Low Ag^+ release for an efficient antibacterial activity

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ABSTRACT

A two-step, easy synthetic strategy in solution has been optimized to prepare authentic monolayers of silver nanoparticles (NP) on MPTS-modified glass surfaces, that were investigated by AFM imaging and by quantitative silver determination techniques. NP in the monolayers remain firmly grafted (i.e. not released) when the surfaces are exposed to air, water or in the physiological conditions mimicked by phosphate saline buffer, as UV–Vis spectroscopy and AFM studies demonstrate. About 15% silver release as Ag^+ ions has been found after 15 days when the surfaces are exposed to water. The released silver cations are responsible of an efficient local microbicidal activity against *Escherichia coli* and *Staphylococcus aureus* bacterial strains.

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1. Introduction

Bacterial infections involving the surface of medical devices (e.g. catheters, artificial prosthetics and subcutaneous implants) and more generally infections spread by materials used in the nosocomial environment are a serious challenge for bio-medical scientists [1]. In the last few decades a considerable effort was made to obtain antibacterial coatings on different surfaces, such as garments and medical devices [2]. The use of silver nanoparticles (NP) as antibacterial agents has been one of the most studied nanotechnology issues in the last decade [3]. Even if the debate concerning the true mechanism of their antibacterial action is still ongoing, it is generally accepted that it should involve Ag^+ release and its interaction with bacteria. Many applicative studies have been published [4]. The "layer-by-layer" (LbL) approach [5] has been applied to obtain surfaces on which thin films of silver NP are deposited or formed in situ on a molecular self-assembled monolayer (SAM) capable of interaction with silver [6]. In some cases the antibacterial activity of such surfaces has been evidenced [4d,7]. On the other hand, the increase of nanoparticle applications has raised the concern for health and environment risks connected to exposition and use of nanoparticles [8]. Nevertheless, with few exceptions [4f] NP layers appear to be weakly bound to the surface, with a consistent risk of NP release in the environment of application, that in perspective may be a human body. These considerations prompted us to find an efficient strategy to prepare glass surfaces with a monolayer of silver NP firmly grafted on a suitable molecular SAM. Our goal is to keep them confined to the surface and capable of exerting an efficient antibacterial activity thanks to Ag^+ release. Noticeably, this activity should be promoted by the high surface/mass ratio typical of NP. In addition, in an applicative perspective, preparing a monolayer of NP on a flat surface, instead of a film or a NP-loaded nanoporous matrix, reduces the amount of an expensive material used (silver) and intrinsically reduces the quantity of potentially dimension-risky materials (nano-objects) contained in the device.

We adopted a two-step process typical of the LbL approach, resembling that already successfully used for the preparation of a silver NP monolayer [9]. First, a SAM of a mercaptosilane is formed on activated glass, according to a procedure that has been optimized in our laboratories [10]. Then, the –SH terminated glass is immersed in a silver nanoparticles colloidal solution. This leads to the self-assembly of a NP monolayer covalently attached to the modified glass, as sketched in Scheme 1 [9b].

The two-step wet synthetic strategy has been optimized, obtaining a reliable protocol to prepare monolayers of silver NP on glass surface. The stability of the obtained NP monolayers under various conditions (including Phosphate Buffered Saline (PBS), mimicking physiological conditions) has been verified with UV-Vis spectroscopy, Atomic Force Microscopy (AFM) and X-ray

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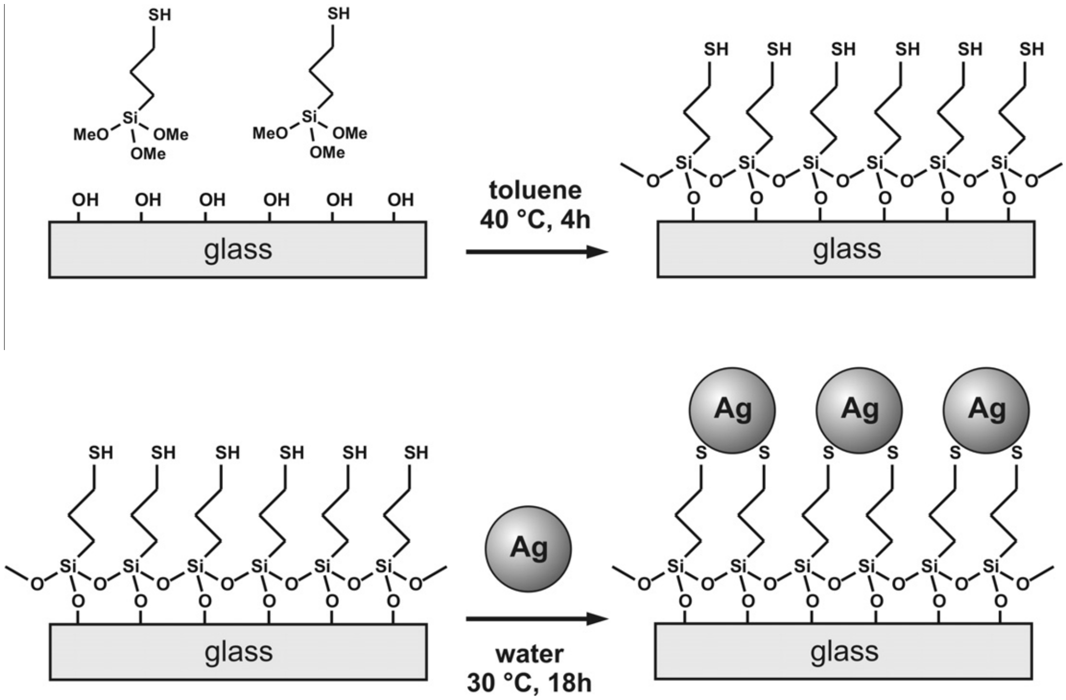

Scheme 1. Pictorial representation of the synthetic "layer-by-layer" approach used to prepare SAM of silver NP on glass substrates.

Photoelectron Spectroscopy (XPS). Ag^+ release and the consumption of the Ag NP monolayer have also been studied by means of inductively coupled plasma atomic emission spectroscopy (ICP-OES) and compared with the total Ag grafted on the surface. The antibacterial activity of the prepared glasses was investigated, finding an efficient microbicidal effect.

2. Material and methods

2.1. Materials

Silver nitrate (>99.8%), sodium borohydride ($\geqslant$99.0%), sodium citrate (>99.0%), (3-mercaptopropyl)trimethoxysilane (>97%, MPTS) and PBS were purchased from Sigma–Aldrich. Reagents were used as received. Microscopy cover glass slides (2.4 × 2.4 cm) were purchased from Forlab (Carlo Erba). Glass cuvettes were standard optical glass cuvettes purchased from Hellma. Water was deionized and then bidistilled.

2.2. Nanoparticle preparation

The synthesis of silver nanoparticles was adapted from a previously reported preparation [9a], see Supplementary data for experimental details. Dimensions (Transmission Electron Microscopy (TEM) images, see Supplementary data) were 7 nm (σ = 4 nm).

2.3. Preparation of a (3-mercaptopropyl)trimethoxysilane SAM on glass surface

The procedure is adapted from Ref. [10], see Supplementary data for full details.

2.4. Silver nanoparticle monolayer preparation

Thiol-modified glasses were immersed into the colloidal suspension of silver nanoparticles and kept at 30 °C for 18 h. In a typical preparation, eight glass slides were prepared at the same time, i.e. they were made to react in the same Ag NP suspension solution, inside a 8-place glass slides holder (where the slides were kept in a vertical position), placed in a large water bath thermostatted with a Julabo heating circulator, gently shaken on a Heidolph Promax 1020 reciprocating platform shaker. After this, the obtained yellow glasses were placed in water and sonicated for 5 min. This procedure was repeated twice, then the glasses were dried under a nitrogen stream and stored in air. The same procedure was applied to –SH terminated modified standard glass cuvettes.

2.5. Characterization

Absorbance spectra of colloidal suspensions were taken with a Varian Cary 100 spectrophotometer in the 200–1000 nm range. Spectra of NP-functionalized glasses were obtained placing the glasses on the same apparatus equipped with a dedicated Varian solid sample holder, or directly using the modified cuvettes. Measurements of absorbance vs. time on modified cuvettes were carried out by filling the cuvette with the chosen solution and keeping it stoppered and in the dark between successive spectra. For the determination of the local refractive index as a function of the solvent refractive index, a step-decreasing gradient of solvent polarity was followed in order to achieve the total removal of the previous solvent, i.e. the solvent was discarded, the cuvette was gently dried in a nitrogen flux and then washed three times with the next solvent before refilling. The following sequence of solvents was used: water, acetonitrile, DMF, *n*-butanol, ethyl acetate, toluene, *n*-heptane.

TEM images were obtained on colloidal solutions of Ag NP prepared as described in Section 2.2 and diluted ten times with bidistilled water, deposited on Nickel grids (300 mesh) covered with a Parlodion membrane and observed with a Jeol JEM-1200 EX II instrument.

Atomic force microscope images were obtained with a Thermo Microscopes CPII AFM, operated in tapping mode with NT-MDT silicon tips NSC05_10° and NSG01. Data analysis (manual width and height calculation on line profiles) was carried out with Image Processing and Data Analysis software – version 2.1.15 by TM Microscopes.

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