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Extended Abstract

Nano science, Nanotechnology, Graphene & 2D material: Sol-gel based surface patterning- David Riassetto, Celine Ternon and Michel Langlet - Grenoble-INP/LMGP, France CNRS-LMGP, France

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Abstract

Photolithography is a well-known and often used technique. However, this technique is mainly used for bulk material or native oxide etching and usually requires an etching step with a strong acid or base. Due to these reasons, photolithography is not well compatible with sensitive substrates like glass or plastic ones. Based on sol???gel route, we formulated and optimized different all-inorganic oxides photo-resists. These photo-resists lead to single-step lithography (i.e. with only one deposition step) of nanometer-scale thin oxides films, etched with solvent or diluted acid. Such method is compatible with the formation of gratings in the range of the millimeter to the sub-micrometric size on rather large surfaces on top of glass or plastic substrates. Our photoresists where made by integrating a photosensitive chelating compound to a ???classical??? sol-gel oxide sol. These photoresists may be deposited by spincoating on various substrates, then insolated through a mask and selectively washed/ etched. On one hand, TiO2 photo-resist was investigated for the functionalization of surfaces with a spatial wettability contrast. On the other hand, ZnO photo-resist was studied for the localized growth of ZnO nanowires. The synthesis principle will be introduced at the conference. The physicochemical and morphological properties of the obtained surfaces, linked to the process parameters, will be presented. Moreover, potential applications will be shown.

Bacterial adhesion to the surface of biomaterials is the first step in colonization and biofilm formation. Once bacteria have colonized a surface and biofilm has formed, a clinical infection around the biomaterial is presented, which will lead to biomaterial failure or chronic infections2. Therefore, a number of alternative approaches have been proposed and investigated to reduce bacterial adhesion to surfaces, since traditional approaches, like antibiotic therapies, are not recommended as biofilms are highly resistant to this conventional therapy. These approaches include immobilization or release of antibacterial substances such as silver, creation of anti-adhesion surfaces5, and fabrication of structured arrays.

A reduction in bacterial adhesion and biofilm formation has been demonstrated by several authors on a variety of modified substrates using different bacterial species. Multiple techniques have been employed to fabricate arrays on the surface of materials, including direct methods like dip-pen nanolithography (DPN), and indirect techniques like microstamping (soft lithography). Most investigations analysing the effect of fabricated surfaces on bacterial adhesion and cellular behaviour share photolithography and soft lithography as the combination of choice to modify the surface of the tested material. Soft lithography is a series of indirect techniques that allow the fabrication of micro and sub micro arrays on the surface of materials using an elastomeric stamp that is usually made of poly(dimethylsiloxane). This PDMS stamp is obtained from a master model, which is usually fabricated using photolithography. However, photolithography presents a series of disadvantages, including high cost, lack of chemical control of the surface, and inapplicability over non-planar surfaces, which render it difficult to use, especially in the biomedical field. DPN has some distinct advantages, including the fact that it is a direct-writing technique that is compatible with many substrates and inks and shows high resolution and registration. It has been proposed that these physical modifications act as barriers or obstacles that hinder the interaction of a single bacterium or a cluster of bacteria with other bacteria as well delaying the cell-to-cell communication, known as quorum-sensing which is recognized to play an important role in biofilm formation by bacterial species

On the other hand, some chemical substances are recognized to be antibacterial. Metals like silver in different forms (silver nitride and silver nanoparticles) have been long recognized as antibacterial substances, as well as copper and zinc. However, these metals present some drawbacks, including cytotoxicity, inflammatory responses and increase in bacterial resistance. Other compounds, such as titanium dioxide (TiO2), have long been studied for their antibacterial properties. TiO2 has received special attention as an antibacterial material, particularly in relation to the photocatalytic effect.

This photocatalytic effect is produced when reactive oxygen species (ROS), such as hydroxyl radicals, hydrogen peroxide,

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and superoxide anion, are generated after TiO_2 is exposed to UV light. Such ROS are known to inactivate bacteria, viruses, and fungi. The basic principle of photocatalysis consists on the formation of an electron-hole pair upon absorption of a photon with an energy equal or higher than the semiconductor's band-gap. Two reactions then occur simultaneously: oxidation from photogenerated holes and reduction from photogenerated electrons. After these electron-hole pairs in the semiconductor particles are formed, the electron migrates to the metal and becomes trapped, therefore electron-hole recombination is inhibited. The photogenerated hole is transferred to the target molecule (usually an organic compound) causing its oxidation or destruction in the case of bacteria or viruses. TiO_2 has been considered as an ideal photocatalyst due to the fact that it is inexpensive, chemically highly stable, and the photogenerated holes are highly oxidizing. Even though TiO_2 exists in three crystalline forms (anatase, rutile, and brookite), the anatase form has shown to have the highest photoactivity. This effect has been largely proposed for disinfection of polluted water, although it has also been proposed in the biomedical field due to promising in vitro results in reducing bacterial adhesion to biomaterials.

Consequently, the combination of a physical surface modification approach with the use of an antibacterial substance to further increase bacterial reduction needs to be addressed. Therefore, the main objective of this work was to assess whether a physical surface modification approach using TiO_2 as antibacterial compound subjected to UV light might reduce Streptococcus mutans adhesion to surgical-grade stainless steel plates

For dip-pen nanolithography (DPN), commercial 10 mm × 10 mm × 1 mm gold wafers (Nanoink Inc., USA) were used as model substrates due to their affinity for the ink.

For soft lithography (microstamping), stainless steel 316L plates (SS316L) 10 mm × 10 mm × 1 mm plates (Onlinemetals, USA) were polished up to 1 µm diamond paste (Leco Corporation, USA) to obtain a mirror-like surface. SS316L plates were sequentially cleaned using surfactant, acetone (99.8% v/v, Merck Millipore, USA), distilled water and absolute ethanol (99% v/v, Merck Millipore, USA) for 8 min each in an ultrasound bath and let dry in air. For simplicity, this surface will be referred as SS polished through the text and used as control

For DPN, a commercial polymeric adhesive (Norland Optical Adhesive 68 T, Norland Products Inc, USA) was used. It was kept at 4 °C throughout the experiments to maintain viscosity.

For microstamping, a silica sol was prepared using the one-stage sol-gel method as previously described. Tetraethylorthosilicate (TEOS) and methyltriethoxysilane (MTES) (ABCR GmbH & Co., Germany) were used as silica precursors for the hybrid sol, 0.1 N nitric acid (Merck Millipore, USA) and acetic acid (glacial, 100% v/v, Merck Millipore, USA) as catalysts and absolute ethanol (99.9% v/v, Merck Millipore, USA) as solvent. The final concentration of SiO_2 was 18 gL^{-1}. Commercial titanium oxide (TiO_2) anatase nanoparticles (<100 nm particle size, NaBond, Hong Kong) were added to the silica sol at 5 and 10% concentrations by weight and the suspension was agitated to reach homogeneity. It was kept at 4 °C

A commercially available polymeric adhesive was used to fabricate patterns on a model gold substrate. A column pattern was created and the dimensions were determined using the DPN system and confirmed by AFM and SEM. Column averaged 2.9 ± 0.1 µm in diameter and 250 to 450 nm in height. SEM and AFM images of a pattern fabricated on gold. As size variability was observed among features in different patterns, care was taken to select those approaching a size near the S. mutans and its arrangement as the bacterial species evaluated. Satellite columns were observed next to the main columns. However, these satellite columns showed sizes that were five to six times smaller than the main columns, which is negligible for the size of the bacterial species used in the current investigation. Furthermore, these satellite columns did not seem to affect the PDMS nor the micro stamping process

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