Development of Alternative Micro– and Nanofabrication Techniques Based on Molecular Self–Assemblies on Solid Surfaces

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Design and development of novel and reproducible strategies for nanopatterning surfaces became one of the most relevant topics involved on the progress of nanotechnology. However, interesting patterning approaches were not able to reach the presumed technological impact as a consequence of lacking the required combination of reproducibility, accuracy, simplicity and more important, suitability for large scale fabrication.

My dissertation focused on development of novel alternative nanofabrication techniques using concepts and tools brought from diverse chemistry–related research fields like surface chemistry, electrochemistry or materials science.

One breakthrough on the development of alternative nanofabrication techniques was brought by “soft lithographic techniques” initially developed by Whitesides’ group at Harvard University about a decade ago. Soft lithography is a set of techniques that rely on printing and molding with rubber stamps to make micro– and nanostructures. However, high–resolution patterning is rather problematic with elastomeric, distortion–prone materials, thus limiting the use of soft lithographic techniques for nanoscale patterning.

During my thesis I worked on extending the concept of “soft lithography” to other stamps different from the traditionally used polydimethylsiloxane (PDMS) stamps. This initial framework was motivated by the idea of overcoming the current limitations of PDMS stamps. In addition, I was much interested on exploring novel nanopatterning routes derived from the use of non–traditional stamps. Following this approach, the idea of using metal–made conductive stamps, instead of rubber stamps, resulted attractive in such a way of exploiting electrochemical deposition as a versatile chemical route to synthesize different patterned materials, ranging from alloys to ceramics.

The beginning of my thesis work aimed on gaining insight on the surface chemical modification of conductive stamps. Direct electrochemical deposition onto the stamp would result on the irreversible adhesion of the electrosynthesized material. Otherwise, common release layers, like teflon–like coatings, would hinder the charge transfer at the electrochemical interface due to they act as insulating films. Thus, interfacial electrochemistry and diverse aspects of materials science became of great importance on understanding the fundamental problems on extending the concept of “soft lithography” to electrochemical systems. In particular, to modify the adhesion properties of the “stamp electrode” we explored the use of alkanethiol self–assembled monolayers (SAMs) as release agents.

Under this focus we started to study the behavior of self–assembled monolayers (SAMs) at electrochemical interfaces. It is well–known that these self–assembled molecular films can be electrodesorbed from the electrode surface under determined electrochemical conditions. Considering that a great variety of technologically–relevant materials are electrodeposited under cathodic conditions, we were particularly interested on understanding the factors ruling the reductive (cathodic) electrodesorption process of alkanethiolate SAMs.

By combining electrochemical and surface–sensitive techniques we studied the critical role of solvent, pH, the hydrocarbon chain length and the metal surface on the electrochemical stability of alkanethiol SAMs.

We observed that the influence of the hydrocarbon chain length on the cathodic stability is closely related to the magnitude of the hydrophobic and van der Waals forces, that act as stabilizing factors. The hydrophobic forces are responsible for keeping the thiol molecules on the SAM as a consequence of the low affinity of hydrocarbon chains to the aqueous electrolyte environment. In the case of van der Waals forces (dispersion forces) they are involved on the attractive adsorbate–adsorbate interactions. Solvents with marked affinity to the organosulfur molecules decrease the cathodic stability of SAMs. This is as a consequence of a diminution on the hydrophobic forces (stabilizing factor) in the electrolyte where the thiol molecules are more soluble.

The influence of the electrolyte pH on electrochemical stability can be easily described considering the thiol–thiolate equilibrium at the electrode interface. By changing the pH, the distribution of thiol and thiolate species, which govern the Nernstian response for the electrodesorption process, is affected.

We used quantum mechanics tools (density functional theory, DFT) to study the influence of the metal surface on the reductive electrodesorption. Different stabilities (Cu>Ag>Au) are due to a balance between the adsorption energy of the thiolate species and the energy to introduce an electron in the metal–thiolate bonding.

After studying the stability of SAMs at electrochemical interfaces the second part of my thesis concerned on studying the influence of SAMs on electrochemical deposition processes.

In presence of long–chain SAMs, metal electrodeposition only occurs at SAM defects. This fact is reflected on a marked decrease of electrocrystallization nuclei. Interestingly, the reduced number of nucleation sites in combination with the poor interaction between the methyl–terminated SAM and the electrodeposited metal film promote a drastic change (decrease) on the adherence of the electrodeposit.

These anti–sticking properties of self–assembled monolayers were used for direct molding of electrodeposited materials using “conductive stamps”. This electrochemical route was successfully used to transfer surface–relief patterns on metals, alloys and ceramic oxides with no repeated implementation of expensive hard lithographic techniques.

Electrochemical soft lithography can be used to mold and replicate surface–relief structures with sub–50 nm and sub 10 nm, lateral and vertical resolution, respectively.

Finally, and more important, these SAM–modified “conductive stamps” can be used in combination with other deposition techniques (different from electrodeposition) for micro– nanomolding surface–relief structures on a wide range of materials. Under this approach, we were able to transfer surface–relief patterns on pulsed–laser deposited ZnO films and to obtain nanostructured AlN and TiN ceramic surfaces deposited by reactive sputtering with a resolution that current hard lithographic techniques are not able to obtain on hard materials.

In summary, my thesis merged tools from surface chemistry, electrochemistry and materials science to gain understanding on the behavior of SAMs at electrochemical interfaces and their influence on electrochemical deposition processes. This insight promoted the development of an electrochemical soft lithographic technique capable of patterning diverse materials with nanoscale resolution in an inexpensive and straightforward manner. These studies on electrochemical systems could be extended to other deposition techniques widening even more the range of materials that can be nanopatterned with the same “soft lithographic concept”.

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