4. Introduction to micro- and nanostructuring of metal surfaces

The modification of surfaces at micrometer and sub-micrometer scales is considered to be a key future technology. This has led in recent years to an interest in the generation of micro- and nanometer sized structures on surfaces [143]. Nanostructured materials may adopt various shapes which are critical factors in determining their basic properties and are of much current interest for extensive potential applications in electronic, mechanical and optical devices.

A variety of methods for the fabrication of micro- and nanostructured materials have been proposed and applied, such as molecular beam epitaxy, microlithography, vapor-liquid-solid growth, solution-liquid-solid growth and template-mediated methods. The latest entails synthesizing the desired material within the pores of a nanoporous material.

In this order of idea, a working place has been developed to modify the metallic surfaces with organocopper(I) complexes through coordinative interaction at micro and nanometer scales. To test the operating of the experimental setup, mesoporous platinum films (with a defined nanostructure) should be electrodeposited from lyotropic liquid crystal phases onto a gold surface under galvanostatic control. The templated electrodeposition was introduced by Attard et al. [41,42,144,145] to produce under potentiostatic control porous nanostructured metals from lyotropic liquid crystal [146-148]. Such modified materials found applications ranging from catalysts, molecular sieves to batteries and electronics [149-153].

4.1. Surfactant templating

Non-ionic surfactants, \( n \)-alkylpolyethylene glycol ethers commonly known as polyoxyethylene surfactants, are widely used as emulsifying agents, as detergents [154] and as template to produce mesoporous and/or mesostructured material [155-159]. They have the general chemical formula \( C_nH_{2n+1}(CH_2CH_2O)_mOH \) [156], \( CH_3CH_{(n-1)}(CH_2CH_2O)_mOH \) [155] or \( n-C_nH_{2n+1}(OCH_2CH_2)_mOH \) [154] and denoted as \( C_nEO_m \); by alteration of \( m \) and \( n \) it is possible to change systematically their chemical structure. The templating aggregates arise because surfactants are bifunctional molecules which contain a polar head group (\( m \)) (water loving or hydrophilic) and a non-polar chain (tail) group (\( n \)) (solvent hating or hydrophobic) as drawn in scheme 38.
Polyoxyethylene surfactants, when mixed with water, form micelles above a critical concentration in water with a wide range of liquid crystals (LC) occurring frequently at high concentrations of non-ionic surfactants (typically more than 40 wt%) \([41,144,145]\). The shape of the micelles depend highly upon surfactant concentration, electrolyte level and temperature.

![Scheme 38 The chemical structure of a non-ionic surfactants.](image)

The amphiphilic nature of non-ionic surfactants results in molecular aggregation forming usually a lyotropic liquid crystalline (LLC) mesophase with a well-defined structure. This occurs because the alkyl group \(C_nH_{2n+1}\) (oil like) of the \(C_nEO_m\) molecule tends to minimize the interaction with water and also the polar EO head group \((-\text{CH}_2\text{CH}_2\text{O})_m\text{OH}\) tends to stay outside to form diluted water solutions. Thus the liquid crystalline phase is formed by water molecules through polar-apolar interactions \([156]\).

The topology of the structure can be varied in a predictable fashion. \cite{Attard144,146} have used at high concentration, the non-ionic surfactant, octaethyleneglycol monodecyl ether \((C_{16}EO_8)\) to produce three liquid crystalline phases: hexagonal \((H_I)\), cubic \((Ia3d)\) and lamellar \((L_\alpha)\). Among these three phases, the hexagonal one, which exists over a wide range of composition and temperature is the most reported.

The hexagonal phase is consisted of long cylindrical micelles of surfactants packed into a hexagonal array with a uniform radius determined by the length of the surfactant molecules (scheme 39). The size of pores and the thickness of metal walls can be modified by varying the alkyl chain length of the surfactant and/or by adding a co-solvent as n-heptane to swell the micellar surfactant rods in lyotropic liquid crystalline phase. So, the range of radii was varied from 1.7 to 3.5 nm by using a variety of non-ionic surfactants (scheme 38) and added hydrocarbon swelling agents, suggesting the dispersion of alkane molecules between the surfactant micellar aggregates \([160,161]\).
The cubic phase does not exist at room temperature. At high concentration of surfactant the lamellar (L\textsubscript{\(\alpha\)}) phase predominates and consists of surfactant molecules aggregated to form infinite continuous planes separated by water layers [160,161].

Consequently, the nanostructures of the metal films deposited from LLC phases depend on the structure of the lyotropic phase used. In the cases of C\textsubscript{12}EO\textsubscript{6}-H\textsubscript{2}O, C\textsubscript{12}EO\textsubscript{8}-H\textsubscript{2}O, C\textsubscript{12}EO\textsubscript{10}-H\textsubscript{2}O, C\textsubscript{16}EO\textsubscript{8}-H\textsubscript{2}O and C\textsubscript{16}EO\textsubscript{1}-H\textsubscript{2}O systems, the sequence of the mesophase follow the hexagonal (H\textsubscript{1}) \(\rightarrow\) cubic (V\textsubscript{1}) \(\rightarrow\) lamellar (L\textsubscript{\(\alpha\)}) order with increasing surfactant concentration at room temperature. The hexagonal phase is the most stable and appears in a range of 40-70 wt% surfactant concentrations [42,144,154,158,162].

4.2. The principle of templated electrodeposition

The principle of the templated electrodeposition consists to dissolve the metal precursor in the hydrophilic domains of the mixture around the hexagonally packed cylindrical surfactant micelles. In these domains the metal salts are solvated by water in the vicinity of the polar EO head groups of the non-ionic surfactant molecules. Upon application of the potential, metal is electrodeposited within these aqueous domains producing a metal film around the surfactant micelles. Once the metal deposition is complete, the electrochemical cell is disassembled and the surfactant is removed by soaking the film in water to leave an adherent nanostructured metal film with a hexagonal array of cylindrical pores as a direct cast of the lyotropic liquid crystalline phase (scheme 40 analog to [149,160,163,164]). Several prerequisites are required for using this method to prepare nanostructured materials: water, choice of surfactant,
precursor molecule and additive. Under the right conditions the precursor molecules react, only within the aqueous domains, to build up a solid mass of product.

![Scheme 40](image)

Scheme 40 The principle of the liquid crystal templating method.

The electrodeposition of metal by templating method usually occurs at a constant potential where the rate of deposition is controlled by the kinetics of the process and not by mass transport. So, the thickness of the deposited film is controlled by varying the total charge passed during the electroplating process [164].

### 4.3. Schematic representation of the working station

The first goal of this work is to achieve galvanostatically microstructures which exhibit a well defined nanostructures. These nanostructured surfaces will be used later for the fixation of metal complexes. For this achievement, the basic of apparatus for metal electrodeposition is shown in scheme 41. The working electrode is attached to the bottom of electrochemical cell which is mounted on a stable platform. The counter electrode is fixed on a Motor Controller which can drive up to 4 DC-motors directly from a PC with C-842 WinMove® programming software. The electrodes are connected to a Potentiostat / Galvanostat which operates remotely from a PC via a IEEE-488 interface port with 352 SoftCorr® III software. The distance between both electrodes (WE and CE) is maintained constant during the experiment by piezoelectric micropositioners which can move in two dimensions (y,z).
4.4. Potentiostatic deposition of the platinum film from the liquid crystalline plating mixture

The first series of experiments in this part is devoted to the electrodeposition of mesoporous platinum film from the liquid crystalline plating mixture onto gold electrode. The plating mixture used consists of a commercially available non-ionic surfactant, Brij©76 that nominally corresponds to decaethyleneoxide monoostadecyl ether (C_{18}EO_{10}), a precursor salt such as hexachloroplatinic acid (HCPA) and water. The first step consists to identify the texture of the ternary salt/water/surfactant system by polarized optical microscopy (POM).

Thin films of the liquid crystals were prepared by sandwiching the mixture between a glass microscope slide and cover slide, and cooling them from 83-85°C to room temperature. The POM image of the mixture displays a typical texture which corresponds to a columnar phase and was found to be stable up to 85°C (Fig. 66). By pressing on the sample sandwiched between glass slides, large dark region are developed which could be refer to hexagonal phases. Unfortunately, images could not be possible from the X-ray, consequently nothing could be said about the mesophase.
The electrodeposition of the platinum film from the liquid crystalline plating mixture is carried out under thermostatic and potentiostatic control. The temperature is maintained constant at 40°C and the potential at –0.1 V for 30 min. After the deposition, the electrode is soaked in water, after the deposition, for at least 48 h to remove the surfactant. The resulting film was adherent, gray and shiny. Atomic force microscopy (AFM) was employed to visualize the structure of the deposited platinum film. The morphology of the deposited film is presented in Fig. 67.
Introduction to micro and nanostructuration

As it is shown, AFM reveals that the deposits were not uniform and present large pores which could not be comparable with that found by Attard et al. [41] for mesoporous platinum films electrodeposited from the hexagonal phase of a nonionic surfactant octaethyleneglycol monohexadecyl ether (C\textsubscript{16}EO\textsubscript{8}). The pore diameters are estimated ranging 220 – 316 nm. The use of the working place presented in the previous paragraph is more complicated for the electrodeposition under potentiostatic control.

4.5. Galvanostatic deposition of the platinum film from the plating mixture

The galvanostatic deposition of the platinum film from the templating liquid crystal has been carried out from the hexagonal phase formed by a mixture of a non-ionic surfactant, C\textsubscript{18}EO\textsubscript{10} denoted Brij\textsuperscript{®} 76, and an aqueous solution of HCPA.

In this part, the structure and the morphology of the electrodeposited platinum films is established by AFM. Fig. 68 represents the 3-dimensional view of the gold working electrode without the deposit.

![Fig. 68 AFM image of the gold electrode without deposit (3-dimensional view).](image)

The ternary plating mixture is prepared from an aqueous solution of 2M HCPA which is mixed, in a ratio 1:1, with 50 wt% of Brij\textsuperscript{®} 76 in water. The platinum films are deposited at a constant current of 9 \( \mu \)A (Fig. 69A) and 50 \( \mu \)A (Fig. 69B) for about 45 min and 3 hours respectively on a polished gold electrode. The morphology of the deposited films is investigated over a range of length scales reported in Fig. 69. The AFM studies show a porosity in the structure although nothing could be said presently about its regularity. It appears that the time of deposition could play an important role with regard to the

87
morphology of the film electrodeposited. The deposit obtained within a short time scale seems to be more structured and flat (Fig 69A) than the long time deposition which present large pores (Fig. 69B).

![AFM image of the electrodeposited platinum films](image)

**Fig. 69** AFM image of the electrodeposited platinum films: (A) 9 µA, 45 min and (B) 50 µA, 3 h.
Introduction to micro and nanostructuration

The diameter of pores are estimated in the range of 115 – 121 nm with a deepness of 4.2 nm for short time deposition (Fig. 69A) and 360 – 365 nm with a deepness of 5.6 nm for long time deposition (Fig. 69B). These values are very different of the theoretical value of 4.5 nm calculated assuming that the diameter of micelle is $2.5n$ for $C_nEO_m$ surfactant [154]. Up to now this difference remains non clarified. A possible explanation may be arise from the composition mixture of the ternary system used.

4.6. Conclusion

The work described in this part, as mentioned before is an introductive work devoted to the testing of a new working place built up for molecular architectures and nanostructures on metal surfaces. The first test was devoted to the electrodeposition of mesoporous platinum films from lyotropic liquid crystalline phases. The plating mixtures consist of non-ionic surfactant Brij® 76 ($C_{18}EO_{10}$), hexachloroplatinic acid and water in a ratio 2:1:1. The morphology of the electrodeposited platinum film investigated only by atomic force microscopy (AFM) presents a porous structure. The AFM studies of the thin films deposited galvanostatically reveal to be in sharp contrast to those achieved potentiostatically. The deposits seem to be uniform and flat over the electrode area but the diameter of pores remains large than expected and could not be compared with the results reported in the literature. Nevertheless, the new workstation can be use to produce porous platinum films from lyotropic liquid crystalline phase. Thus, this porous electrode could be use for microstructuring of metal complexes onto its surface.