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Conditions that bicontinuous microemulsions must fulfill to be used as template for electrodeposition of nanostructures

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ABSTRACT

The conditions to obtain metal micro/nanostructures by templated electrodeposition using bicontinuous microemulsions have been proposed. For this, different microemulsions have been tested to discover, analyze and generalize the conditions that must fulfill in order to act as a template for metal electrodeposition. Bicontinuous microemulsions were selected to provide enough conductivity to permit the process at significant velocity. Using the cobalt deposition process from a single bath in the aqueous component of the microemulsion as a test, the relation between the nature of the microemulsions and the template capacity in the electrodeposition process has been deduced. Depending on the characteristics of each selected microemulsion, either continuous or nanostructured deposits (porous films or particles of 20–50 nm) were obtained. The conditions for which the microemulsions act as templates in the electrodeposition are: (1) immiscibility of oil and aqueous solution components, (2) low dielectric constant of the oil to favor the non-dissolution of the electroactive species, (3) the use of a surfactant that avoids the solubilization of electroactive species. Also, the possibility of using an electrodeposition method to characterize the structure of some microemulsions has been demonstrated.

1. Introduction

The development of nanometer-sized materials (nanoparticles, nanowires, nanorods, nanostructured thin films, etc.) has been intensively studied due to their considerable technological and fundamental scientific interest [1–3]. Many strategies and techniques to prepare nanomaterials and control their characteristics have been developed because composition [4–8], shape, thickness and crystalline phase of the nanostructures determine their optical, chemical, magnetic and catalytic properties.

Electrodeposition is proved as a promising technique to prepare nanomaterials (alloys, intermetallic, oxides and composites) that could be grown directly on the devices because it is an advantageous [9,10], simple and cost-efficient technique as its experimental setup does not require high temperatures and vacuum conditions. Furthermore, it allows an easy control of composition, thickness and growth process. The architectural growth can be controlled by the use of templates or lithographed substrates. In the last years, the use of alumina or polycarbonate membranes has permitted the control of the separation and aspect-ratio of the nanostructures, providing the possibility to define nanowires with different length and width [11–16]. Recently, there are some studies that analyze the capability of soft template systems like microemulsions and self-assembled monolayers [17,18].

Microemulsions are thermodynamically stable liquid solutions of water, oil and amphiphile which are optically single isotropic systems. Depending on the temperature, the electrolyte concentration, etc. microemulsions could exist as oil-swollen direct micelles dispersed in water (*o*/*w* microemulsions), water-swollen inverse micelles dispersed in oil (*w*/*o* microemulsions), or with both aqueous and oily continuous domains as interconnected sponge-like channels (bicontinuous microemulsions) [19–22]. Microemulsions have been used as a reaction medium, a soft template, for the chemical synthesis of small nanoparticles or other nanostructures using reducing substances [23–27].

In previous studies the possibility to use microemulsions media to electrodeposit alloys was tested [28,29]. This procedure could be a new method for preparation of nanostructures, avoiding the use of aggressive reducing substances. It could allow preparing nanostructures of different shape and size. However, the conditions in which this is possible must be analyzed. The aim of this work is to discover, analyze and generalize the conditions that bicontinuous microemulsions must fulfil in order to act as a template for

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metal electrodeposition defining nanostructures. Bicontinuous microemulsions are selected to provide enough conductivity to allow significant deposition rate. Different microemulsions systems with different characteristics have been selected to this aim [28–32]. Moreover, electrodeposition could be proposed as a morphological characterization technique to visualize microemulsion morphology of some type of microemulsions in the case that electroactive species could be dissolved in aqueous or organic component. Cobalt electrodeposition has been selected for this study.

2. Materials and methods

2.1. Materials

2.1.1. Surfactants

Non-ionic surfactant p-octyl polyethylene glycol phenyl ether a.k.a. Triton X-100 (Acros Organics, 98%), polyoxyethylene lauryl ether a.k.a. Brij 30 (Sigma), polyoxyethylene sorbitan monooleate a.k.a. Tween 80 (Aldrich).

2.1.2. Oils

Diisopropyl Adipate (Croda), Isopropyl Myristate (Sigma-Aldrich), Isohexadecane (commercial name Arlamol HD, UNIQEMA), Isohexadecane (Fluka, 98+%), oleic acid (Sigma Aldrich, 99+%).

2.1.3. Electrolytes

Cobalt chloride (Carlo Erba, 99+%), Sodium Hydroxide (Panreac, 99+%).

2.1.4. Other additives

Butyl-L-Lactate (Sigma-Aldrich), Rhodamine B (Sigma-Aldrich), Sudan Black HB (Sigma-Aldrich), n-propanol (Acros Organics, 99.6%).

All solutions were prepared with deionized water (Millipore Q-system) with a resistivity of 18.2 MΩ cm.

2.2. Procedures and apparatus

Microemulsions systems (MS) described in the bibliography have been selected to perform the electrodeposition (Table 1), but substituting the water with the cobalt (II) electrolytic solution (0.5 M $CoCl_2$; pH adjusted to 4.0 with a NaOH diluted solution) and selecting the adequate aqueous component percentage from conductivity measures. The microemulsion regions in the aqueous solution component (W), organic component (O) and/or surfactant (S) systems were prepared by the stepwise addition of aqueous solution (or organic component, in system D) to oil/surfactant mixtures (or water/surfactant mixture, in system D) at controlled temperature, under magnetic stirring at 400 rpm. The microemulsion compositions and the ratio of components are expressed in weight by systems SA, SB and SC and in volume at system SD throughout the text. The conductivity was measured using a Crison conductimeter GLP31 with a 52-92 (Crison) conductivity cell (1 cm^{-1} of cell constant). Measurement of conductivity was carried out with an absolute accuracy up to ±0.05 °C by a CAT Crison temperature sensor (model 55-31).

The electrochemical study has been carried out in different microemulsion systems. Cyclic voltammetry and potentiostatic electrodeposition was done with microcomputer-controlled potentiostat/galvanostat Autolab PGSTAT30 with GPES software and a three-electrode cell containing a Si/Ti (10 nm)/Au (50 nm) (0.50 cm × 0.50 cm of exposed area) working electrode, a Ag/AgCl/3 M KCl reference electrode and a platinum wire counter electrode under temperature controlled conditions. Each system was de-aerated by argon bubbling before each experiment and maintained under argon atmosphere during the electrochemical process. The deposition charge density and current density are calculated with a virtual exposed area in all the cases. Voltammetric experiments were performed at a scan rate of 50 mV s^{-1} without stirring of the solution.

The morphology analyses of the obtained deposits were examined by using Field Emission Scanning Electron Microscopy (JEOL JSM-6510), Scanning Electron Microscopy (JEOL JSM-7100F) or Transmission Electron Microscopy (Hitachi 800 MT). For the TEM analysis it is essential to release the nanostructures from the substrate. This was achieved by removing the Au layer using a saturated I_2/I^- solution. The nanostructures were later retained by an external magnetic field and washed with water and ethanol.

Table 1
Selected systems based on described microemulsions in the bibliography, but substituting water for Co(II) solution.

Bicontinuous microemulsion	Components	References
Classical	Aqueous solution, Triton X-100, Diisopropyl Adipate	[28]
	Aqueous solution, Brij 30, Isohexadecane	[30]
	Aqueous solution, Tween-80, Butyl-L-Lactate, Isopropyl Myristate	[31]
Surfactant-free	Aqueous solution, propanol, Oleic acid	[32]

3. Results and discussion

Four different bicontinuous microemulsions have been tested as soft templates in the electrodeposition process. In each case, the proportions of the components have been selected to obtain ME regions, based on the literature studies, identified as optically transparent regions, isotropic mixtures and thermodynamically stable. The direct mixture of all the components and the system reversibility when the temperature changes (increase or decrease) and returns to the initial stage corroborate the microemulsion nature. The formation of bicontinuous, described in the bibliography, was assessed by conductivity and dye diffusion test with Black Sudan HB and Rhodamine B. Moreover, conductivity measures, in the selected dilution lines, permit to identify the effect of substituting pure water by the electrolytic Co(II) bath as the aqueous component on each microemulsion type.

3.1. Classical bicontinuous microemulsions

We select three microemulsions, described in the bibliography [28,30,31], but replacing aqueous component for cobalt (II) solution, to study the cobalt electrodeposition and the type of deposit attained from them. In order to satisfy the template capability we seek in all cases an organic medium (O) immiscible in water, with low dielectric constant (ε) to avoid the solubilization of the cobalt salt as the manner that we expect that cobalt electrodeposition will occur only from the aqueous component. The three microemulsions (SA, SB and SC) contain different oils and surfactants (Table 2).

The conductivity of the systems SA and SB as a function of the percentage of aqueous component was analyzed to determine the composition for which bicontinuous microemulsion is formed. For the analyzed dilution line ($R_{S:O}$) (Table 2), the electrical conductivity of the microemulsions (systems SA and SB) changes with increasing water content (Fig. 1). For low percentages of Co(II) aqueous solution, conductivity remains very low as corresponds to oil continuous microemulsion (w/o microemulsion); the posterior gradual increase of conductivity reveals the existence of a percolation phenomenon and the next slow increase of conductivity is