

Review

Microemulsion-Based One-Step Electrochemical Fabrication of Mesoporous Catalysts

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Abstract: Electrochemical technology has been proposed as an alternative or complementary method to classical inorganic synthesis for the fabrication of effective metallic solid catalysts. Microemulsion-based electrodeposition is a novel, fast, and one-step procedure to obtain mesoporous catalysts with extraordinarily effective areas, which can be used in heterogeneous catalysis for degradation of pollutants and clean energy production. The fabrication process involves conducting microemulsions containing ionic species (dissolved in aqueous solutions) as precursors of the metallic catalysts. The presence of nanometric droplets of organic or ionic-liquid components in the microemulsion defines the mesoporosity of the catalysts during a one-step electrodeposition process. This method also allows the fabrication of metal catalysts as supported mesoporous films or mesoporous nanowires with very high effective areas. Additionally, reactants have excellent accessibility to the overall surface of the catalysts. The different catalysts fabricated with the help of this technology have been tested for competitive degradation of organic pollutants and anodes' materials for fuel cell devices.

Keywords: mesoporous; electrodeposition; microemulsion; heterogeneous catalysis; soft-templating; alcohol electrooxidation; water decontamination

1. Introduction

The synthesis and design of mesoporous materials is one of the hottest topics being researched in the fields of materials science and heterogeneous catalysis, as they extend the horizon for developing advanced technology to meet the most relevant global challenges (e.g., energy sources, water decontamination, and others) to people, the planet and, prosperity [1–4]. According to the definition of the *International Union of Pure and Applied Chemistry* (IUPAC), mesoporous materials are nanoporous materials, ordered or disordered, with pores of diameters ranging from 2 to 50 nm [5,6]. Their potential to eliminate or at least dramatically curb pollution from industrial, chemical, and biological processes, especially for ordered mesoporous materials, is understood based on the enlarged surface area, large pore volumes, relatively low density, chemical functionalities, and permeability properties, among others [7–9]. These special characteristics, which are more relevant in well-ordered mesoporous materials, have attracted intensive research interest in the development of many new mesoporous solids since the discovery of the first hexagonally ordered MCM-41 (Mobil Composition of Matter No. 41) in 1992 by the Mobil Oil Corporation [1–11]. However, the history of ordered mesoporous materials dates back to 1969, when the synthesis of an ordered mesoporous material was first described in a patent literature. However, the extraordinary properties of the synthesized materials were not recognized due to the lack of analysis done at that time [10,11]. Over the last three decades, mesoporous materials have

been fabricated utilizing a wide variety of fabrication approaches that are based on templated synthesis by using various synthesis techniques such as sol-gel, hydrothermal, solvothermal, direct oxidation, chemical vapor deposition, physical vapor deposition, electrodeposition, sonochemical, microwave, and so on [12,13]. The intensive research conducted in terms of synthesizing and developing more efficient mesoporous materials has allowed the exploration of a wide range of chemical natures and stoichiometries (e.g., silica, aluminosilicates, carbon, metals, metals oxides, metal sulfides, metal carbides, metal nitrides, polymers, zeolites), different shapes and architectures (e.g., films, nanomaterials, composites) and structure dimensions and pore geometries (e.g., cylindrical, spherical, cage-type structures) [12–15]. However, to date, no comprehensive classification of mesoporous materials has been done on the basis of nature, shape, architecture, or fabrication approach.

Mesoporous materials are excellent candidates for catalysis because of the high number of reactions they can undergo or the number of interaction sites with the reactants due to the large surface area. Note that a large surface area does not necessarily imply an improved catalytic performance, as accessibility and surface chemistry are also relevant for catalytic purposes. By extension, nanoarchitectonics have also attracted much attention for heterogeneous catalysis, as an increase in the number of active sites with high accessibility and overcoming the issue of size restriction was encountered with bulk samples (even if these samples are nanoporous) [16–18]. The improved catalytic performances are demonstrated in nanostructured catalysts. For instance, highly mesoporous Co_3O_4 nanoflakes synthesized applying a microwave-assisted hydrothermal and low-temperature conversion method produced excellent electrochemical performance as an anode in lithium batteries and as an electrocatalyst in the oxygen evolution reaction (OER) [19]. Mesoporous Rh nanoparticles (NPs) fabricated by conducting chemical reduction on polymeric micelles resulted in an improved catalytic performance for the electro-oxidation of methanol [20], and mesoporous Pt-based nanowires (NWs), which were prepared by means of electrodeposition with enhanced catalytic performance for water decontamination [21–23] demonstrate the potential of mesoporous materials. Nanostructured materials, especially inorganic, are expected to, therefore, play an important role in fabricating competitive mesoporous catalysts. The general means to create mesoporous nanomaterials include multistep processes that inhibit their potential applicability or scalability as well. Thus, research has focused on the development of new strategies that facilitate the fabrication of competitive mesoporous materials in terms of time, scalability, and cost. In this regard, electrochemistry has opened an important door for the research of the mesoporous world in terms of both characterization and electrochemical growth of mesoporous structures [8,24,25]. In general, electrochemical methods allow the characterization of some aspects of reactivity and the properties of mesoporous materials, such as electroactive surface areas, double layer capacities, mass or charge transport processes, and so on. However, electrochemistry was recently proven as one of the most competitive and versatile ways to prepare ordered or disordered mesoporous materials, especially in the nanoscale, due to its simplicity, and the green and economic procedure. Different approaches have actually been proposed to build mesoporous structures by means of electrochemical methods such as direct electrodeposition, electrodeposition using porogen agents (pore directors) and soft and/or hard templates or electrochemical dealloying [8]. Note that the electrochemical methods allow the preparation of a wide variety of materials, such as metals, semiconductors, metals oxides, and polymers among others.

This review discusses the methods and approaches for synthesizing different types of mesoporous materials, especially metallic mesoporous materials, which can be used as efficient catalysts in several reactions. First, it summarizes the main approaches used up until now for the fabrication of mesoporous heterogeneous catalysts. Second, it highlights the possibilities and developments of the electrochemical creation of metallic mesoporous structures. In addition, an overview of microemulsion-assisted electrochemical fabrication, progress, and perspectives are extensively reviewed in this section. Third, it analyses the potential as well as perspectives of the electrochemical growth of metallic mesoporous materials for heterogeneous catalysis and covers the recent developments in this area. Finally,

the challenges to and perspectives on the anticipated developments surrounding the electrochemical synthesis of mesoporous structures and their potential in catalysis are also provided.

2. Synthesis of Mesoporous Materials

Mesoporous materials can be synthesized using various methods, such as sol-gel or hydrothermal. Different shapes, qualities, elemental compositions, architectures or pore definitions can be obtained applying various strategies; however, it is difficult to opt of an option, as each specific material, shape, or application may be more appropriate for one or another approach. Note that all the different methodologies come with advantages and disadvantages. The direct synthesis of mesoporous materials requires the use of templates or porogen agents (pore directors) to define the pore. To date, these strategies have been classified as endotemplate (soft-templating approach), exotemplate (hard-templating approach), and template-free approach (Figure 1) [1–6,25–29]. Here, we summarize the principal advantages, disadvantages, and resulting materials of each approach:

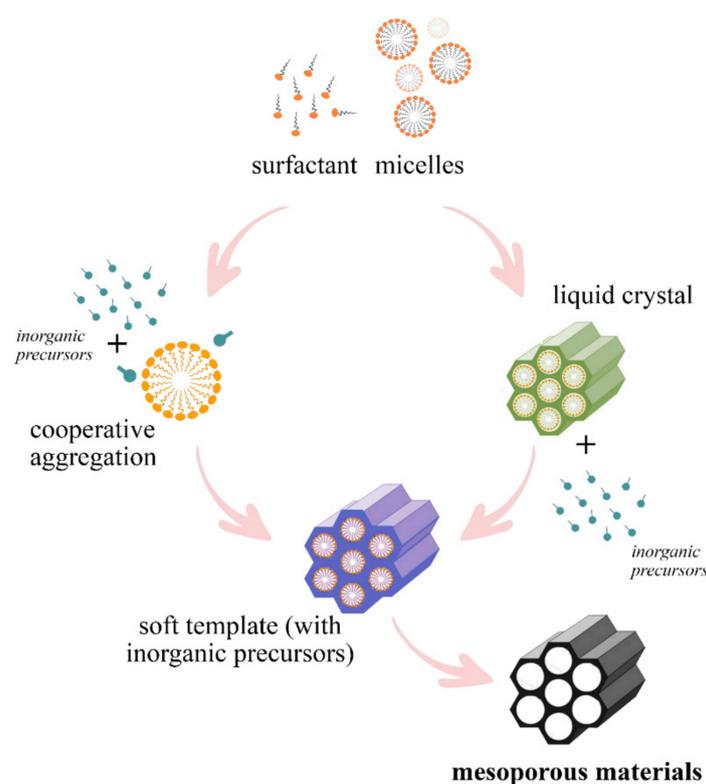


Figure 1. Schematic representation of endotemplate or soft-templating approach for synthesizing mesoporous materials. Adapted with permission from [30], Elsevier, 2017.

2.1. Endotemplate or Soft-templating Approach

To date, silica, aluminosilicates, organo-silica, carbon, metals, metal oxides, polymers, and phosphates have been synthesized by using soft-templates as porogen directors (surfactant, block copolymer, supramolecular aggregates, microemulsions) (Figure 1) [31–34]. Inorganic precursors react in a non-homogeneous medium (a solution containing one of the named porogen directors), as the manner that the shape of the final solid material (mesoporous material) follows the dynamic structure of soft-systems, which act as a nano/microreactor. Soft-systems are formed with at least two components and precursors dissolved in the aqueous component (including a wide variety of possibilities) or the non-aqueous component (e.g. evaporation-induced self-assembly). The main advantages are as follows: (i) the relatively high control over pore size and mesostructure by controlling the dynamic structure of the selected soft-system; (ii) simplicity because of soft-templating requires fewer synthetic steps than hard-templating approach, and low cost; (iii) versatility because of diverse

morphologies and tunable pore architectures can be easily obtained by means of soft-templating approach; (iv) scalability because of this approach facilitates the large-scale production of mesoporous materials; and (v) high quality (well-defined mesoporous materials have been prepared). Moreover, the main issues are as follows: (i) difficulty in eliminating surfactants or other organic species adsorbed on the surface; (ii) the use of surfactants; (iii) the high sensibility of soft-systems, which can affect the mesopores; and (iv) the relatively low crystallinity of the obtained materials [31–36].

2.2. Exotemplate, Hard-templating, or Nanocasting

It is the most robust strategy for fabricating mesoporous materials. In this synthesis, the reaction of the precursors, contained in a solution, to obtain the final solid material takes place inside the holes of a porous solid acting as a hard-template. Therefore, the synthesized material grows following the structure of the template. During the last few decades, a great variety of porous materials have been manufactured using the hard-templating approach, being the most represented in carbon, metals, metal oxides, metal sulfides, metal nitrides, metal carbides, non-oxide ceramics, and zeolites [28,37–40]. The term nanocasting is especially illustrative (Figure 2), as the process entails of filling a hard template, which defines the porosity, to obtain a negative replica of a rigid template (the initial template is removed afterwards). Note that this approach only includes the use of rigid templates. The main advantages are as follows: (i) the high quality of the obtained mesoporous materials in terms of crystallinity, pore definition, pore distribution and order; and (ii) the relatively high insensibility and independence of the mesoporous structure in relation to the reaction conditions, which allow it to work at high temperatures for example. However, this approach requires the use of preformed rigid templates, and it is a multistep and time-consuming procedure [37–40].

The combination of soft- and hard-templating approaches, also known as multiple-templating strategy, is a powerful tool for the creation of complex and hierarchical porous materials, with different properties and enhanced capability and competitiveness for several applications, being particularly useful in heterogeneous catalysis [1,5,21–23,41,42]. The multi-templating approach can be adopted for two different reasons: (i) for the generation of multiple porosity, i.e., to obtain porous materials with various well-defined porous shapes or sizes; or (ii) for the fabrication of porous materials with a desired shape (e.g., mesoporous nanowires or nanorods synthesized using a hard-template as a shape director and a soft-template as a porogen agent). Therefore, the main advantage is the possibility to obtain complex or hierarchical porous materials, but this approach also has limitations: for example, it requires multiple templates, and the multistep procedure is time consuming [1,5,21–23,41,42].

2.3. Template-Free Approach

This approach is widely implemented in the synthesis of mesoporous materials, especially in the fabrication of mesoporous nanomaterials. In this kind of synthesis, no type of permanent template is used in the solution containing the reagents. This methodology encompasses several options, many of them being specific for the manufacture of a material. However, we can generalize that in most cases it consists of the following: (i) the generation of porosity through the formation of a gas during the synthesis process (e.g., the hydrogen evolution approach); (ii) the formation of porosity by means of selective etching of a composite material or alloys (e.g., the dealloying method); and (iii) the manufacture of mesopores through aggregation of nanoscale building blocks (e.g., template-free packing method). The main advantages are as follows: (i) the simplicity of the method, which does not require any hard or soft-template; (ii) it allows creating products with high crystallinity; and (iii) it is easily scalable and processable. However, note that it is difficult to obtain ordered mesostructures. To date, this approach is extensively used to synthesize mesoporous materials of carbon, metals, metal oxides and metal sulfides [28,29,43–45].

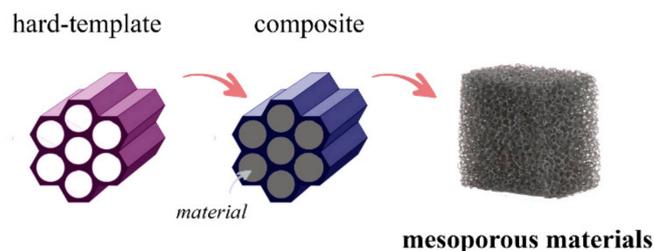


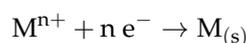
Figure 2. Schematic representation of exotemplate or hard-templating approach for synthesizing mesoporous materials.

These are the principal strategies used for synthesizing mesoporous materials. However, in the literature, you can find other classifications that include some extra approaches, such as the in-situ templating pathway or reticular chemistry guiding approach. However, these pathways can be grouped under soft-templating, hard-templating, or template-free approach [1–5]. In addition, these strategies are always an instrument for a specific synthesis route, such as sol-gel or precipitation. During the last two decades, the mesoporous domain has attracted increasing interest from electrochemistry due to their potential applications, especially in heterogeneous catalysis for energy conversion and storage. Conversely, electrochemistry has also attracted interest in mesoporous world, as it offers simple, green, and non/expensive methods to characterize the properties of mesoporous materials and synthesize simple and complex mesostructured materials through electrodeposition (or other electro-assisted possibilities, such as electro-polymerization) [8].

3. Electrochemical Synthesis of Mesoporous Materials

Electrochemical methods have been developed recently to fabricate mesoporous materials, especially from metals (and alloys) or oxides. The fundamental basis of these methods is the use of solutions containing precursors in the form of soluble species (electrolytic baths), which can be transformed into solid mesoporous materials through electrochemical reactions induced by the application of potential/current densities on adequate electrodes. The procedure requires electrodeposition processes but with the particularity that specific strategies allow the obtaining of materials on the electrode that shows mesoporosity instead of compact materials. Electrochemical synthesis has been proposed to simplify the fabrication process, by minimizing, or even restricting to one, the number of steps necessary to obtain the mesoporous materials that can be used as effective catalysts.

Electrochemical synthesis is especially useful for the fabrication of metallic materials. Pure metals or alloys have been frequently fabricated on electrode' surfaces by the reduction of the ion precursors contained in an electrolytic solution. The material is formed on the electrode through of only one operational step, comprising in the electrochemical reduction of the precursor/s:



where M^{n+} represent the ionic species that can be reduced (for example, Ni^{2+} , Ag^{+} , $PtCl_4^{2-}$ $AuCl_3^{-}$) on a substrate to form the metallic catalysts M (Ni, Ag, Pt, Au). When different species contained in the solution can be simultaneously reduced by adjusting the potential/current density, alloy catalysts (NiPt, CoAu) can be formed on the substrate. In order to get the porosity of the metallic catalyst electrodeposited, the following different strategies have been used:

3.1. Dynamic Hydrogen Bubbling Templating

Electroformation of metals/alloys from aqueous electrolytic solutions under conditions in which simultaneous hydrogen evolution takes place (very negative potential/current densities) such as the manner in which the hydrogen bubbles formed during solid formation create porous metals or alloys

(schematically illustrated in Figure 3). Therefore, gas bubbles create a dynamic bubble template on the electrode surface. This strategy is especially relevant for the synthesis of mesoporous films, but it can be also used for nanostructured materials. The pores in the electrodeposited material will approximately be like the size of the released gas bubbles [46–49]. Mesopores can be easily obtained at short distances from the electrode surface, and in general, the pore size increase as the films grow. However, in this case, the control over the pores size and their uniformity is difficult. To date, a wide range of porous, especially macroporous, metals and alloys have successfully been synthesized through hydrogen bubble template-assisted electrodeposition [46–49].

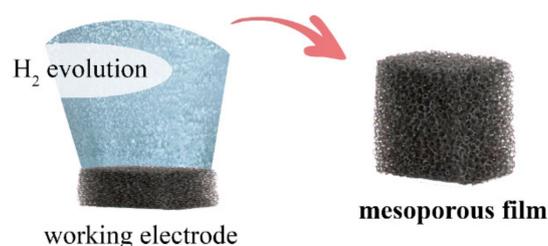


Figure 3. Schematic representation of dynamic hydrogen bubbling templating for electrochemically synthesizing microporous and mesoporous materials.

3.2. Electrodeposition and De-alloying

Electrodeposition of at least two metals from a single solution is induced to form a mixture of these metals in the solid state. After that, the selective etching of one of the components leads to a porous matrix with a highly effective area, which can be used as effective catalyst for defined reactions. Two different de-alloying processes have been distinguished (Figure 4): (i) chemical de-alloying, in which an aggressive dissolution (e.g., an acidic solution) is used to remove the less noble element; and (ii) electrochemical dealloying, in which the electrochemical etching of the less noble element is performed in a non-aggressive medium (it is also possible that the selective etching of the more noble element occurs in a system where the less noble component is passivated) [5,50–54].

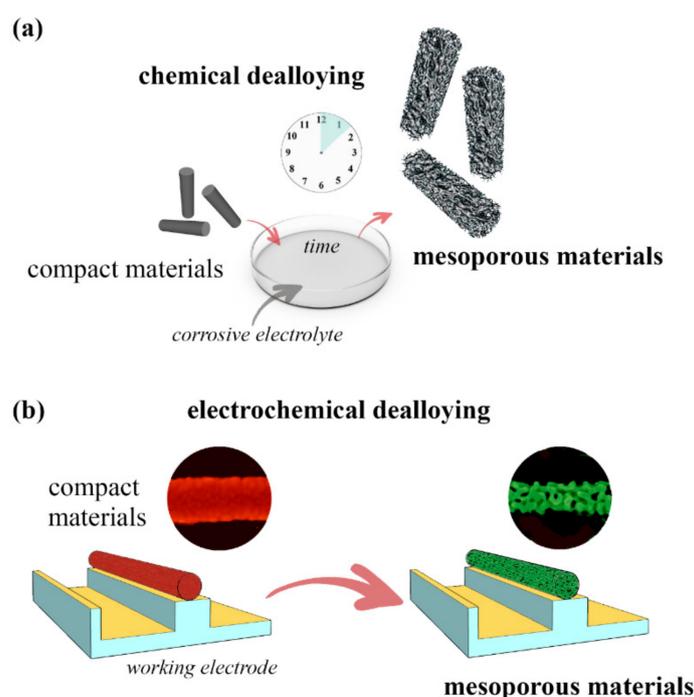


Figure 4. Schematic representation of (a) chemical and (b) electrochemical dealloying for synthesizing mesoporous materials, especially nanomaterials. Adapted with permission from [5], Elsevier, 2018.

3.3. Electrodeposition of Composites and Posterior Etching

The presence of particles (e.g., polystyrene ones) dispersed in the electrolytic solution, which could be incorporated in the metallic deposit during the reduction process, have been used to fabricate the composites with a metallic matrix and included particles. The posterior etching of the particles by means of chemical treatments leads to the synthesis of porous metals and alloys [5].

3.4. Electrodeposition in Structured Electrolytic Baths

The electrolytic medium acts as a template during the deposit formation, as the manner that its structure is practically replicated in the corresponding solid material. Three different strategies have been developed for this objective:

3.4.1. Electrodeposition in Lyotropic Liquid Crystals

Mesoporous films of metals and metal oxides are successfully electrodeposited using hexagonal or lamellar-structured lyotropic liquid crystals as a porogen directors (Figure 5a). This methodology is mainly employed for the synthesis of mesoporous films such as cobalt hydroxide films for electrochemical capacitor applications [55,56]. In a less generalized way, some researchers have also successfully electrodeposited mesoporous nanowires of manganese dioxide (Figure 5) or cobalt hydroxide using alumina membranes (shape director) and liquid crystals as porogen agents [57,58]. However, this strategy is restricted to the electrodeposition of thin films due to the high viscosity of this electrochemical medium (in general, liquids crystals are made with high concentration levels of surfactant) inhibiting their potential usage for shape-controlled electrodeposition using hard-templates.

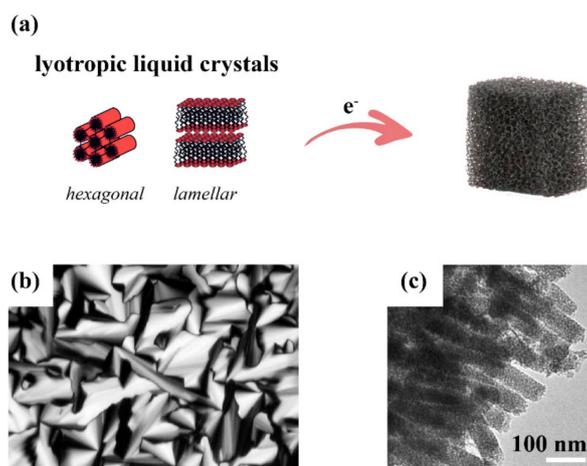


Figure 5. (a) Schematic representation of electrodeposition in hexagonal and lamellar lyotropic liquid crystals approach. (b) Polarized optical microscopy image of hexagonal (H_1) containing manganese precursors. Adapted with permission from [58], Springer Nature, 2009. (c) Transmission electron microscopy micrograph of the mesoporous H_1 -e MnO_2 electrodeposited nanowire arrays. Adapted with permission from [58], Springer Nature, 2009.

3.4.2. Electrodeposition in Micelles Systems

Micellar solutions are formed when the concentration of a surfactant exceeds a certain critical level, known as critical micellar concentration. The structures of the micelles can acquire different shapes: spherical, cylindrical, laminar, and so on. The shape and size depend on the surfactant molecules that form them as well as the physical-chemical conditions of the solution (e.g., the concentration of surfactants, pH, temperature and ionic strength). In polar solvents, such as water, the surfactants form an aggregate with the hydrophilic head regions in contact with water and the hydrophobic tail regions oriented to the micelle center. This option helps overcome the problem of high viscosity of liquid crystals and electrosynthesizes mesoporous nanowires, nanorods, or other nanoscale architectures

or shapes through the multi-templating approach. This strategy is based on the use of the spherical micelles of the surfactants (e.g., Brij 58) or the di- or tri-block copolymers (e.g., poly(ethylene glycol)-block-poly(propyleneglycol)-block-poly(ethylene glycol) (PEG-PPG-PEG) known as P-123) in water as soft-templates for the electrodeposition of mesoporous films or nanostructures (Figure 6). This approach has been demonstrated to be useful for the electrodeposition of several metals, such as Au, Pt, Pd, or Cu and alloys, such as Pt-Cu, Pt-Ru, Pt-Fe, or Cu-Ni. However, it is not a generalizable option for any material, since in order to maintain the porogen capacity, the existence of an interaction between the precursors and the surfactants or the di- or tri-block copolymers micelles is necessary. This requirement is an important limitation that inhibits their potential usage, as certain precursors are extremely expensive [42,59–63]. However, excellent and highly competitive electrocatalysts have been synthesized with this approach, such as mesoporous Pt nanorods with accessible and large effective surface areas of approximately $50 \text{ m}^2 \text{ g}^{-1}$ and excellent catalytic performance towards methanol electrooxidation [42] or mesoporous Fe–Pt thin films with enhanced electrocatalytic activity towards the hydrogen evolution reaction [63].

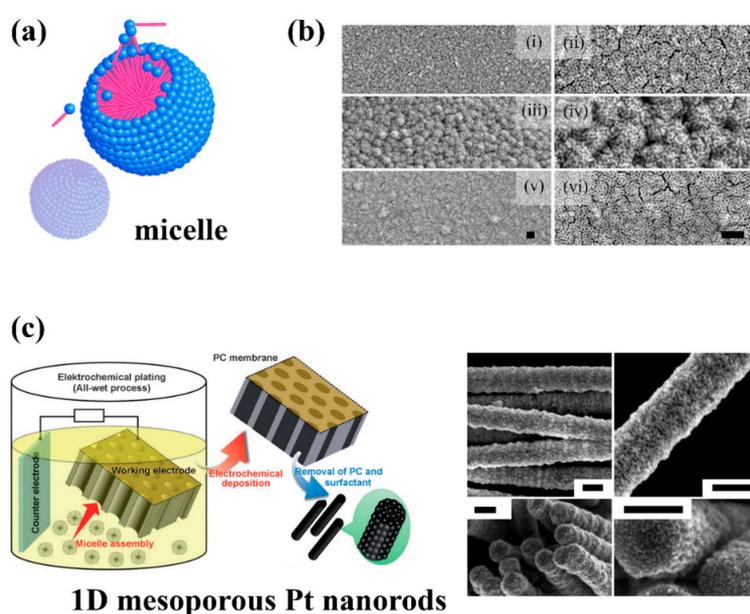


Figure 6. (a) Schematic representation of micelles. (b) Scanning electron microscopy micrographs of Fe-Pt films electrodeposited on the surfaces of Au (i, ii), Al (iii, iv) and Cu (v, vi). Scale bar: 100 nm. Adapted with permission from [42], John Wiley and Sons, 2013. (c) Schematic representation of electrochemical assembly of micelles in the confined space of a polycarbonate membrane for the electrodeposition of 1D mesoporous Pt nanorods. Transmission electron microscopy images of 1D mesoporous Pt nanorods. Scale bar: 100 nm. Adapted with permission from [63], John Wiley and Sons, 2018.

3.4.3. Microemulsion-Based Electrodeposition

Microemulsions are isotropic thermodynamically stable colloidal systems that are formed with two immiscible (or quasi-immiscible) liquids and surfactant(s). Microemulsions are single phase at the macroscopic level and a nanoheterogeneous system at the nanoscopic scale. Three different type of microemulsions can be obtained: oil-in-water (O/W microemulsions, also known as direct microemulsion), water-in-oil (W/O microemulsions, also called reverse micelles/microemulsions), where the droplets of oil or water, respectively, vary from 1 to 100 nm, or bicontinuous, where similar water and oil domains are interconnected, thereby forming a tridimensional dynamic network [64–67]. This option overcomes the limitations of the liquid crystal and micellar solution approaches, as it offers a robust and independent system as a soft-template to generate pores, i.e., the microemulsions act as nanoreactors for the electrodeposition of porous materials. In general, the electroactive species are dissolved in the aqueous solution, and the electrodeposition only occurs in the aqueous domains of

the microemulsion. Nanoparticles and macroporous and nanoporous materials have been successfully synthesized using microemulsion-based electrodeposition [64–67]. However, from an electrochemical point of view, classical microemulsions are not realistic or competitive electrochemical media due to their high ohmic resistance, which is introduced by the oil and surfactant components. In this regard, the substitution of oil dielectric component with an ionic liquid allows the main limitation of this approach to be overcome for the shape-controlled electrodeposition of nanostructured materials and for the electrosynthesis of well-defined porous nanostructures (Figure 7) [21–23,68,69].

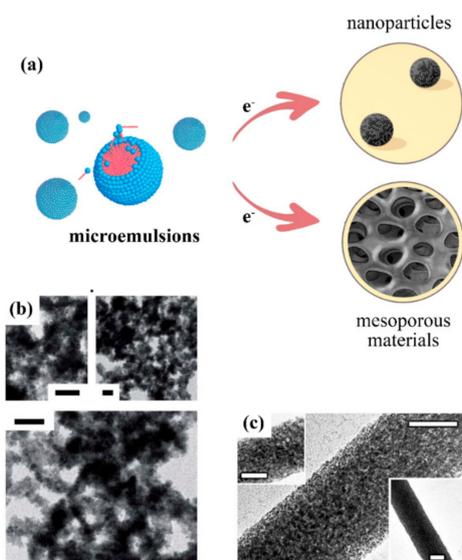


Figure 7. (a) Schematic representation of microemulsion-assisted electrodeposition. Adapted with permission from [5], Elsevier, 2018. (b) Transmission electron microscopy micrographs of CoPt₃ films electrodeposited using IL/W microemulsions. Scale bar: 10 nm. Adapted with permission from [70], The Royal Society of Chemistry, 2016. (c) Transmission electron microscopy images of mesoporous Co-Pt nanowires. Scale bar: 50 nm. Adapted with permission from [21], Elsevier, 2017.

4. Detailed Analysis of the Microemulsion-Based Electrodeposition Method

Microemulsion-based electrodeposition has been proposed as a novel, quick, and one-step procedure to obtain mesoporous metallic catalysts, with significantly effective areas, that can be used in heterogeneous catalysis for pollutant degradation and clean energy production [21–23]. The proposal was derived from initial studies, in which the possibility of using microemulsions as electrolytic media to obtain porous materials was recommended. Microemulsions are stable-structured liquid media usually composed of droplets of oil (O) or aqueous (W) components that are dispersed in aqueous or oil components to, respectively, form O/W or W/O systems [64–67]. Surfactants are necessary to stabilize the microemulsion. Some microemulsions were tested as electrolytic media, containing the W phase the electrolytes precursors of the metallic deposits. These studies demonstrated that the shape of the solid deposits was controlled by the microemulsion structure, and the nanoparticulated or porous materials, depending on the microemulsion type, was obtained on the electrode. The electrodeposition occurred from the W component and the O component defined the porosity or shape. The classical chemical wet approach for synthesizing nanoparticles by using colloidal systems, especially with reverse microemulsions, as nanoreactors and reducing agents (e.g., sodium borohydride) inspired the first studies pertaining to electrodeposition of metallic nanoparticles. The electrochemical pathway offered an alternative route that eliminates the use of aggressive reducing agents as well as introduce the possibility to directly grow supported nanoparticles on the surface of conductive electrodes, which is important for electrocatalysis, as that enables a simple recyclability and reusability of electrocatalysts. Au, Ni, Pd, Pt, Co-Ni or Pt-Ru nanoparticles have been synthesized using reverses microemulsions [64–67,71]. However, the low conductivity and high ohmic resistance leads to very

low electrodeposition rates. Note that the continuous medium in reverse microemulsions is an oil component (dielectric component). In this respect, the possibility of dissolving ionic species in the oil component and the use of ionic surfactants or reverse percolated microemulsions have been explored to enhance conductivity (i.e., to improve the efficiency of the electrodeposition process) [64,72]. However, the determining element in terms of conductivity remains the microemulsion structure.

Then researchers explored the uses of conductive microemulsions (bicontinuous or O/W structures) for the electrochemical synthesis of metallic nanoparticles, microporous films, mesoporous films, or foams [73–75]. The microemulsions were revealed to feasible soft-templates to obtain porous or discontinuous deposits. However, the difficulties of the initial proposal were as follows: (1) the selection of the proportions of oil, aqueous solution and surfactant to obtain a stable microemulsion; and (2) the low conductivity of the microemulsions due to the presence of the oil component that leads to the low rate of deposit formation. The microemulsion-based electrodeposition using classical microemulsions facilitates the obtaining of mesoporous materials (possible mesoporous catalysts) when the microemulsion comprises nanometric oil droplets dispersed in an aqueous electrolytic solution (O/W) and stabilized by surfactant. The structure of the microemulsions partially replicates in the deposit formed, where the presence of the oil droplets on the electrode surface during the deposit formation allows the electrochemical synthesis of metallic deposits containing a three-dimensional lattice of mesopores [71,72]. This procedure is defined as soft-templated electrodeposition in microemulsion. It is a one-step procedure to obtain mesoporous metallic materials, although the most significant limitation is the low rate of synthesis. To overcome this limitation, the substitution of oil with ionic liquid (IL) was proposed. This strategy allowed the use of all the microemulsion types as efficient electrochemical media. The initial studies were focused on the synthesis of nanoparticles or composites (Figure 8). For example, W/IL microemulsions allowed the synthesis of Co-Pt nanoparticles with a tunable size, composition, and magnetic properties by modifying the composition of the aqueous component and the water droplet size [68] and the synthesis of Au nanoparticles with excellent catalytic performance towards glycerol oxidation [76] or Ni/Co-Pt composites [69]. The conductivity of these new microemulsions as electrolytic media is significantly greater than that of the classical ones, implying a clearly enhanced electrochemical synthesis rate.

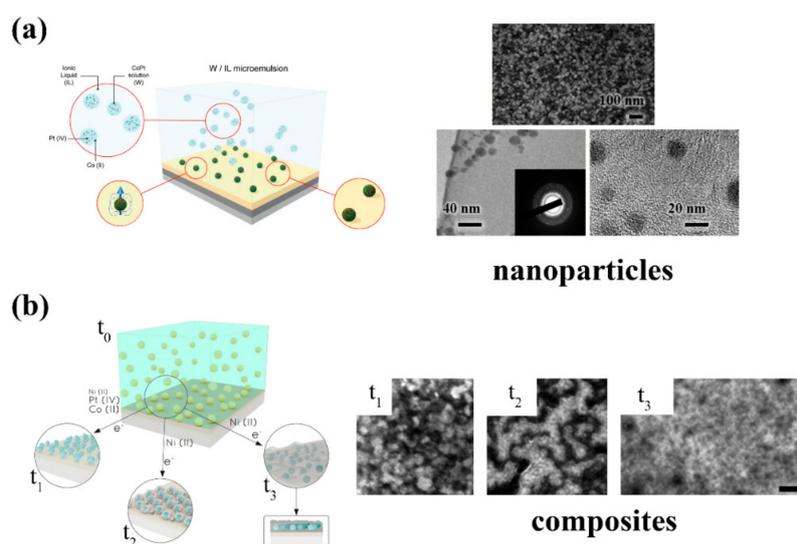


Figure 8. (a) Schematic representation of electrochemical synthesis of magnetic CoPt nanoparticles in W/IL microemulsions. Field-emission electron scanning micrograph (above) and transmission electron micrographs (below) of CoPt nanoparticles. Adapted with permission from [68], American Chemical Society, 2014. (b) Schematic representation of the proposed electrochemical synthesis of composites using ionic liquid microemulsions and FE-SEM micrographs of deposits at different times. Bar scale: 100 nm. Adapted with permission from [69], Elsevier, 2014.

More recently, microemulsion-assisted electrodeposition was explored for the synthesis of mesoporous materials, which can act as heterogeneous catalysts. The first studies were based on the use of IL/W microemulsions to synthesize mesoporous films and catalyze the oxidation of methanol in alkaline and acidic media, thus obtaining effective surface areas that are significantly higher than those obtained when films were synthesized in aqueous or micellar solutions (Figure 7b) [70]. The metal or alloy deposits from only the aqueous component of the microemulsion and the droplets of the IL of a few nanometers define the mesoporosity of the metals or alloys. To compare the potential of the microemulsion-based electrodeposition with the micellar solution approach, Co- and Pt-rich films have been synthesized in aqueous solutions, micellar solutions, and IL/W microemulsions. The FE-SEM micrographs helped to note that compact films, interconnected nanopowdered deposits, and mesoporous films can be obtained when the aqueous solutions, micellar solutions, or IL/W microemulsions were used respectively as electrochemical media. The various effective electrochemical surface area (ECSA) for CoPt₃ deposits for aqueous solution (3 m² g⁻¹), micellar solution (43 m² g⁻¹) and IL/W microemulsion (66 m² g⁻¹) confirmed the formation of a tridimensional mesoporous sponge structure when ionic liquid microemulsions were used. Moreover, the structure of the microemulsion, which does not require an interaction between the surfactant/micelle and the precursor (as in the case of the micelle solutions method), configures this synthesis path as a more robust route than other soft-templating electrochemical approaches for synthesizing mesoporous films [70].

Once we demonstrated the possibilities of the electrochemical method to obtain mesoporous metallic materials with excellent effective area and accessibility of the reactants, the electrochemical proposal has been refined to obtain mesoporous materials in the micro/nanoscale, in the form of nanorods or nanowires, to dramatically increase the global surface effectiveness for catalysis. The catalysts will present, in this case, a very large effective area impacted by both the aspect ratio of the nanorods/nanowires and the mesoporosity of the material. The first studies in this line were based on the use of IL/W microemulsions to manufacture nanorods with diameters of 200 nm (Figure 9), using polycarbonate membranes (hard-template) with nanometric channels to define the nanorods' shape during the electrodeposition. It should be noted that the obtained nanorods exhibited a relatively low-defined porosity. According to these previous results, the porogen capability is not clearly demonstrated, although the resulting nanorods exhibited improved catalytic performance towards methanol oxidation when compared to the more compact type obtained in the aqueous solution. Then, the experimental conditions were evaluated, especially the differences with respect to the synthesis of the mesoporous films, which revealed two important experimental effects related to the following: (i) the previous immersion of polycarbonate membranes over 24 h (this practical was common for the synthesis of nanorods in aqueous media to favor the entry of the electrolytic solution into the pores of the membrane) seems to not be optimal in the microemulsion media [77]. It is possible that this time can promote a sufficiently significant diffusion of the electroactive species to the ionic liquid domains, which can allow deposition from both the aqueous domains and from the ionic liquid droplets and, therefore, inhibits the formation of pores; and (ii) the stirring conditions (argon bubbling) in the bulk of the media to favoring the process.

To consolidate the microemulsion-based electrodeposition approach to obtain mesoporous nanorods, the possibility of using other types of microemulsions, which may have greater ability to define pores, was also explored. The use of bicontinuous, W/IL, and different IL/W microemulsions was analyzed. Moreover, the previous time taken to ensure that the nanochannel of hard template was filled was reduced to 4 h, and the conditions of stirring in the bulk of the media were maintained. Semi-agitation (argon bubbling near the surface of hard-template) is fundamental, because when W/IL microemulsions are used in non-agitation conditions, it is observed that the current density decays asymptotically to zero after several minutes, as a result of the consumption of the electroactive species dissolved in the water droplets, which were directly in contact with the surface of the electrode. In contrast, when this semi-stirring condition is applied to the proximity of the membrane, it is observed that the current density decays much more slowly, which translates to a higher growth rate

of the nanorods. However, the semi-stirring conditions in the bulk of the medium is an important element of the confined structure's distortion in the microemulsion. The semi-stirring condition is, therefore, necessary in the case of W/IL microemulsions, but it could be one of the main reasons for low definition in the case of IL/W microemulsions. In these conditions, it is found that all microemulsion systems lead to nanoporous structures with different morphologies, but only the W/IL microemulsions help obtain well-defined mesoporous nanowires (Figure 10a). In all the cases, the nanoporous Co-Pt nanowires presented improved the catalytic performance of the electrolysis of methanol due to the large effective surface areas [78,79].

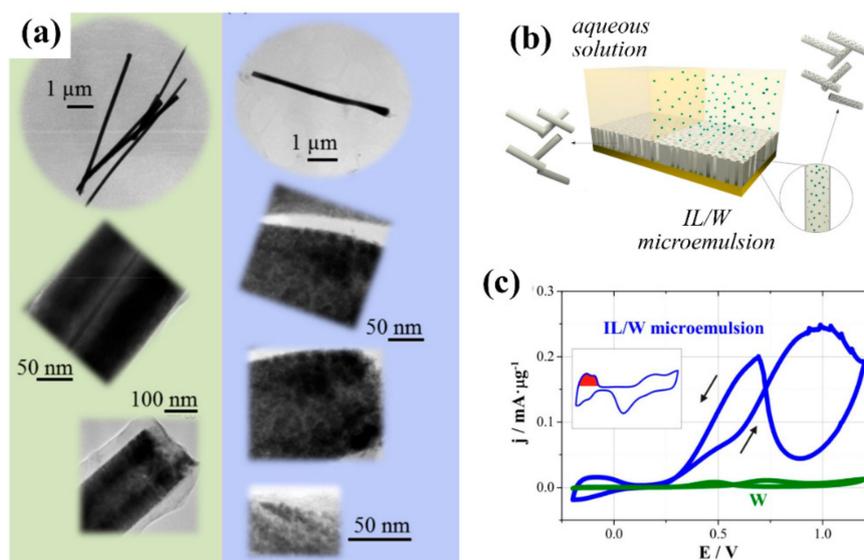


Figure 9. (a) Transmission electron microscopy micrographs of CoPt nanowires electrochemically prepared in aqueous solution (left) and IL/W microemulsion (right) systems on Au sputtered 20 μm -thick polycarbonate membranes with 200 nm pore diameters size after circulating the same deposition charge. (b) Schematic representation of electrochemical synthesis of mesoporous and non-mesoporous CoPt nanowires on polycarbonate membranes coated with gold layer. (c) Test of the fabricated nanowires as catalysts for fuel cells application: Cyclic voltammograms for methanol oxidation on CoPt nanowires obtained from W and IL/W systems in argon saturated 1.0 M CH_3OH + 0.5 M H_2SO_4 solution at 100 mV s^{-1} . Adapted with permission from [77], MDPI, 2014.

To verify the formation of mesoporous nanowires independently on the aqueous bath composition, mesoporous nanowires of Co-Ni were also electrodeposited utilizing W/IL microemulsions (the test of the methodology with other electrolytic baths as components of the microemulsions). In addition, to reduce the cost of electrocatalysts, core@shell mesoporous nanowires, through the formation of a Pt shell over the entire area of Co-Ni nanowires by galvanic displacement, was also explored. Therefore, W/IL microemulsions allowed the electrodeposition of mesoporous nanowires of Co-Pt ($228 \text{ m}^2 \text{ g}^{-1}$) and Co-Ni@Pt ($224 \text{ m}^2 \text{ g}^{-1}$) with higher effective electrochemical surface areas - significantly higher than those obtained through the micelle template approach (mesoporous Pt nanowires with areas as high as $53 \text{ m}^2 \text{ g}^{-1}$) [79]. Then, ionic liquid microemulsions allowed the synthesis of tridimensional networks of interconnected mesopores (not only surface porosity), which exhibited a catalytic activity toward methanol oxidation that was three times higher than that obtained with mesoporous Pt nanowires synthesized by micellar approach. Therefore, W/IL microemulsion-assisted electrodeposition allows the synthesis of metals, alloys (magnetic electrocatalysts) and core@shell structures, which are characterized by excellent catalytic activity for the oxidation of alcohols in acidic and alkaline media, exceptional stability and low poisoning of the catalyst (Figure 10b). However, this methodology is constrained due to the low deposition rate, which is approximately 50 times lower than that in micellar solution media.

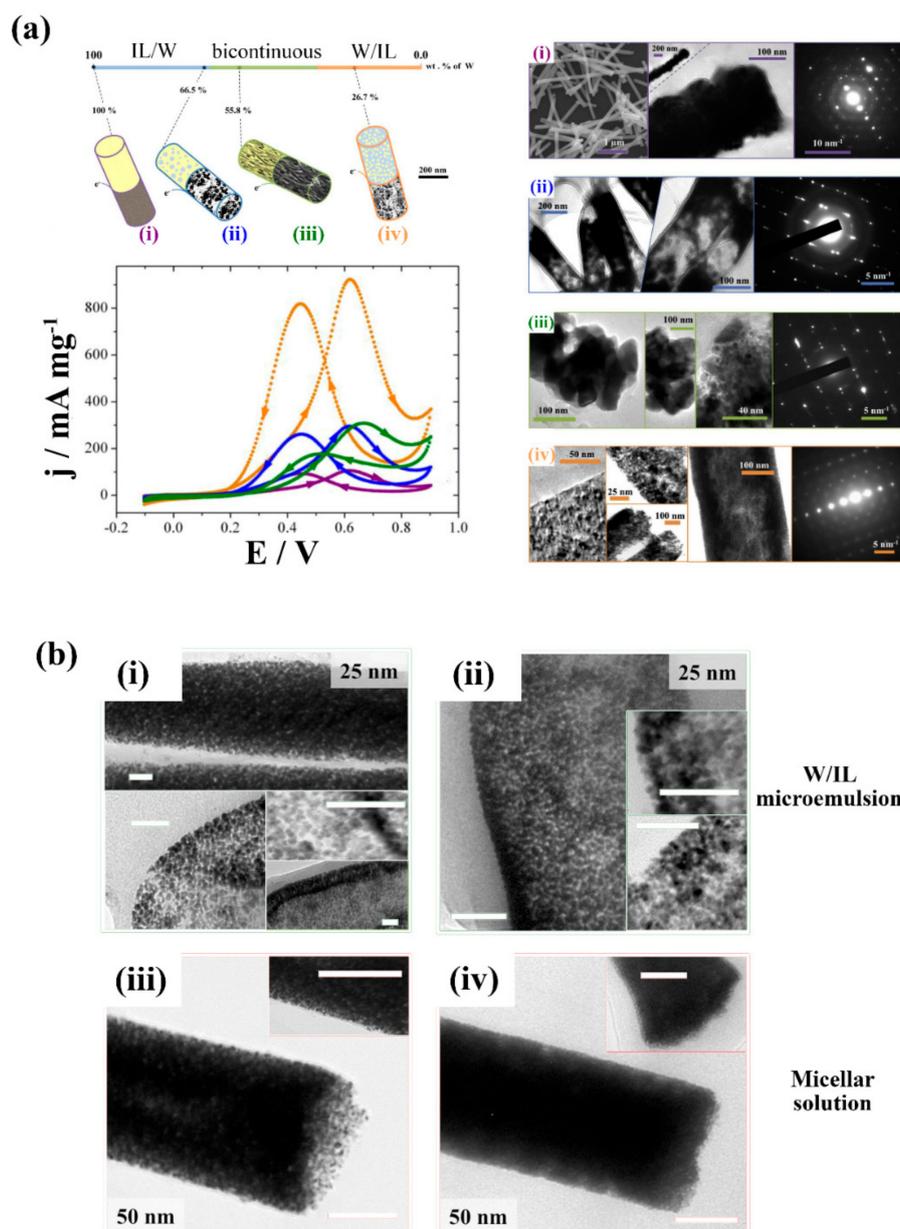


Figure 10. (a) Schematic representation of the different selected systems (W and IL/W, bicontinuous or W/IL microemulsions) to electrochemical fabrication of compact and porous nanorods. Secondary electron microscopy, high resolution transmission electron microscopy and selected area electron diffraction images of (i) W, (ii) IL/W, (iii) bicontinuous and (iv) W/IL nanorods (right). Test of the fabricated nanowires as catalysts for fuel cells application: Cyclic voltammograms (recorded at 50 mV s^{-1}) in $0.5 \text{ M H}_2\text{SO}_4$ containing 1 M methanol (left). Adapted with permission from [78], Elsevier, 2015. (b) Transmission electron micrographs of (i,iii) Pt and (ii,iv) CoNi@Pt nanorods prepared in (i,ii) water-in-ionic liquid microemulsion (W/IL) and micellar solution (iii, iv). Adapted with permission from [79], Elsevier, 2015.

Finally, for the development and consolidation of this new electrochemical pathway and the synthesis of mesoporous nanomaterials as well as to solve the limitations relevant to the low electrodeposition rate of W/IL microemulsions (lower than other proposals that can be found in the literature) the use of IL/W microemulsions was re-explored. In this respect, non-stirring conditions have been explored as the previous results proved that this parameter distorts the structure of microemulsion inside the confined space of the nanochannel membrane. Pt and Co-Pt nanowires

of 100 nm in diameter and a good definition of pores as well as excellent catalytic properties for the oxidation of ethanol in alkaline medium was obtained. Therefore, IL/W microemulsions, under the condition of non-agitation, have proved to be effective electrochemical media for the synthesis of mesoporous nanomaterials with well-defined pores and high deposition rates (however, slightly lower than that of aqueous media but acceptable). The control of the structure of the microemulsion (size of the ionic liquid droplets) permits defining the size of the pores of thin films or nanowires (even in the case of nanowires of 25 nanometers in diameter) (Figure 7). Note that the possibility to electrodeposit nanowires of 25 nm diameter demonstrate that IL/W also maintains the porogen capability when the size of the nanochannel is very similar to the hydrodynamic diameter of the microemulsions droplets [21–23,80]. Therefore, microemulsion-assisted electrodeposition as a soft-templating approach for the synthesis of mesoporous nanostructures is a simple, economical and sustainable synthesis procedure that facilitates the synthesis of new electrocatalysts for the commercial exploitation of methanol fuel cells or direct ethanol with high catalytic activity. Table 1 summarizes the advantages, disadvantages and experimental conditions that must be considered while carrying out microemulsion-assisted electrodeposition to manufacture mesoporous nanowires.

Microemulsion-assisted electrodeposition using IL/W microemulsions allowed the synthesis of magnetic mesoporous nanocatalysts of the following:

Pt, Co-Pt, Co-Ni, Co-Ni@Pt, Co-Ni@Au as excellent electrocatalysts for alcohol electrooxidation in acidic and alkaline media with very high electrochemically active surface areas (around $240 \text{ m}^2 \text{ g}^{-1}$) due to the accessible three-dimensional interconnected network formed by the mesopores. Mesoporous photocatalysts exhibited enhanced catalytic performance with significant improvements over the performance of the compact nanowires/nanorods or commercial PtRu nanoparticles. These structures provided an oxidation current/mass ratio that is significantly higher than other mesoporous nanowires prepared by the micellar solution approach and the onset potential of the ethanol or methanol electrooxidation is clearly advanced (Figure 11) [78–80].

The CoPt, CoNi, and CoNi@Pt core@shell mesoporous nanowires also demonstrated excellent catalytic activity in generating hydrogen and as magnetic nanocleaners of persistent organic pollutants in contaminated water. In particular, by employing sodium borohydride, the mesoporous nanowires catalyzed the reduction of organic compounds such as 4-nitrophenol, methylene blue, and rhodamine B, in turn, enhanced hydrogen formation [21–23]. Moreover, the magnetic character of the nanowires allowed their rotation with the application of rotating magnetic fields, as represented in Figure 12 for CoPt mesoporous nanowires (Figure 12b), which enhanced the destruction of organic pollutants (Figure 12c) and the generation of hydrogen (Figure 12d) [21]. Synthesizing magnetic mesoporous nanowires could be crucial to fabricating heterogeneous catalysts with highly active surface areas accessible to pollutants and that can act as nanostirrers to improve the local flow of material towards active sites of the catalyst. Moreover, the magnetic character of the nanowires allows easy recyclability and reusability. By facilitating the control of the velocity and directionality in relation to contaminated solution following the application of controlled magnetic fields, synthesized magnetic mesoporous nanowires can be also used as nanocleaners of persistent organic pollutants [23]. Figure 12e illustrates how the reduction in organic pollutants can enhance hydrogen generation with borohydride when the catalyst (i.e., 25-nm mesoporous nanowires) is magnetically stirred. The figure also shows the degradation of different pollutants when the nanowire catalysts advance into test channels.

Table 1. Experimental conditions, advantages and disadvantages of W/IL and IL/W microemulsions for microemulsion-assisted electrodeposition of mesoporous nanowires.

Microemulsion Type	Experimental Conditions	Advantages	Disadvantages
W/IL	It requires semi-stirring conditions during the electrodeposition process. It is important to fill the nanochannels of the hard template prior to starting the electrodeposition.	Porogen activity does not depend on the concentration of the aqueous component. The pore size can be controlled by modifying the droplet size. Well-defined mesopores are obtained.	Deposition rates are low. Viscosity is relatively high. Electrodeposition efficiency is low. It is a temperature-dependent procedure.
IL/W	Non-stirring (silent) conditions are required. No previous immersion of the hard template in the electrochemical media is required.	Porogen activity does not depend on the concentration of the aqueous component. Pore size can be controlled by modifying the droplet size. High deposition rate is observed. It has relatively low viscosity. High electrodeposition efficiency (similar than in aqueous solution) is noted. Well-defined mesopores are obtained.	It is a temperature-dependent procedure.

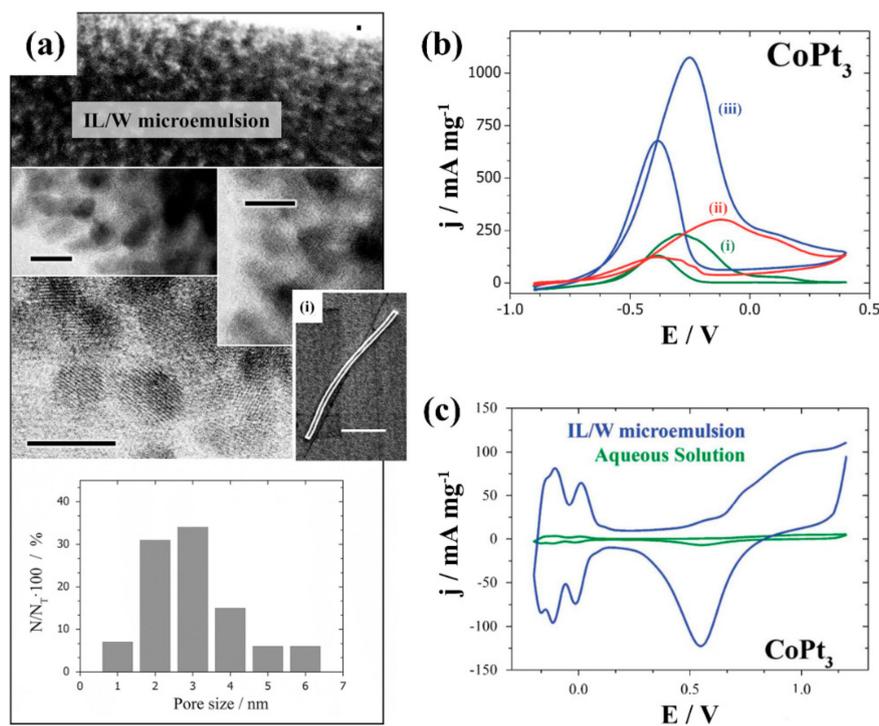


Figure 11. (a) Transmission electron microscopy, (i) field-emission scanning micrographs and pore size distribution of mesoporous CoPt₃ nanorods prepared in IL/W microemulsions. Scale bars: 5 nm (black) or 1 μm (white). (b) Cyclic voltammograms at 50 mV s^{-1} of CoPt₃ nanorods prepared using (i) aqueous solution, (ii) micellar solution and (iii) IL/W microemulsion. (c) Cyclic voltammetry (first cycle) of CoPt₃ nanorods in 0.5 M H₂SO₄ solution at room temperature at a scan rate of 100 mV s^{-1} . This experiment allows the determination of the electrochemical active surface areas (ECSAs) of both catalysts. Adapted with permission from [80], The Royal Society of Chemistry, 2016.

Thus, microemulsion-assisted electrodeposition is an interesting soft-templating approach that can be adopted for the manufacture of competitive new heterogeneous catalysts for energy and water decontamination applications.

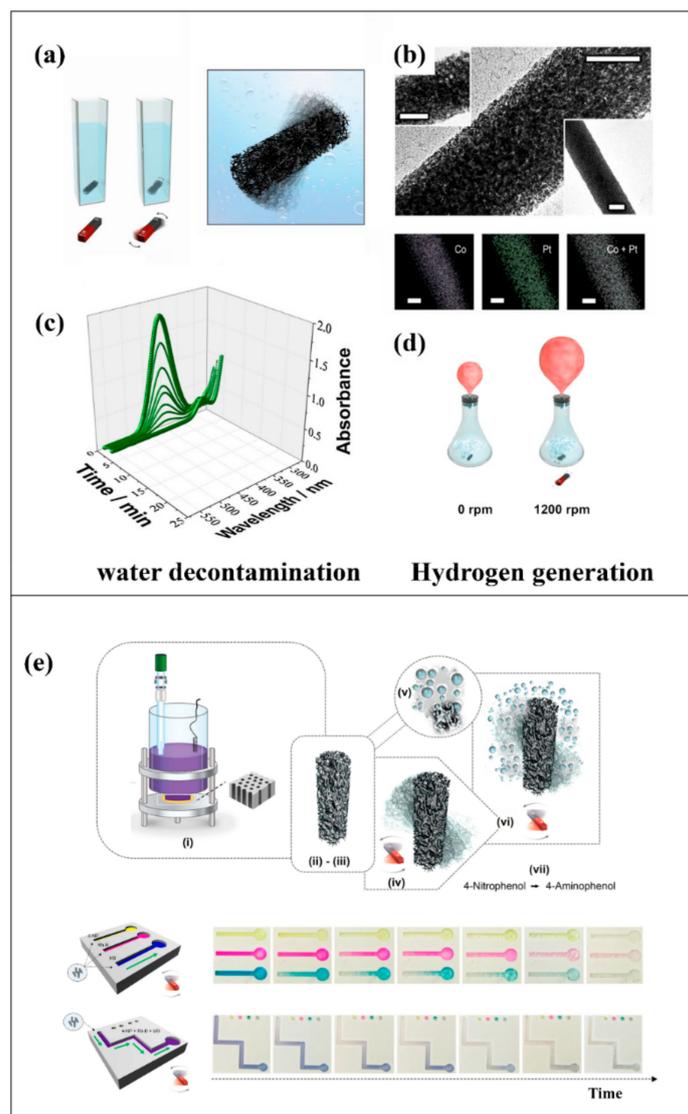


Figure 12. (a) Schematic representation of the magnetically-actuated metallic mesoporous nanowires for enhanced heterogeneous catalysis. Adapted with permission from [21], Elsevier, 2017. (b) High resolution transmission electron microscopy micrographs and elemental mapping of mesoporous nanowires. Scale bar: 50 nm. Adapted with permission from [21], Elsevier, 2017. (c) Time-dependent UV-visible spectra of methylene blue catalyzed reduction with borohydride. Adapted with permission from [21], Elsevier, 2017. (d) Schematic representation of hydrogen generation. Adapted with permission from [21], Elsevier, 2017. (e) Schematic representation of the magnetically-actuated and controlled mesoporous nanowires for water decontamination. Adapted with permission from [23], American Chemical Society., 2017.

5. Conclusions

In this review, we have presented the potential of the defined electrochemical strategies to fabricate mesoporous metal and alloy structures that are useful as effective heterogeneous catalysts for reactions involved in clean energy production or degradation of organic pollutants in water remediation. Electrochemical fabrication is a competitive approach for producing mesoporous metal or oxides catalysts because by means of a one-step procedure, it is possible to directly transform the precursors in a solution to a solid catalyst, through electrodeposition process. In this approach, the electrodeposited solid must be a mesoporous structure as a consequence of the presence of a porogen-inducer agent that is active during the electrodeposition process. One or more electroactive species are reduced

by the application of potential/current densities. Therefore, the electrochemical method is a cheap and simple synthesis procedure that further substitutes aggressive reducing agents by electricity to transform ions in solution to the solid mesoporous catalysts.

Between the different electrochemical proposals, one of the most effective is the microemulsion-based one-step electrochemical fabrication. In the optimized approach, a microemulsion containing droplets of an ionic liquid dispersed in an aqueous solution containing the ions precursors is used as an electrolytic medium to electrodeposit metals, oxides, or alloys. The electrodeposition occurs only from aqueous component of the microemulsion and the droplets define the lattice of the mesopores of the electrodeposited catalysts. This three-dimensional lattice of the mesopores allows the reactant access to the catalyst in a heterogeneous catalysis process, with an extraordinary effective area for the reaction.

Microemulsion-based electro-fabrication presents excellent results in the fabrication of catalysts in the form of nanorods/nanowires, through a double-templated electrodeposition process: a hard-template (membrane with nanometric channels) is used to synthesize the deposit in the form of nanorods/nanowires, and a soft-template (the microemulsion of ionic-liquid in an aqueous solution) is employed as electrolytic medium to obtain the mesoporous nanorods/nanowires. These porous nanostructures (nanowires of 200, 100, or even 25 nm of diameter) of metals such as Pt, Pt and Ni alloys, or metal@Pt and metal@Au have been demonstrated to be excellent catalysts for the electro-oxidation of alcohols in fuel cell reactions, possessing extraordinary electrochemical surface area. When the core metal or alloy is magnetic, the catalyst can be manipulated and recycled. Furthermore, similar mesoporous nanorods with magnetic characteristics have been proposed as magnetic nanocleaners, which can be concentrated in defined positions for the destruction of organic pollutants. The effectiveness of microemulsion-assisted electrodeposition presents the possibility of fabricating new mesoporous films or nanorods of metals, oxides, or alloys of adequate nature to be utilized as catalysts in different reactions of heterogeneous catalysis. It is possible to combine metallic surfaces with vector cores (electric, magnetic) to control the movement and recyclability of the highly mesoporous nanometric catalysts.

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