Mesoporous silicon oxide films and their uses as templates in obtaining nanostructured conductive polymers

R Salgado¹, G C Arteaga² and J M Arias³
¹Corporación Universitaria del Caribe, Sincelejo, Colombia
²Universidad del Sinú, Montería, Colombia
³Institución Educativa Marceliano Polo, Cereté, Colombia

E-mail: rodrigo.salgado@cecar.edu.co; rdsalgad@uc.cl

Abstract. Obtaining conductive polymers (CPs) for the manufacture of OLEDs, solar cells, electrochromic devices, sensors, etc., has been possible through the use of electrochemical techniques that allow obtaining films of controlled thickness with positive results in different applications. Current trends point towards the manufacture of nanomaterials, and therefore it is necessary to develop methods that allow obtaining CPs with nanostructured morphology. This is possible by using a porous template to allow the growth of the polymeric materials. However, prior and subsequent treatments are required to separate the material from the template so that it can be evaluated in the applications mentioned above. This is why mesoporous silicon oxide films (template) are essential for the synthesis of nanostructured polymers since both the template and the polymer are obtained on the electrode surface, and therefore it is not necessary to separate the material from the template. Thus, the material can be evaluated directly in the applications mentioned above. The dimensions of the resulting nanostructures will depend on the power, time and technique used for electropolymerization as well as the monomer and the surfactant of the mesoporous film.

1. Introduction
Recently, nanostructured materials from conductive polymers have attracted special attention from disciplines related to science and engineering due to a number of factors such as their large surface area, transport properties, chemical specificity, low cost, ease of processing and large-scale production, which makes them the main candidates to replace materials in the production of micro/nano devices, as well as chemical and biological sensors.

These new morphologies not only reduce the dimensions of the polymeric materials but also contribute to improving their properties for applications such as the manufacture of OLEDs, solar cells, electrochromic devices, sensors, etc., which makes it necessary to implement new synthesis methods to develop nanostructures with even smaller dimensions. Some synthesis methods, including Hard Template and Soft Template, have been developed to obtain nanostructured CPs.

1.1. Hard template
Martin was the first explored this method as a way to produce conductive polymer nanofibers, nanotubes and nanowires [1]. This technique is based on the synthesis of the desired material within the pores or channels of a membrane that acts as a template or reactor so that the desired material grows in each pore of the membrane and then the template is removed resulting in materials with a morphology such as that of nanostructures. Commercial Anodic Aluminum Oxide (AAO) and polycarbonate (PC) membranes...
are usually used as templates. Porous AAO membranes are generated electrochemically from metal aluminum, and their pores are arranged in the form of a regular hexagonal network, with a density of $10^{11}$ pores/cm$^2$ [2]. PC membranes are manufactured using track-etching technology. These membranes have surfaces with pores up to 10nm in diameter and a density of about $10^9$ pores/cm$^2$ [3]. However, although they are commercially available, these membranes have a limited number of pore diameters. This technique has the following advantages:

A. It is a widely used method to make metallic nanomaterials, as well as semiconductors and conductive polymers.

B. The diameter of the nanostructures is controlled by the pore size of the membrane used as template, while the length is adjusted by changing the polymerization time. This method allows making nanotubes and nanowires with different diameters.

C. Nanostructures can be generated either chemically or electrochemically by this method, although the chemical process makes it difficult to separate the nanostructured material from the impurities. The membrane is immersed directly in the solution containing the oxidant and the monomer, and then polymerization within the pores of the membrane is generated using a suitable disturbance.

D. Electrochemical deposition is a cleaner technique. This method involves the use of a metallic film that covers the surface of the membrane to carry out the electrochemical polymerization within the membrane pores.

A large number of nanostructures have been developed using both chemical and electrochemical methods. However, the complex membrane production processes, in addition to the subsequent template removal treatments, which can deform or even destroy nanostructures, sometimes limit their use.

1.2. Soft template

Also called self-assembly, it is a simple, powerful technique for the manufacture of nanostructured conductive polymers that uses surfactant-based micelles to confine the polymerization of the conductive polymer in nanometric dimensions. This method is based on the selective control of non-covalent interactions such as hydrogen bonds and Van der Waals forces, which are the driving forces responsible for self-assembly. There are different types of processes to produce conductive polymer nanostructures using self-assembly including the surfactant as soft-template, which stands out as one of the most widely used methods.

1.2.1. Surfactant as soft-template. Surfactants are molecules that form thermodynamically stable aggregates with intrinsically nanoscale dimensions both regarding dissolution and interfaces. The morphology of the surfactant aggregates can be spherical, cylindrical, or a flat bilayer, depending on the type of surfactant used. [4,5]. This technique has been used to make nanowires, nanospheres, and nanotubes. Compared to techniques such as the hard template, this is a relatively simple, low-cost method. However, it also has disadvantages due to the difficulty in separating the desired product.

On the other hand, electrochemical methods have been used to make CP films of controlled thickness according to the electrochemical technique used (potential cyclic voltammetry, fixed) with positive results in different applications as those mentioned above (OLEDs, solar cells, electrochromic devices, sensors, etc.). Chemical and electrochemical methods have also been used. Although good results have been obtained with current CP materials, new studies aim to improve these materials and produce miniaturized device components to manufacture polymers in the form of nanostructures such as nanofibers, nanotubes, and nanowires. Compared to conventional polymer films these materials exhibit improvements in their conductive properties, as well as a higher value in the surface/volume ratio and a decrease in impedance at the electrode-electrolyte interface. Other methods have been evaluated to avoid complex separation processes when using Hard Template and Soft Template techniques. Hence the importance of mesoporous silicon oxide films, which develop on the surface of the working electrode, thus allowing to evaluate and compare their usefulness in different applications concerning conventional polymers.
In recent years, the electrochemical community has become interested in developing techniques for modifying electrodes using oxide films with nanostructured surfaces [5-7]. This process can be carried out through some techniques [5,8-10] especially those using cationic surfactants capable of accumulating on the electrode surface in the form of semi-micelles due to electrostatic attraction [11-13].

The manufacture of oxide films requires the use of an acid solution composed of cationic surfactant and metal salts capable of forming insoluble hydroxides in basic medium. The application of a cathodic potential to electrolyze water and generate OH⁻ species on the electrode surface will result in the precipitation of the metal oxide in the vicinity of the electrode, which is molded by the physical space occupied by the surfactant semi-micelle [14]. This process is known as surfactant-assisted polycrystalline and allows to generate nanoscale metal oxide films [8,15-17]. The channels are formed perpendicular to the electrode and will grow as the potential step is maintained. The pore diameter will depend exclusively on the radius of the semi-micelle, that is, the type of surfactant used.

Recent efforts in this field have resulted in a significant improvement in electrosynthesis of silica or silicon oxide (SiO₂), films by using a cationic surfactant (cetyltrimethylammonium bromide) as a template [18-20]. The polycrystalline of silica follows the same principle as that of metal oxides. Since silica is practically inert to chemical attacks and solvents and is also resistant to high temperatures, electrodes modified with these nanoporous films can be used for other purposes. On the other hand, factors such as mass transfer and electrode activity are not affected by the presence of this material [21]. In 2007, Walcarius et al. [18] were able to produce nanoporous silica films of 2.9nm pore diameter on various electrode surfaces. This type of processes has also been used in analytical electrochemistry [22,23].

Modified electrodes could also be used to form deposits whose morphology is determined by the shape of the nanoporous film, that is, nanowires. This type of structures exhibits very good permeability to oxidation-reduction or redox reactions of electrochemical, nonpolar and charged molecules that have a known response (ferrocene, potassium ferricyanide, etc.).

2. Experimental
The aqueous silica precursor solution was prepared using 5.0×10⁻²molL⁻¹KNO₃ and 5.0×10⁻⁴molL⁻¹HCl. 1 volume of ethanol was added to the solution to form a 50:50 mixture. A 10.0mL aliquot of the solution was taken and poured into a distilling flask together with 0.4187g cetyltrimethylammonium bromide (CTAB) and 760μL tetraethyl-orthosilicate (TEOS). A magnetic stirrer was used to stir the solution constantly for 2.5 hours so that it can be used in electrochemical experiments.

Using a potentiostatic method the silicon oxide film was placed on different electrode types including platinum (Pt) electrodes by applying -0.9V potential for 5s [18,24-26]; conductive glass (CG) electrodes by applying -1.1V potential for 5s [27]; and stainless steel (SS) electrodes, whose optimum potential is currently being analyzed.

3. Results
Platinum, CG and SS electrodes were deposited in a precursor solution. Cyclic voltammetry (CV) was used to carry out potential scanning ranging from the relaxation potential to more negative potentials thus obtaining voltammetric profiles as shown in Figure 1.

Figure 1 shows a decrease in the current after completion of each cycle, which is consistent with the deposition processes described for low conductive materials. Once the range of potentials in which the template-assisted electrodeposition begins is defined (around -700mV to -1200mV) it is necessary to find out the potential and time required for the formation of the template, which ranges from -700mV to -1200mV, and 5 to 10s, respectively. This procedure is carried out through the application of fixed potential (EP). The application of cathodic potential promotes the formation of hydroxyl ions which are necessary to catalyze the polycrystalline of the precursors in the silica film. Once the film was obtained, the electrode is washed to prevent the reaction from continuing and then dried in an oven at 130°C for at least 12 hours.
Experiments were carried out to demonstrate the permeability of the film due to ion transport. For this purpose, electrodes are immersed in a solution of ferrocene (FeCe) in acetonitrile (ACN). Figure 2 compares the voltammetric responses. It also shows significant reduction of the FeCe current in the modified electrodes.

Permeability can be improved by stirring the electrodes in an ethanol-HCl solution which solubilizes CTAB [18] and allows better ion transport through the resulting film. The appropriate potentials for template generation are as follows: -0.9V for Pt, and -1.1V for CG. This is because mesoporous silicon oxide films exhibit higher permeability in FeCe tests by using these potentials, which suggests that nanostructures can be generated within these films. Tests with template-modified Pt electrodes resulted in the formation of PEDOT [24] and Polythiophene [25] in the form of nanowires, which were later used as specific dopamine (DA) sensors and in electrocatalysis of formic acid [24-26]. Tests with CG electrodes modified with silicon oxide films resulted in polythiophene nanowires [27]. Tests with PEDOT, a conductive polymer with recognized properties, are currently taking place. Experiments are being carried out with SS electrodes to obtain the potential needed for the formation of silicon oxide films in the electrode surface.

Figure 1. Voltammetry profile of precursor (a) SS|solution, (b) Pt|solution (c) CG|solution. v=100mVs⁻¹. 10 cycles=cycles 2, 5, 7, 9.

Figure 2. Comparison between the voltammetric responses shows significant reduction of the FeCe current in the modified electrodes Pt|Template and CG|Template. The red line shows the unmodified electrode (a), (b) and (c) =Pt|Template (d), (e) and (f) =CG|Template. The black line shows the modified electrode.
4. Conclusions
The modification of electrodes using mesoporous silicon oxide films allows producing conductive polymers, specifically nanowires, with nanostructured morphology. This technique also allows to evaluate the resulting material directly and prevents the material from being deformed by subsequent treatments.

Recommendations
It is advisable to carry out studies using the same type of surfactant with different length chains that promote the formation of templates with larger and smaller pore sizes, which could, therefore, form nanowires of both larger and smaller diameters. This work would allow studying the potential effect of these dimensions on electrocatalysis of elements such as formic acid, and how they can impact the production of DA sensors.

Acknowledgements
The authors would like to thank their respective academic institutions for the support given to their research work.

References
[1] Martin C R, Parthasarathy R, and Menon V 1994 Electrochim. Acta 39 1309-1313
[2] Chakarvarti S K 2009 Indian J. Phys. 83(6) 737-749
[3] Apel P 2001 Radiat. Meas. 34 559–566
[4] Grant L M, Ederth T and Tiberg F 2002 Langmuir 16 2285
[5] Carswell A D W, O'Rear E A and Grady B P 2003 J. Am. Chem. Soc. 125 14793-14800
[6] Zhao D D, Xu M W, Zhou W J, Zhang J and Li H L 2008 Electrochim. Acta 53 2699-2705
[7] Mazaj M, Costacurta S, Zabukovec Logar N, Mali G, Novak Tusar N, Innocenzi P, Malfatti L, Thibault-Starzyk F, Amentisch H, Kaucic V and Soler-Illia G J A A 2008 Langmuir 24 6220-6225
[8] Tan Y, Srinivasan S and Choi K S 2005 J. Am. Chem. Soc. 127 3596-3604
[9] Newalkar B L, Komarneni S and Katsuki H 2002 Mater. Lett. 57 444-447
[10] Huczko A 2000 Appl. Phys. A Mater. Sci. Process 70 365-376
[11] Thomas A, Goettmann F and Antonietti M 2008 Chem. Mater. 20 738-755
[12] Choi K S and Steinmiller E M P 2008 Electrochim. Acta 53 6953-6960
[13] Sánchez-Rivera A E, Vital-Vaquier V, Romero-Romo M, Ramírez-Silva M T and Palomar- Pardave M 2004 J. Electrochem. Soc. 151 C666-C673
[14] Goux A, Etienne M, Aubert E, Lecomte C, Ghanbaja J and Walcarius A 2009 Chem. Mater. 21 731-741
[15] Wang Y D, Ma C L, Wu X H, Sun X D and Li H D 2002 Talanta 57 875-882
[16] Liu P, Lee S H, Tracy C E, Turner J A, Pitts J R and Deb S K 2003 Solid State Ionics 165 223-228
[17] Boeckler C, Oeckermann T, Feldhoff A and Wark M 2006 Langmuir 22 9427-9430
[18] Walcarius A, Sibottier E, Etienne M and Ghanbaja J 2007 Nat. Mater. 6 602-608
[19] Etienne M, Quach A, Grosso D, Nicole L, Sánchez C M and Walcarius A 2007 Chem. Mater. 19 844-856
[20] Kwon S Y, Kim J C and Choi B I 2008 Thin Solid Films 516 2843-2847
[21] Etienne M, Sallard S B, Schröder M, Guillemin Y, Mascotto S, Smarsly B M and Walcarius A 2010 Chem. Mater. 22 3426-3432
[22] Walcarius A and Kuhn A 2008 Trends Anal. Chem. 27 593-603
[23] Etienne M, Goux A, Sibottier E and Walcarius A 2009 J. Nanosci. Nanotechnol. 9 2398-2406
[24] del Valle M A, Salgado R and Armijo F 2014 Int. J. Electrochem. Sci. 9 1557-1564
[25] del Valle M A, Ramos A C, Diaz F R and Gacitúa M A 2015 J. Braz. Chem. Soc. 26 2313-2320
[26] Salgado R, del Valle M A, Duran B G and Pardo M A, Armijo F 2014 J. Appl. Electrochem. 44 1289-1294
[27] del Valle M A, Gacitúa M, Díaz F R, Armijo F and Rio R D 2009 Electrochem. Commun. 11 2117-2120