Electrochemically assisted self-assembly of ordered and functionalized mesoporous silica films: impact of the electrode geometry and size on film formation and properties

Grégoire Herzog, Emilie Sibottier, Mathieu Etienne and Alain Walcarius*

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Surfactant-templated mesoporous silica thin films can be deposited onto solid electrode surfaces by electrochemically assisted self-assembly (EASA). The method involves a cathodically triggered self-assembly of cationic surfactants (cetyltrimethyl ammonium bromide, CTAB) and local pH increase leading to the polycondensation of silica precursors (i.e., tetraethoxysilane, alone or in the presence of (3-mercaptopropyl) trimethoxysilane (MPTMS)) and concomitant growth of the ordered mesoporous silica or organosilica film. The present work shows that the EASA method can be applied to film deposition on electrode supports of various morphologies, geometries and sizes (large and flat discs or non-flat streaked supports, i.e., gold CD-trodes, as well as several kinds of ultramicroelectrodes, including carbon fibers, platinum wires, and platinum microdiscs). Galvanostatic conditions were mainly preferred to potentiostatic conditions to avoid problems related to various overpotentials and surface areas experienced with the various working electrodes used here. The results indicate that film deposition was possible on each electrode support but also that both the film formation and properties were dependent on the experimental conditions for EASA. For example, passing from large electrodes to ultramicroelectrodes required the application of larger current densities to ensure film deposition, which can be due to faster loss of the hydroxyl species in solution in the case of radial or spherical diffusion, in comparison to the linear. Highly porous deposits were obtained after template removal, as ascertained by cyclic voltammetry using Ru(NH$_3$)$_6$$^{3+}$ as a redox probe. The advantage of better signal-to-background current ratios for ultramicroelectrodes relative to the macroscopic ones was maintained after film deposition, also resulting in higher sensitivity when used in conditions of preconcentration electroanalysis (using silver(i) or mercury(ii) as a probe being accumulated by complexation to MPTMS-based films).
1. Introduction

Nanostructuration of electrode surfaces via a bottom-up approach has become a well-established area of modern electrochemistry. Recently, the use of templates such as supramolecular assemblies, packed colloidal crystals or hard porous materials, appear to be increasingly attractive for the generation of nanosystems with ordered pore structure at the meso- or macro-scale. Among the more versatile templates are the packed colloidal crystal assemblies (to prepare periodic macroporous solids by the so-called sphere templating method\textsuperscript{2–4}) and the molecular or supramolecular aggregates (that can be used as soft templates for the generation of ordered mesoporous materials, such as silicates\textsuperscript{5} or other metal oxides and organic–inorganic hybrids,\textsuperscript{6,7} non oxide inorganic mesostructures,\textsuperscript{8} or mesoporous polymers and carbons\textsuperscript{9}). Both approaches can be also applied to the generation of ordered macro-\textsuperscript{10} or mesoporous\textsuperscript{11} metallic structures. Template-based ordered materials, especially those deposited as thin films on electrode surfaces, are highly promising for applications, notably in the fields of electroanalytical chemistry and sensors,\textsuperscript{12–18} and energy conversion and storage.\textsuperscript{18–22}

Besides the various existing chemical methods to generate such nanostructured thin films,\textsuperscript{2–11} electrochemistry has become an attractive, and sometimes unique, means to synthesize ordered mesoporous (and also macroporous) deposits on electrode surfaces. This can be basically achieved by direct electrodeposition or indirect electro-assisted deposition of selected precursor compounds (to give metals, semiconductors, metal oxides, polymers, or sol–gel-derived materials) through soft and/or hard templates.\textsuperscript{14,16,18,23} The soft templates are typically lyotropic liquid crystalline phases\textsuperscript{24} (made from highly concentrated surfactants or block copolymers) or more diluted surfactant solutions containing precursors, which are likely to undergo self-assembly co-electrodeposition in the form of a nanostructured thin film.\textsuperscript{11} The hard templates are mainly preformed mesoporous films, whose mesopores are filled with the precursors, which are then subjected to electrochemical deposition in the void volumes of the template material (formation of a structural replica).\textsuperscript{25} An alternative approach is electrodeposition through packed colloidal crystal assemblies,\textsuperscript{14} which was mainly applied to the generation of ordered macroporous deposits rather than the mesoporous ones.\textsuperscript{24} One can distinguish three mechanisms that have been exploited to electrogenerate mesoporous thin films around supramolecular assemblies or through hard templates: (1) the direct electrodeposition of metals, which is usually performed by electro-reduction of metal cations in solution; (2) the indirect precipitation of metal hydroxides or oxides by electrogenerated hydroxide ions; (3) sol–gel film deposition by polycondensation of hydrolyzed precursors (e.g., Si(OH)\textsubscript{4}) catalyzed by electrogenerated hydroxide ions.\textsuperscript{18}

An interesting breakthrough in the field is the discovery that ordered mesoporous metal, metal oxide or metal hydroxide thin films can be generated by electrodeposition from dilute surfactant solutions containing the appropriate inorganic/metal precursors according to a cooperative templating mechanism.\textsuperscript{26} It takes advantage of the possible assembly of ionic surfactants onto electrode surfaces under potential control (i.e., electrochemical interfacial surfactant templating).\textsuperscript{27} The driving force to incorporate a mesostructure into the inorganic films is determined by cooperative interactions between the surfactant, inorganic ions, and the working electrode during electrodeposition. The first examples were
mesostructured ZnO films\textsuperscript{28} and 2D hexagonal ordered platinum mesostructures,\textsuperscript{29} as successfully obtained using sodium dodecyl sulfate as a template.

More recently, the electrochemical interfacial surfactant templating approach was combined with the electro-assisted deposition of sol–gel materials, to give the first example of electrogenerated highly ordered mesoporous silica films.\textsuperscript{30} In this case, the elecrogenerated species (e.g., OH\textsuperscript{−}) do not serve to precipitate a metal hydroxide but they act as catalysts to gelify a sol onto the electrode surface. Indeed, applying a cathodic potential to an electrode immersed in a hydrolyzed sol solution is likely to generate locally OH\textsuperscript{−} species at the electrode/solution interface, inducing thereby the polycondensation of the silane precursors and growth of silica films onto the electrode surface.\textsuperscript{31–34} If operating in the presence of a cationic surfactant (i.e., cetyltrimethylammonium bromide, CTAB), one can obtain hexagonally packed mesoporous silica channels growing perpendicularly to the electrode surface, as a result of electrochemically driven cooperative self-assembly of surfactant micelles and concomitant silica formation. This new method has been called “Electro-Assisted Self-Assembly” (EASA).\textsuperscript{35} Such vertically aligned mesopores are very difficult to obtain by other sol–gel synthesis methods (such as evaporation-induced self-assembly),\textsuperscript{36} and often require substrate patterning,\textsuperscript{37} magnetically induced orientation,\textsuperscript{38} epitaxial growth,\textsuperscript{39} or a Stobêr-solution growth approach.\textsuperscript{40} Mesoporous silica films obtained by EASA generally show granular domains, each of which is composed of hexagonally packed one-dimensional channels oriented uniquely perpendicular to the film surface,\textsuperscript{41} with uniform thicknesses ranging typically between 50–200 nm.\textsuperscript{35} Aminopropyl-, mercaptopropyl- or methyl-functionalized mesoporous silica films can be produced by EASA, keeping a high degree of mesostructural order up to a maximum functionalization level depending on the nature of the organic group (i.e., 10% for amino groups\textsuperscript{42} and 50–60% for the methyl ones\textsuperscript{43}). The films can be prepared on various conducting supports (carbon, platinum, gold, indium–tin oxide),\textsuperscript{30,35} and even on insulating supports using higher electric fields.\textsuperscript{44} The EASA approach was also exploited for the preparation of bimodal macro–mesoporous films\textsuperscript{45} and the deposition of micron sized mesoporous silica spots using a scanning electrochemical microscope\textsuperscript{46} (in a parallel way to that applied to the generation of non-templated silica deposits at a local scale\textsuperscript{47}).

Following these pioneering approaches, the present investigation aims at showing that EASA can be basically applied to the generation of templated and ordered silica and organically modified silica films of electrode supports exhibiting non-planar topography (e.g., gold CD-trodes made from recordable CDs\textsuperscript{48}) or variable shape and size (e.g., from macro- to ultramicrowelectrodes with tubular or disk geometry) and different natures (carbon, platinum). The effect of the electrode size and shape on both the deposition process (influence of the electrochemical deposition conditions on the film formation) and the permeability properties of the resulted coatings will be discussed. Using thiol-functionalized films and silver(I) or mercury(II) as model redox probes, attempts will be made to define the most promising systems for electroanalytical applications.

2. Experimental

2.1 Chemicals, reagents and electrodes preparation

Tetraethoxysilane (TEOS, 98%, Alfa Aesar), (3-mercaptopropyl)trimethoxysilane (MPTMS, 95%, Alfa Aesar), ethanol (95–96% Merck), NaNO\textsubscript{3} (99%, Fluka), HCl
(Riedel de Haan, 1 M solution) and cetyltrimethyl ammonium bromide (CTAB, 99%, Acros) were used for film synthesis. Ruthenium hexamine chloride (Ru(NH₃)₆³⁺, 98%, Aldrich) was used for the film permeability characterisation. Silver(i) stock solutions were prepared from silver nitrate powder (99.8%, Prolabo) while mercury(II) stock solution was a standard solution (1000 ppm in 2% HNO₃, VWR International). All solutions were prepared with high purity water (18.2 MΩ cm⁻¹) obtained from a Purelab Option-Q from ELGA.

Four types of electrodes (macroscopic, µwire, µdisc and Au-CD-trode) were used. Macroscopic electrodes were discs made of either Pt (Ø = 2 mm) or glassy carbon (Ø = 3 mm). µwire electrodes were made of carbon fiber (Ø = 7 µm) or Pt wire (Ø = 25 µm), which were attached to a copper wire for connection purposes using a silver epoxy (EPOTEK H2SO from Epoxy Technology USA). The epoxy was then cured at 80 °C for 16 h. The wire was inserted in a borosilicate capillary and then elongated using a home-made pipette puller. The aperture between the capillary walls and the electrode is sealed with glue (Araldite, Bostik, France). The Pt µdiscs were prepared as follows: a 1 cm long Pt wire (Ø = 25 µm) was inserted in a borosilicate capillary, which had an end sealed in a Bunsen burner flame. The capillary was melted around the Pt wire over a distance of 5 mm. A copper wire was connected to the Pt wire end using the silver epoxy. The borosilicate capillary was then polished using sandpaper of two granularities (starting with 2500 and then 4000) until a Pt microdisc was apparent. Gold CD-trodes were prepared by attaching the gold film taken from a recordable compact disc (CD) onto a polyvinyl chloride slide (PVC). Each CD-trode was connected using a copper wire and a plastic slide with a disc opening of 9 mm of diameter. The gold surface was then cleaned in 65% nitric acid. The geometry of the gold electrode prepared this way was a succession of troughs (1 µm wide and 100 nm high) separated by 500 nm.

2.2 Preparation of surfactant templated thin films

The mesoporous silica films were prepared by the electrochemically assisted self-assembly (EASA) method described elsewhere. A typical sol was prepared as follows: ethanol and 0.1 M NaNO₃ were mixed in 1 : 1 v/v ratio. Silanes (TEOS, or TEOS:MPTMS 9 : 1 molar ratio) and CTAB were added to the mixture. Total silane concentrations varied between 25 and 340 mM. The molar ratio of CTAB : silanes was maintained at 0.32 as it was reported to form regular mesoporous structures. The pH of the sol was adjusted to 3 by addition of HCl and the sol was hydrolysed under stirring at room temperature for 2.5 h prior to use as electrodeposition medium. The sol was prepared on the day of its use for electrode modification. The electrodes were modified in the hydrolysed sol either by a potentiostatic or a galvanostatic method. A current density, j, of −0.74 mA cm⁻² (unless stated otherwise) or a potential of −1.3 V for Au, −2.2 V for carbon and −0.9 V for Pt was applied at the working electrode with respect to a silver wire acting as pseudo-reference electrode and a gold disc as a counter electrode (note that on Pt µdiscs, a galvanostatic conditioning step (i = 30 nA, t = 5 s) was applied prior to successful deposition of the silica film). After film formation, the electrodes were treated overnight at 130 °C (to ensure good cross-linking of the silica network). Template removal was achieved using 0.1 M HCl in ethanol, as previously described.42
2.3 Electrochemical methods

All electrochemical experiments were done with a PGSTAT 12 or a µAutolab from Ecochemie (Metrohm, Switzerland). The bare and modified electrodes were characterised by cyclic voltammetry (CV) at 10 mV s⁻¹ in a de-aerated solution of 5 mM Ru(NH₃)₆³⁺ in 0.1 M NaNO₃, in order to obtain information on the film permeability properties. In these experiments, a stainless steel rod was used as a counter electrode and the reference electrode was Ag|AgCl|1 M KCl (purchased from Metrohm, Switzerland). Ag⁺ and Hg²⁺ ions were also used as probes to assess the electroanalytical properties of the modified electrodes. Ag⁺ and Hg²⁺ were detected as described in previous publications.⁴⁹,⁵⁰ Briefly, the modified electrodes were immersed at open-circuit potential for 2 min (unless stated otherwise) in a solution containing a known concentration of Ag⁺ (or Hg²⁺) in 0.1 M HNO₃. Detection was performed in a metal-free 0.5 M HCl solution for Ag⁺ or in a 3 M HCl solution for (Hg²⁺). The potential was held at −0.3 V for 60 s to allow deposition of metal species on the electrode surface prior to anodic stripping by differential pulse voltammetry (experimental conditions: step potential: 2 mV, modulation amplitude: 25 mV, modulation time: 50 ms; interval time: 100 ms) from −0.3 to 0.3 V. For Ag⁺ detection, a silver wire was used as a pseudo-reference electrode and a stainless steel rod as a counter electrode. For Hg²⁺ detection, a Ag wire electrode was used as a pseudo-reference electrode and a platinum mesh as a counter electrode.

2.4 Microscopy

Scanning electron microscopy (SEM) images were obtained using a Philips XL30 microscope, while transmission electron microscopy (TEM) images were achieved with a Philips CM20 microscope at an acceleration voltage of 200 kV. Atomic force microscopy measurements were carried out at room temperature using a commercial microscope (Thermomicroscope Explorer Ecu+, Veeco Instruments SAS), using V-shaped silicon nitride tips (MLCT-EXMT-BF, Veeco Instruments) with a spring constant of 0.1 N m⁻¹ (manufacturer specifications). The images were collected in contact mode with a scan size ranging from 10 to 50 µm.

3. Results and discussion

3.1 Electrochemically assisted self-assembly on non-planar electrodes

As illustrated at the top of Fig. 1, the EASA method involves the immersion of an electrode into a surfactant-containing hydrolysed sol (stable at pH 3) and the application of a cathodic potential likely to generate hydroxyl ions at the electrode/solution interface, causing thereby a local pH increase resulting in the precursors’ condensation and concomitant growing of a surfactant-templated mesoporous silica film. Such an electrochemically triggered pH change inducing the sol–gel transition is now a well-established process.⁴¹–⁴⁴ In the presence of ionic surfactants, however, the applied potential not only plays the role of generating the basic catalysts (i.e., hydroxyl groups), but also contributes to the self-assembly of the surfactants onto the electrode surface.⁴⁶ Such assemblies were claimed to induce an unique orientation of silica mesopore channels perpendicularly to the underlying support (see bottom of Fig. 1), a configuration ideal for many applications but difficult to get by other methods.²³

A first objective of this work was to check if EASA allows the achievement of uniform silica thin films, which are also mesoporous and organised, on
heterogeneous non-flat surfaces. Fig. 2 shows the modification by EASA of 3D Au structures obtained from compact discs (i.e., gold CD-trodes). SEM images, respectively obtained before (Fig. 2A) and after (Fig. 2B) modification of the gold surface, reveal that although the thin film is not visible, the presence of small beads of silica can be noticed, indicating that there is a modification of the surface. The 3D structure of the electrodes is still visible despite the modification process. This is even more noticeable on the AFM picture (Fig. 2C) and the cross-sectional SEM view (Fig. 2H), demonstrating that the streaked microstructure was not significantly affected after film deposition by EASA, whereas the same support covered with a similar mesoporous silica film prepared by spin-coating did not exhibit the pristine topography (it is obvious from the image depicted in Fig. 2D that the troughs are filled with silica, confirming the limitation of traditional sol–gel techniques (e.g. drop- and dip-coating methods) to be applied to non-flat surfaces). More overwhelming is the fact that a uniform film (80 nm thick) was deposited by EASA over the whole non-flat surface exhibiting a step height between moulds and hills of the same magnitude as the film thickness (i.e., 100 nm step height between 0.5 μm wide moulds and 1.0 μm wide hills). The AFM profiles of cross-sections recorded before and after film deposition indicate that the vertical sidewalls of the CD-trode are indeed uniformly coated with a 80-nm thick film (Fig. 2E). The modified surface obtained by EASA was also analysed by TEM (Fig. 2F and 2G). On Fig. 2G, a dark area is visible, which corresponds to the sidewalls of the 3D structure. Fig. 2G shows that the film formed by EASA is highly ordered throughout the film, and the electron diffraction pattern confirms the existence of a hexagonal packing of mesopore channels over the whole surface.

3.2 Electrochemically assisted self-assembly on microdisc and microwire electrodes

The above results demonstrate that EASA is likely to deposit surfactant-templated silica films at the micron scale, suggesting that the method could be also
applicable to the modification of ultramicroelectrodes. The first attempts were made using microwire electrodes based on either carbon fiber (Ø = 7 µm) or Pt wire (Ø = 50 µm). Typical SEM and TEM micrographs of the modified microwires are shown in Fig. 3. The modification of the microwires is clearly visible by comparing the SEM images obtained before (Fig. 3A and 3D) and after (Fig. 3B and 3E) film deposition. It should be noted that the formation of H₂ gas bubbles was not observed during the film electrogeneration, otherwise significant macropores would have formed in the film, as reported elsewhere.\(^\text{55}\) As shown, an important amount of silica beads and aggregates are formed on the surface of both carbon fiber and platinum wire electrodes. Nevertheless, underneath the beads/aggregates, an ordered mesoporous film is formed as is revealed by TEM (Fig. 3C and 3F). These micrographs indicate indeed the existence of hexagonally packed silica mesochannels. The sample shown in Fig. 3F was obtained after ultramicrotomy of the film and the resulting cross-sectional view demonstrates that mesopores were oriented perpendicular to the surface of the wire. Due to the different hydrogen evolution on carbon and platinum (distinct potentials for reduction of protons/water), the applied potential likely to induce film formation on these two electrodes was also different (i.e., \(-0.9\) V for Pt and \(-2.2\) V for C). To overcome this problem, and to offer a generic way to generate mesoporous silica films on electrodes of different nature and size, galvanostatic conditions have been used on the basis of the application of an adequate cathodic current density (values determined from the previous potentiostatic experiments and corrected by the real electroactive surface area of the electrode). Note that the electroactive surface area of the microfiber electrodes was determined from CV experiments, and determined using the following equation:\(^\text{56}\)

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**Fig. 2** Modification of Au CD-trodes by EASA. SEM images of a bare Au CD-trode (A) and the same electrode modified by EASA (–1.3 V for 5 s) (B). AFM images of Au CD-trodes coated with a mesoporous silica film prepared by EASA (C) or by spin-coating (D). AFM profiles (E) of the cross-section of Au CD-trode prior to (dotted line) or after (plain line) film deposition by EASA. TEM images (F–G) of mesoporous silica films obtained by EASA (–1.3 V for 10 s) at two different enlargements; insert of G is the corresponding electron diffraction pattern. Field emission SEM image (H) of the cross section of the same thin mesoporous silica film as in (C).
\[ i = \frac{2nFADC}{r\ln\tau} \]

\( C \) is the concentration (in mol cm\(^{-3}\)), \( D \) the diffusion coefficient (in mol cm\(^{-2}\)), \( A \) the surface area of the electrode (in cm\(^2\)), \( F \) the Faraday constant, \( n \) the number of electrons transferred in the reaction, \( r \) the radius of the fibre (in cm). Finally, \( \tau \) is defined by \( \tau = 4Dt/r^2 \) where \( t \) is the duration of the experiments (calculated from potential difference from the foot of the wave up to the reverse potential divided by the scan rate). Once the surface area was determined, microfiber electrodes were then modified by applying a current for a duration, which varied typically between 5 and 15 s. For instance, a current density of \(-3.7 \times 10^{-3} \) A cm\(^{-2}\) gave rise to the generation of similar films as in Fig. 3 for the carbon fiber and Pt wire. The next step is the evaluation of the quality and permeability properties of the films, which can be made using CV of a redox probe in solution, with an expected absence of signal prior to surfactant removal in case of good quality films covering the entire electrode surface and significant CV responses observed after template removal due to the porous nature of the mesoporous film.\(^{35}\)

Microwire electrodes made of carbon fibers modified by a mesoporous silica film generated by the galvanostatic method were first characterised by CV in 5 mM Ru(NH\(_3\))\(_6\)\(^{3+}\) (in 0.1 M NaNO\(_3\), see typical curves in Fig. 4). CV curves were recorded before and after surfactant extraction from the pores. The first observation is that prior to surfactant removal, the signal was never totally/efficiently blocked by the presence of the electrodeposited film onto the electrode surface, contrary to what was observed on larger electrodes.\(^{30,35}\) This suggests either an incomplete coverage of the underlying electrode with the mesoporous film (some heterogeneous growing?) or the generation of some defects/damages during the curing step (stress/strain or lattice contraction, which would be more
constraining for the curved surface of a microfiber in comparison to the flat electrodes?). This second hypothesis is probably more plausible as SEM images (Fig. 3) seem to indicate full coverage of the fiber by the mesoporous film (the aggregates are not present everywhere but the thin film seems to be). The gain/increase in CV currents recorded after template removal (which was expected as a result of the mesoporosity of the film) was not so obvious (yet clearly noticeable in some cases, see right part of Fig. 4), pointing out some restricted diffusion of the probe through the film to the electrode surface. Similar results were obtained from pure silica films (i.e., prepared with TEOS alone) and for the mercaptopropyl-functionalized ones (i.e., prepared from a 9:1 TEOS–MPTMS mixture). A most intricate issue is the lack of reproducibility for both film formation and properties. Indeed, Fig. 4A and 4B represent the CV characterisation for two carbon fibers using the same film formation conditions. It is clear that the same experimental conditions lead to different electrochemical behaviours, which is basically unacceptable for practical applications. These film imperfections could be partly due to the rather poor adhesion of the silica material to the carbon support and/or to the curved shape of the fiber surface which could induce additional stress during post-treatment heating. In attempting to circumvent some of these limitations, platinum electrodes (macro- and ultramicroelectrodes) were used in the following.

Three Pt electrodes with three distinct geometries and sizes (macrodisc, microwire and microdisc) were used as electrode substrates for mesoporous silica film deposition and CV was then applied to characterise their permeability properties using Ru(NH₃)₆³⁺ as redox probe (Fig. 5). It should be first reminded that the bare electrodes already behave differently as they are characterised by the distinct mass transport behaviours that are observed at these electrodes: linear diffusion of species was achieved at a Pt macrodisc electrode, whereas spherical diffusion was operating at a Pt microwire electrode and cylindrical diffusion at a Pt microdisc. As expected, the highest current density was observed for the CV of Ru(NH₃)₆³⁺ at a microdisc, its limiting current density being 15 times greater than...
the peak current density recorded at the macrodisc and 7.5 times greater than the limiting current density at the Pt microwire (Fig. 5A). All three kinds of electrodes were modified by EASA and characterised by CV. As above (i.e., for carbon microfibers), CV curves for Ru(NH$_3$)$_6^{3+}$ were recorded at the bare electrodes and after film deposition, before and after extraction of the surfactant (Fig. 5B). At both the macro- and microdisc, the presence of the film before surfactant removal results in an almost complete blocking of the electrode surface by inhibiting drastically any electron transfer between the species in solution and the electrode (Fig. 5B1 and 5B3), confirming complete coverage of the electrodes surface with a defect-free (or few defects) templated mesoporous silica film obtained by EASA, respectively before (dash line) and after extraction of the surfactant (dotted line), at (B1) a Pt macrodisc ($j = -0.74 \times 10^{-3} \text{ A cm}^{-2}$, $t = 15 \text{ s}$; [TEOS + MPTMS] = 340 mM), (B2) a Pt microwire ($j = -1.5 \times 10^{-3} \text{ A cm}^{-2}$, $t = 15 \text{ s}$; [TEOS + MPTMS] = 110 mM) and (B3) a Pt microdisc ($j = -5.0 \times 10^{-3} \text{ A cm}^{-2}$, $t = 15 \text{ s}$; [TEOS + MPTMS] = 110 mM). $\nu = 10 \text{ mV s}^{-1}$.
Another point that should be mentioned and discussed is the fact that larger current densities must be applied when passing from the Pt macrodisc to a microwire and to a microdisc (see caption in Fig. 5) in order to observe the formation of the mesoporous silica film onto the electrode surface. Indeed, for instance, applying a current density of $-0.74 \times 10^{-3}$ A cm$^{-2}$ (which is a typical value leading to good electro-assisted deposition on the macroscopic electrode) did not result in any film deposition on the Pt microdisc. Keeping in mind that the applied current induces the generation of the sol–gel polycondensation catalyst (OH$^-$), it seems that the diffusion regime (linear, cylindrical or spherical), which controls the OH$^-$ gradient at the electrode/solution interface, also affects the polycondensation rates of the sol–gel precursors. A plausible explanation is a faster “loss” of OH$^-$ species in the bulk of the solution in the case of spherical diffusion with respect to the linear one, requiring thereby the application of higher current densities (i.e., to generate more OH$^-$ species per unit area) or increasing the deposition time (to counterbalance the slower polycondensation kinetics) to ensure effective polycondensation catalysis and concomitant film deposition.

A more detailed investigation of the factors affecting the deposition process and film permeability properties has thus been performed on the Pt microdisc. As for classical electro-assisted deposition of sol–gel materials,\textsuperscript{31,34,57,58} the EASA process is expected to be mainly affected by three parameters: the deposition time, the applied potential (for potentiostatic mode) or current (for galvanostatic mode), and the concentration of silane precursors.\textsuperscript{35} Fig. 6 illustrates the effect of deposition time (A) and deposition current density (B) on the mesoporous silica film quality, via the variations of limiting currents observed before template removal (significant/high current values would indicate poor quality of the film because the probe (Ru(NH$_3$)$_6$)$^{3+}$) can reach the underlying electrode surface through defects/holes, whereas low current values would indicate good coverage of the electrode surface by a film covering the whole surface). The results clearly point out that sufficiently long deposition times ($t_{dep} > 14–15$ s) and current densities large enough ($j_{dep} \geq 5 \times 10^{-3}$ A cm$^{-2}$) are required to get thin films likely to block the access of the redox probe to the electrode surface. Actually, one can distinguish three limiting cases (Fig. 6C): (C1) too short deposition time and/or too low current density leading to an important CV signal before surfactant extraction (film incompletely covering the Pt surface) and no real enhancement of the limiting current after template removal; (C2) good film quality at intermediate $t_{dep}$ and $j_{dep}$ values resulting in complete suppression of the CV signal before surfactant extraction and good permeability (high limiting current) after template removal; (C3) longer $t_{dep}$ and/or larger $j_{dep}$ values giving rise to rather good electrode coverage with the mesoporous film which is however much thicker, inducing thereby restricted diffusion of Ru(NH$_3$)$_6$)$^{3+}$ species across the film to the underlying electrode surface (see lower currents on the dotted curve in part C3 in comparison to C2 in Fig. 6). The optimal ranges (leading to films covering completely the electrode surface and remaining highly open after template removal) for $t_{dep}$ and $j_{dep}$ values are respectively between 14 and 18 s and between $-5$ and $-8$ mA cm$^{-2}$, for electro-assisted self-assembly of mesoporous silica films on a Pt microdisc. Finally, the influence of the precursors (90 : 10 TEOS–MPTMS) concentration was studied in the range between 25 and 340 mM (using $t_{dep} = 15$ s and $j_{dep} = -6$ mA cm$^{-2}$). The results (not shown) indicate that mesoporous films covering well the whole electrode surface area (i.e., resulting
in mostly (>90%) blocked CV signals prior to template removal) can be obtained in the 50 to 200 mM silane precursor concentration range. Below 50 mM, the amount of deposited material was not enough to cover the whole electrode surface area, while too high precursor concentrations (>200 mM) resulted in much thicker deposits which are known to induce significant cracks upon drying, as already observed for mesoporous silica films generated by EASA on macroscopic electrodes. In conclusion, the optimal conditions for film preparation by EASA on Pt microdiscs are: deposition times in the range 14–18 s, applied current densities between ~5 and ~8 mA cm$^{-2}$, and precursor concentrations ranging between 50 and 200 mM.

3.3 Functionalised films for accumulation – detection by stripping voltammetry

In order to check the potential interest of depositing mesoporous silica films on ultramicroelectrodes instead of macroelectrodes for electroanalysis purposes, some preliminary experiments have been performed using model analytes (silver or mercury ions) that have been accumulated at mercaptopropyl-functionalized
mesoporous silica film obtained by EASA prior to their voltammetric detection. The first attempts were made using modified carbon fiber electrodes for the detection of Ag⁺ after open-circuit accumulation. The presence of 10% MPTMS in the mesoporous silica thin film was responsible for the accumulation of Ag⁺ ions by complexation to the thiol binding sites. The modified electrode was then transferred to a silver-free detection solution (0.5 M HCl) and silver species were detected by anodic stripping voltammetry in the differential pulse mode (DPASV). A cathodic potential was applied to reduce the Ag⁺ ions to form metallic Ag which was then stripped from the surface of the electrode. Typical DPASV curves are shown in Fig. 7A for increasing concentrations of Ag⁺ in the accumulation medium. The stripping peak currents increased linearly with concentrations of Ag⁺ between 2.5 and 20 µM at both modified macroscopic glassy carbon and carbon fiber electrodes (inset of Fig. 7A). The carbon fiber electrode is clearly more sensitive than the macroscopic one as the slope of the calibration curve is 3.4 times steeper than the one obtained at the modified glassy carbon electrode. It should be noted that the accumulation step was done under stirring for the macroscopic electrode, whereas the solution was still for the accumulation step using modified carbon fiber electrodes. Under cylindrical diffusion at the carbon fiber electrodes, accumulation of Ag⁺ ions is more efficient, even in the absence of stirring. The second example concerns the preconcentration electroanalysis of either Ag⁺ or Hg²⁺ at Pt macro- or microelectrodes covered with a similar mercaptopropyl-functionalized mesoporous silica film obtained by EASA (Fig. 7B). Again, in both cases, a higher stripping peak current density was obtained at the microelectrodes in comparison to the macroelectrodes. This advantage is attributed to the spherical diffusion regime at the ultramicroelectrodes, which is maintained after modification of the electrode surface thanks to the fast mass transport ensured by the highly porous organosilica film.

Fig. 7 (A) Differential pulse anodic stripping voltammetry (DPASV) of Ag⁺ ([Ag⁺]) ranging from 2.5 to 20 µM after open-circuit accumulation (for 2 min) at a modified carbon fiber modified with a mercaptopropyl-functionalized mesoporous silica film obtained by EASA (j = –3.69 × 10⁻³ A cm⁻², t = 15 s). Left inset: DPASV of 20 µM Ag⁺ at a modified glassy carbon macrodisc (Ø = 0.3 cm); Right inset: calibration curves for Ag⁺ obtained by DPASV at a modified carbon fiber (■) and glassy carbon macrodisc (●). (B) DPASV of Ag⁺ (B1) or Hg²⁺ (B2) at a modified (EASA conditions as in Fig. 5) Pt macrodisc (a) or Pt microdisc (b). [Ag⁺] 15 µM or [Hg²⁺] = 10 µM; tacc = 7 min (Ag⁺) or 2 min (Hg²⁺); detection medium: 0.5 M HCl for Ag⁺ and 3 M HCl for Hg²⁺; other conditions as in part (A) of the Figure.
4. Conclusions

In this work, we have shown that the EASA method can be basically applied to the generation of mesoporous silica and organosilica films on electrodes of various topographies, shapes and sizes. The experimental conditions (deposition time and applied potential/current) have to be carefully adapted to ensure the formation of defect-free films covering the whole electrode surface as well as to maintain good permeability properties after template removal. Preliminary experiments in preconcentration electroanalysis suggest a significant increase in sensitivity when passing from macroelectrodes to ultramicroelectrodes coated with functionalized mesoporous silica thin films.

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Notes and references
