



# Clay-mesoporous silica composite films generated by electro-assisted self-assembly



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## ABSTRACT

This work describes the electro-assisted generation of clay-mesoporous silica composite films onto glassy carbon electrodes (GCEs). The method involved the deposition of clay particles by spin-coating on GCE and the subsequent growing of a surfactant-templated silica matrix around these particles by electro-assisted self-assembly (EASA). EASA typically consisted in applying a cathodic potential to the electrode immersed into a hydrolyzed sol (containing tetraethoxysilane, TEOS, as the silica source, and cetyltrimethylammonium bromide, CTAB, as surfactant) in order to generate the necessary hydroxyl catalysts inducing the formation of the mesoporous silica. In such conditions, alongside the silica deposition process, the inter-layer distance between the clay sheets was found to increase as a result of CTAB ion exchange. After removal of the surfactant template, the composite film became highly porous (i.e., to redox probes) and the clay recovered its pristine interlayer distance and cation exchange properties. This made it promising for application in preconcentration electroanalysis, as pointed out here using copper(II) as a model analyte, especially because it offered much better long-term operational stability than the conventional (i.e., without silica binder) clay film electrode.

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## 1. Introduction

Structuration of electrode surfaces with inorganic thin films has become a well-established field of interest, notably for applications in electroanalysis [1–21]. Various materials have been used for that purpose, including zeolites [2–5], clays [6–9] and layered double hydroxides [10,11], silica [3,12,13] and silica-based organic–inorganic hybrids [13,14], sol–gel materials [14–17] and, more recently, ordered mesoporous materials [3,18–21]. The driving force to select one or another of these electrode modifiers often relies on the particular properties (ion exchange, selective recognition, hosting capacity, size selectivity, redox activity, permselectivity, etc.) which can be useful to the final application (preconcentration electroanalysis, electrocatalysis, permselective coatings, biosensors, ...).

As most of these materials are electronic insulators, their use in connection to electrochemistry requires a close contact to an electrode surface, which can be basically achieved via dispersion of as-synthesized powdered materials in a conductive composite

matrix (e.g., carbon paste electrodes [22]) or deposited as thin films on solid electrode surfaces. In the latter case, a critical point is the uniformity and long-term mechanical stability of the thin coatings, which might be challenging when attempting to deposit particulate materials onto electrodes, requiring often the use of an additional polymeric binder [23]. This is especially the case of zeolite film modified electrodes, the situation being somewhat less problematic for clay film modified electrodes because of the particular platelet morphology of clay particles and their self-adhesive properties toward polar surfaces [24] ensuring better interaction with most electrode materials and consequently more durable immobilization. Nevertheless, besides the classical physical attachment of a clay film to a solid electrode surface (through solvent casting, spin-coating or layer-by-layer assembly as the mainstream techniques [6,24,25], or electrophoretic deposition [26]), other strategies based on covalent bonding (via silane or alkoxy silane coupling agents) have been also developed [27,28].

On the other hand, the versatility of the sol–gel process makes it especially suitable to coat electrode surfaces with uniform deposits of metal or semimetal oxides (mainly silica) and organic–inorganic hybrid thin films of controlled thickness, composition and porosity. The method is intrinsically simple and exploits the fluidic character of a sol (typically made of alkoxy silane precursors for silica-based

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materials) to cast it on the surface of a solid electrode, allowing gelation, and drying to get a xerogel film [14–17]. The driving force for film formation is thus solvent evaporation and this approach is often sufficient to yield high quality films of flat surfaces [29], including the ordered mesoporous ones generated by evaporation-induced self-assembly in the presence of surfactant templates [30]. Sol-gel thin films can be also generated onto electrode surfaces by electrolytic deposition. The method involves the immersion of the electrode into a hydrolyzed sol solution (i.e., typically in moderate acidic medium) and the application of a suitable cathodic potential likely to generate hydroxyl ions locally at the electrode/solution interface, such local pH increase contributing to catalyze the precursors polycondensation and the growth of the silica film on the electrode surface [31–33]. This approach can be extended to the generation of organically-functionalized silica films [34,35] or to the co-deposition of sol-gel/metal nanocomposites [36] or conductive polymer-silica hybrids [37], and is compatible with the encapsulation of biomolecules to build bioelectrocatalytic devices [38,39]. When applied in the presence of surfactant template (i.e., cetyltrimethylammonium bromide, CTAB), the method enables the deposition of highly ordered mesoporous silica films with mesopore channels oriented normal to the underlying support [40,41], a configuration ensuring fast mass transport for analytes from the solution through the film to the electrode surface, thus offering great promise for the elaboration of sensitive electroanalytical devices [42]. Moreover, contrary to the evaporation method, the electro-assisted generation approach enables to get uniformly deposited sol-gel layers onto electrode surfaces of complex geometry or complex conductive patterns (i.e., gold CD-trodes [35], macroporous electrodes [43], metal nanofibers [44] or printed circuits [45]) or at the local scale using ultramicroelectrodes [46,47]. The method was also proven to be suited to the generation of sol-gel materials through nano- or micro-objects deposited onto electrode surfaces, such as nanoparticles [48] or bacteria [49], thus acting somewhat as a template for film growing.

In the present paper, we have further extended the electro-assisted deposition method to generate clay-mesoporous silica composite films and characterized their permeability properties toward selected redox probes (cationic, neutral, and anionic). The synthesis procedure involves at first the deposition of clay particles montmorillonite-rich natural clay from Romania) onto a glassy carbon electrode surface, and the subsequent electro-assisted self-assembly of a surfactant-templated mesoporous silica around the clay particles. The use of a cationic surfactant (i.e., CTAB) in the synthesis medium was driven by at least two points, the fact that it contributes to template the silica film (which exhibits distinct permeability properties before and after extraction [40–42]), and its possible incorporation into the interlayer region of the clay by cation exchange (which is known to modify the interlayer spacing between the clay sheets [50]). Even if some silica-clay composites have been described in the literature [51–53], including two as thin layers on electrode [54,55], the present work provides, to the best of our knowledge, the first example of electrogenerated clay-mesoporous silica composite films. Their permeability properties and long-term operational stability of the modified electrodes are discussed regarding their physico-chemical characteristics.

## 2. Experimental

### 2.1. Reagents and materials

Tetraethoxysilane (TEOS, 98%, Alfa Aesar), ethanol (95–96%, Merck),  $\text{NaNO}_3$  (99%, Fluka), HCl (37%, Riedel de Haen) and cetyltrimethylammonium bromide (CTAB, 99%, Acros) were used as received for sol-gel films synthesis. The redox probes

employed for permeability characterization were analytical grade: ferrocene dimethanol ( $\text{Fc}(\text{MeOH})_2$ , Alfa Aesar); potassium hexacyanoferrate(III) ( $\text{K}_3\text{Fe}(\text{CN})_6$ , Fluka); and hexaammineruthenium chloride ( $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ , Sigma–Aldrich); they were typically used in 0.1 M  $\text{NaNO}_3$  solution. A certified copper(II) standard solution ( $1000 \pm 4 \text{ mg L}^{-1}$ , Sigma–Aldrich) was used to prepare diluted solutions for preconcentration studies. The electrolytes KCl (99.8%) and HCl (36% solution) were obtained from Reactivul București. All solutions were prepared with high purity water ( $18 \text{ M}\Omega \text{ cm}^{-1}$ ) from a Millipore milli-Q water purification system.

The clay sample used in this study was natural Romanian clay from Valea Chioarului (Maramureș County), which consisted mainly of smectite, with minor amounts of quartz. Its physico-chemical characterization is provided elsewhere [56]. The structural formula is  $(\text{Ca}_{0.06}\text{Na}_{0.27}\text{K}_{0.02})_{\Sigma=0.35}(\text{Al}_{1.43}\text{Mg}_{0.47}\text{Fe}_{0.10})_{\Sigma=2.00}(\text{Si}_{3.90}\text{Al}_{0.10})_{\Sigma=4.00} \text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ . It is characterized by a surface area ( $\text{N}_2$ , BET) of  $190 \text{ m}^2 \text{ g}^{-1}$ . Only the montmorillonite-rich fine fraction of the clay ( $<0.2 \mu\text{m}$ , as collected by sedimentation according to Stokes law, after the raw clay was suspended in water, ultrasonicated for about 15 min and allowed to settle, centrifugation and ultracentrifugation of the supernatant phase) was used here. This fine fraction has a cation exchange capacity (CEC) of  $0.78 \text{ meq g}^{-1}$ . Its XRD diffractogram showed a high content of montmorillonite (with its characteristic peaks at  $2\theta$ :  $6.94^\circ$ ;  $19.96^\circ$ ;  $21.82^\circ$ ;  $28.63^\circ$ ;  $36.14^\circ$ ;  $62.01^\circ$ ) and also confirmed the almost negligible presence of other minerals.

### 2.2. Preparation of the clay-mesoporous silica films

Glassy carbon electrodes (GCE, 5 mm in diameter) were first polished on wet silicon carbide paper using 1 and  $0.05 \mu\text{m}$   $\text{Al}_2\text{O}_3$  powder sequentially and then washed in water and ethanol for a few minutes, respectively. GCE were afterwards coated with a clay film, which was prepared by depositing a  $10 \mu\text{L}$  aliquot of an aqueous clay suspension ( $5 \text{ mg mL}^{-1}$ ) by spin-coating onto the GCE surface, as in [57]. The film was dried for 1 h at room temperature prior to any further use. This electrode is denoted below as “GCE-clay”. A mesoporous silica film was then electrogenerated through this film, around the clay particles, onto the electrode surface under potentiostatic conditions. This was typically achieved from a precursor solution containing 20 mL ethanol, 20 mL aqueous solution of 0.1 M  $\text{NaNO}_3$  and 0.1 M HCl, to which 13.6 mmol TEOS and 4.35 mmol CTAB were added under stirring (optimized conditions as in [40–42]) and the resulting sol was aged for 2 h prior to use. The GCE-clay electrode was then immersed in this sol solution and electro-assisted deposition was performed by applying  $-1.3 \text{ V}$  for 10 s. The electrode was then quickly removed from the solution, rinsed with water, and dried/aged overnight in an oven at  $130^\circ\text{C}$ . The resulting composite film electrode is denoted “GCE-clay-mesop $\text{SiO}_2$ ”. It can be used as such or after template removal; in this latter case, the CTAB template is solvent-extracted with an ethanol solution containing 0.1 M  $\text{NaClO}_4$  for 5 min under moderate stirring. For comparison purposes, a template-free silica film was also deposited onto the GCE-clay electrode, exactly under the same aforementioned conditions but in the absence of CTAB in the starting sol. It is denoted “GCE-clay- $\text{SiO}_2$ ”.

### 2.3. Apparatus and characterization procedures

All electrochemical experiments were performed using a PGSTAT-12 potentiostat (EcoChemie) monitored by the GPES software. A conventional three electrode cell configuration was employed for the electrochemical measurements. Film modified GCEs were used as working electrodes, with a saturated Ag/AgCl (Metrohm) and a platinum wire as reference and counter electrode, respectively. Cyclic voltammetry (CV) measurements were

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