Mesoporous silica networks with improved diffusion and interference-rejecting properties for electroanalytical sensing

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Mesoporous silica materials characterized by well-ordered microstructure and size- and shape-controlled pores have attracted much attention in the last years. These systems can be used for the development of functional thin films for advanced applications in catalysis and electrocatalysis, sensors and actuators, separation techniques, micro- and nano-electronic engineering [1-2].

In this work, “insulating” and mesoporous silica films were prepared by spin coating a home-made silica sol on a cleaned ITO glass support. The mesoporosity was controlled by the use of Polystyrene (PS) latex beads with different dimensions (30-60-100 nm) as template. The number of successive multi-layer depositions was varied (1-2-3-5 layers) and after the template removal, stable, homogeneous and reproducible transparent films were obtained, characterized by an interconnected porous structure. The morphological features and the physicochemical and optical properties of the films and/or sol-precursors were studied by DLS, FE-SEM, AFM, UV-vis transmittance spectroscopy and wettability analyses. Moreover, a deep electrochemical characterization was also performed by Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS). In particular, the use of two redox mediator probes [($K_4Fe(CN)_6$) and ($Ru(NH_3)_6Cl_3$)], presenting opposite charge and different diffusional behaviour, allowed the comprehension of the mass transport and charge transfer phenomena, evidencing the effects of spatial confinement and charge selection.

In the case of “insulating” films prepared without the use of PS latexes, we proved an experimental evidence for theoretical models [3] concerning electroinactive layer-modified electrodes, with a scan-rate-dependent variation of the CV shape due to a progressive increase in the diffusion coefficient inside the insulating layer. A complex balance between diverging effects (higher hydrophilicity and insulating behavior effects of silica) when increasing the numbers of layers was also observed [4].

In the case of mesoporous layers, a better electrochemical response of smaller pores and of thicker layers was found, due to two main cooperative phenomena: i) a diffusion modification from fully planar to radial-convergent at the pore-silica interface due to surface porosity; ii) the presence of pores in a hydrophilic matrix which leads to a capillary pull effects, stronger in the case of smaller hydrophilic pores.

The easiness of preparation and the interesting properties of these devices pave the way towards their use in many fields, particularly trace electroanalysis in real matrices. In fact, for example, the porous and properly charged network is able to exclude interfering macromolecules (mucin in our case), preventing electrode biofouling and enhancing the performances of the sensor towards dopamine detection.

References

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