SUPPLEMENTARY INFORMATION

Electrochemically-assisted self-assembly of mesoporous silica thin films

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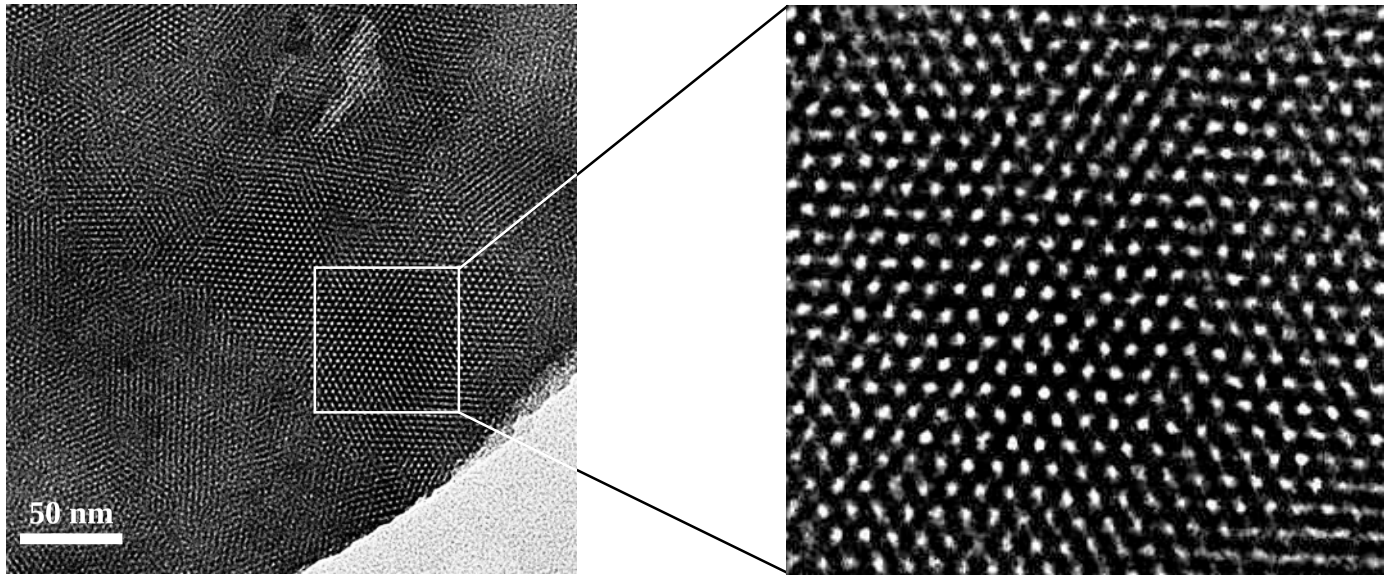

Fig. S1. TEM image of an electrodeposited surfactant-templated mesoporous silica film contaning thiol groups. The image was obtained from a piece of film which was removed mechanically from the support and deposited on the copper grid so that the inherent flatness of the plane surface of the sample is likely to have been affected, leading to some heterogeneous aspects on the TEM image; nevertheless, well-preserved parts can be observed yet (see enlargement). The film was prepared by electrodeposition at -1.3 V for 5 s on a gold surface, from a precursor solution containing TEOS and MPTMS at a 95:5 molar ratio with a CTAB/precursor molar ratio of 0.32.

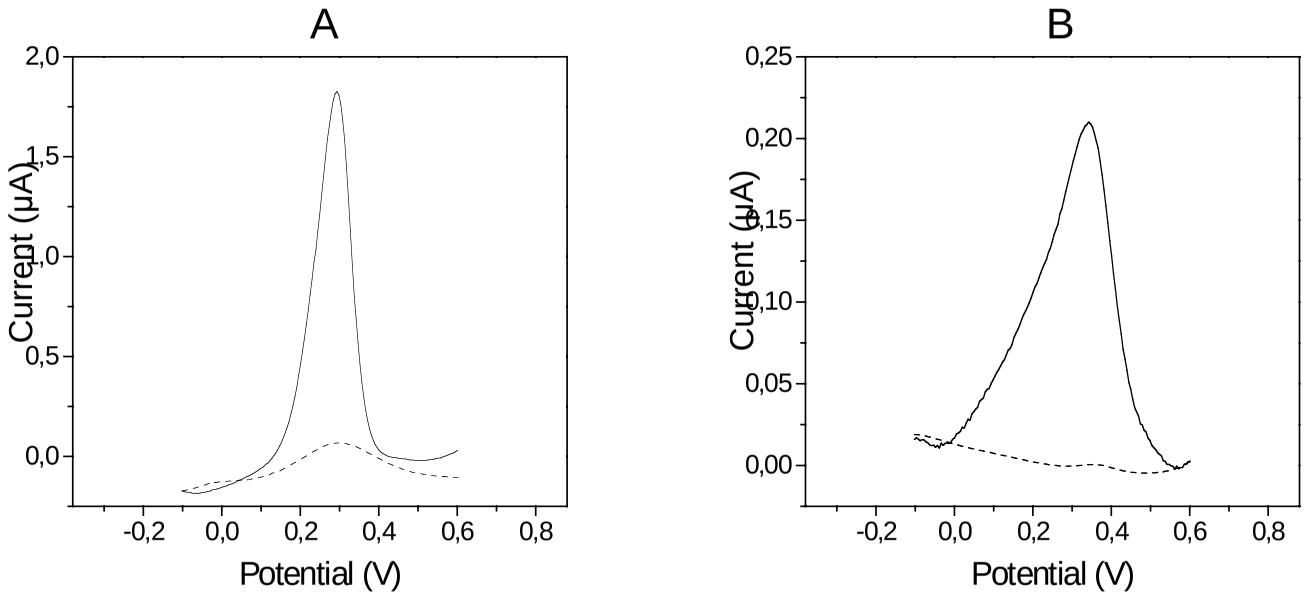

Fig. S2. Anodic stripping differential pulse voltammograms obtained for Cu^{2+} at gold electrodes covered with either an ordered surfactant-templated mesoporous silica film contaning amine groups prepared by the present electrodeposition method (plain curves) or a non-templated amine-functionalized silica film prepared by the same method but in the absence of the surfactant template (dashed curves). Data were obtained after 2 min accumulation at open-circuit from 1×10^{-6} M Cu^{2+} (**A**) and after 15 min preconcentration from 1×10^{-8} M Cu^{2+} solution (**B**).

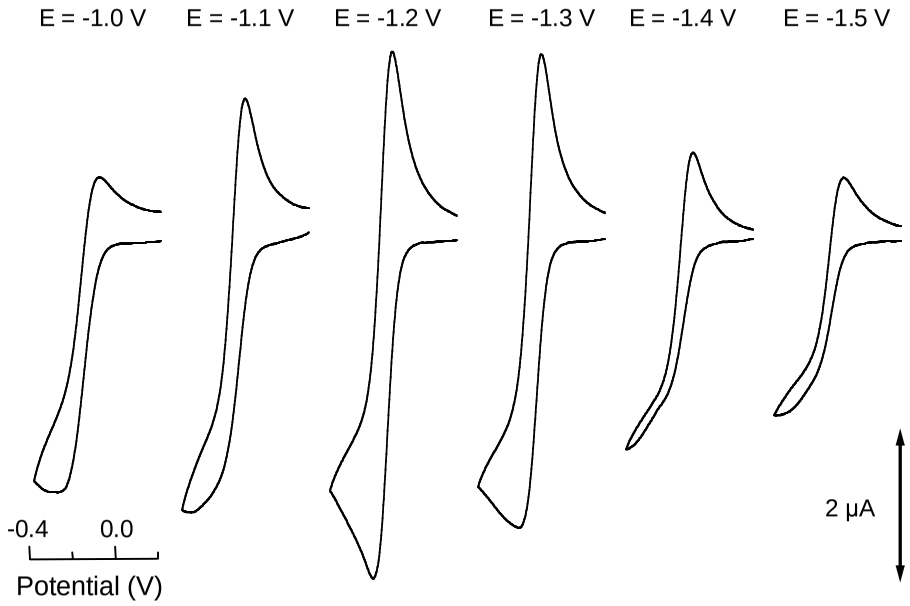

Fig. S3. Influence of the potential value (E = -1.0 V up to -1.5 V) applied to generate surfactant-templated mesoporous silica films on their permeability properties towards an external redox probe ($Ru(NH_3)_6^{3+}$). The films were electrodeposited for 5 s on a gold surface. Cyclic voltammograms were recorded after film aging and surfactant removal, in a solution containing 5 mM $Ru(NH_3)_6^{3+}$. This experiment constitutes an easy way (yet indirect) to find the optimal potential value to apply to perform electrodeposition (i.e, -1.2 V to - 1.3 V for gold).

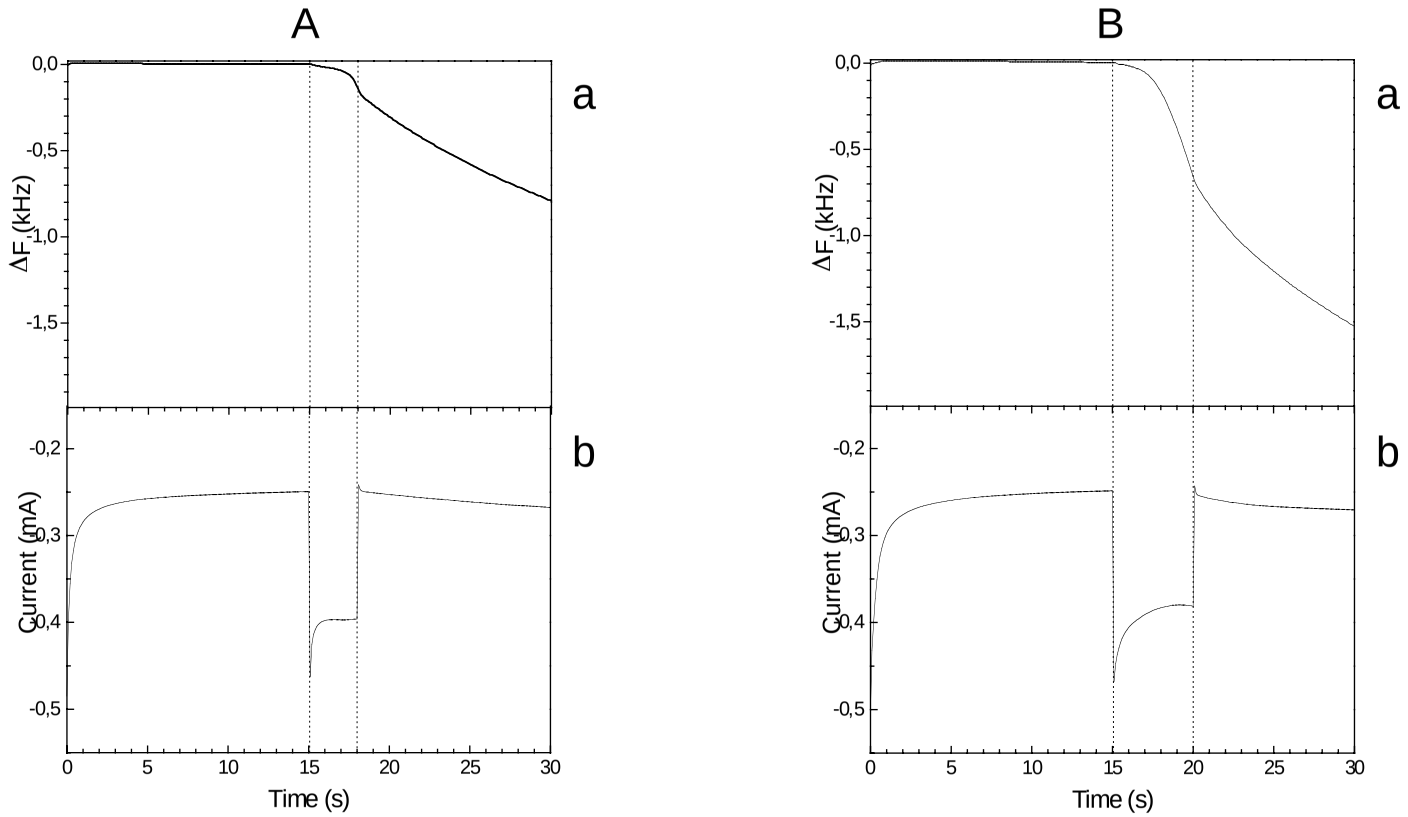

Fig. S4. *In situ* EQCM characterization of the electrodeposition process. **a**, Frequency-time plot (as mass deposits on the substrate, frequency drops). **b**, Corresponding current-time plot. Data have been obtained following a potential step from -0.4 V to -1.3 V, which was applied at time = 15 s for 3 s (**A**) or 5 s (**B**).
After stopping the application of the cathodic potential, the film continued to deposit as a consequence of remaining OH^- species in the diffusion layer at the electrode/solution interface, and this effect was as much more important as longer was the application of the potential (due to a higher amount of catalyst generated at the interface). Meanwhile, this demonstrates that deposition is due to electrocatalysis of the sol-gel process (by local electrochemical manipulation of pH) and not to any electrophoretic deposition process, which was otherwise applied to deposit sol-gel films but under high electric fields.

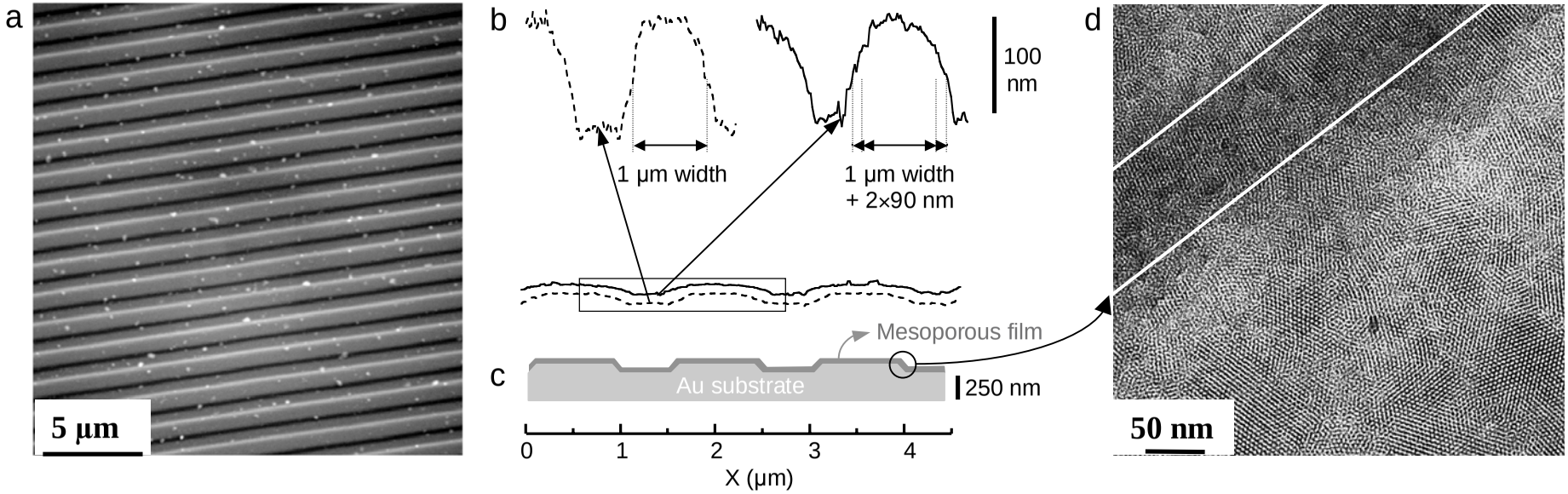

Fig. S5. Microscopic characterization of a film electrodeposited on a gold CD-trode (gold electrode made from recordable CD,44 displaying a regular streaked morphology at the µm-size level). **a**, SEM image. **b**, AFM height profiles measured perpendicularly to the streaked gold substrate before (dashed line) and after (plain line) deposition of the mesoporous silica film, showing clearly the uniform thickness (ca. 90 nm) of the thin film deposited on the whole surface of the regular streaked support. Dotted lines indicate the thickness of the film deposited on the vertical parts of the substrate. **c**, scheme of the underlying substrate. **d**, TEM image of the film showing that mesostructuration is retained on nonplanar portions of the surface (between the white lines).

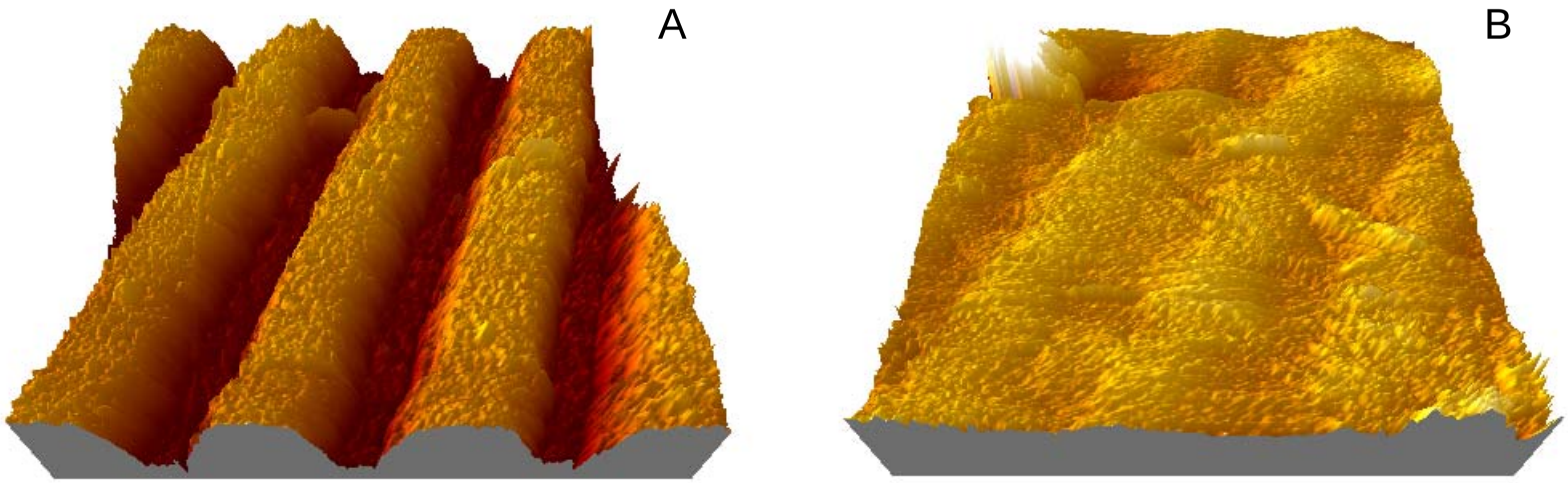

Fig. S6. 3D AFM images (images size 5 by 5 µm, x/y/z ratios taken as 1/1/5) of a bare gold CD-trode (**A**) and the same streaked support covered with a mesoporous silica film prepared by spin-coating evaporation-induced self-assembly (**B**). These results point out the limitation of the spin-coating process to deposit uniform films on non-flat surfaces as the streaked profile of the underlying gold substrate is not maintained after film deposition, contrarily to what was observed for the electrodeposited mesoporous silica films proposed in the present paper (see Fig. S5).