CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

Laboratoire de Chimie Physique et Microbiologie pour l'Environnement

LCPME

Université Henri Poincaré Nancy 1

Electrochemistry with Functionalized Mesoporous Materials

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Advanced micro- and mesoporous materials
September 6-9, 2007, Varna, Bulgaria

Silica-based organic-inorganic hybrids

Combined properties

- Mechanical stability
- Tailored chemical reactivity

Two preparation routes

- Post-synthesis grafting
- One-step synthesis by sol-gel

Interest of mesostructured materials

Some target applications

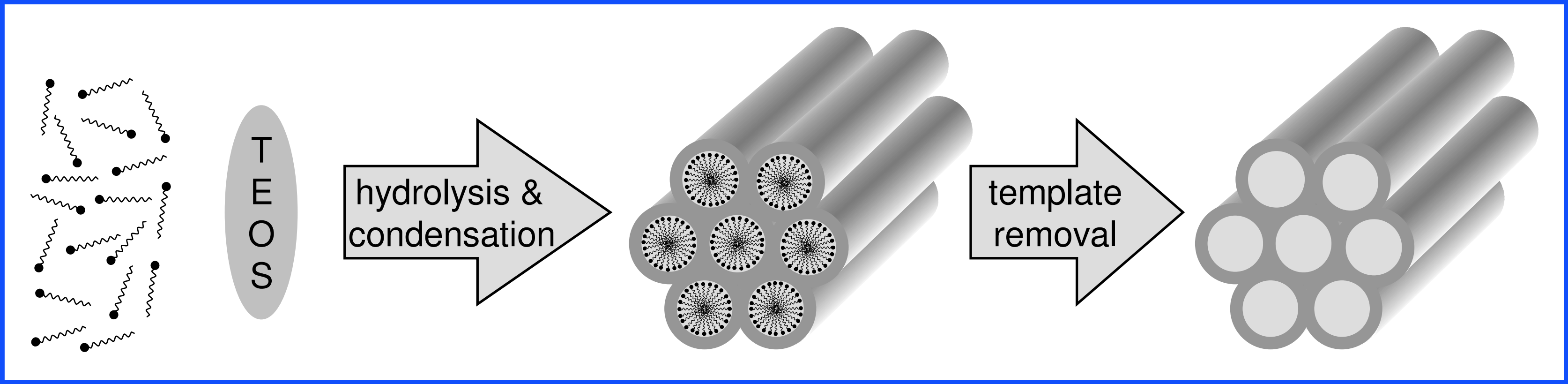
- Remediation
- Electrochemistry
- Catalysis

Some relevant requirements

- High capacity, great affinity for target species
- Recognition and host properties, fast diffusion
- High surface areas, many reactive centers

Ordered mesoporous silica

Sol-gel formation of silica around a surfactant template:
the example of MCM-41 displaying a hexagonal structure



Kresge *et al.*, *Nature* 359 (1992) 710

<u>Attractive characteristics</u>:

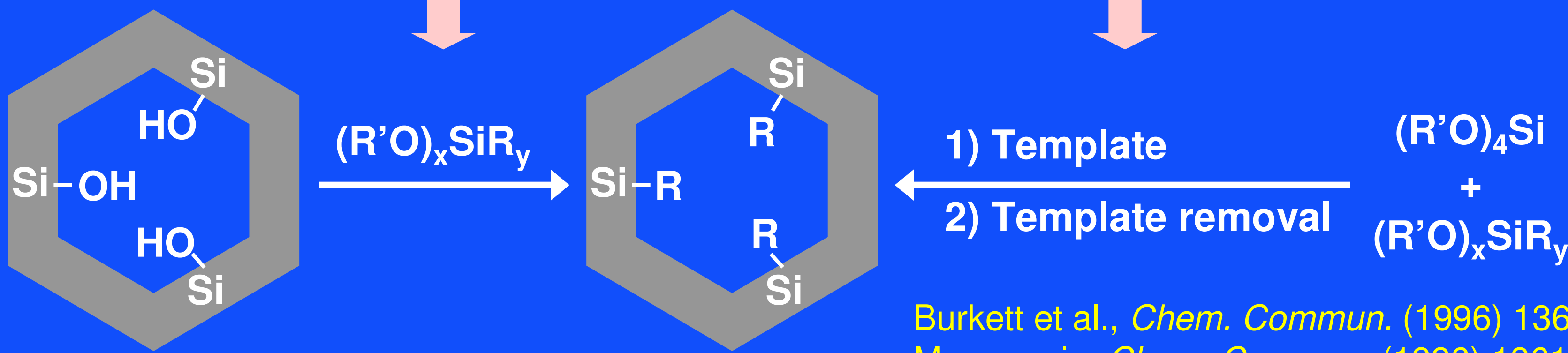
- Regular pores of monodisperse size (2-10 nm range)
- High specific surface area (500-1500 $m^2\ g^{-1}$)
- Surface reactivity similar to that of amorphous silica (e.g. possibility of grafting organic groups)

Hybrid organic-inorganic mesoporous silica

How to prepare organically-modified mesoporous silicas ?

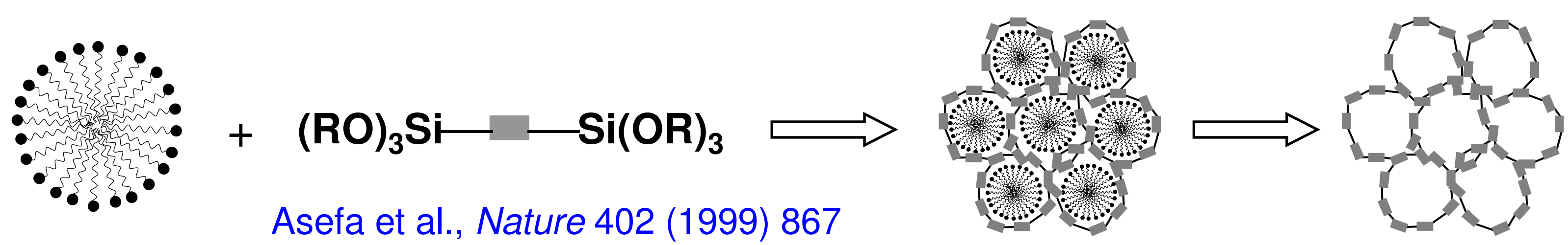
Post-synthesis grafting

Direct synthesis



Burkett et al., *Chem. Commun.* (1996) 1367
Macquarrie, *Chem. Commun.* (1996) 1961

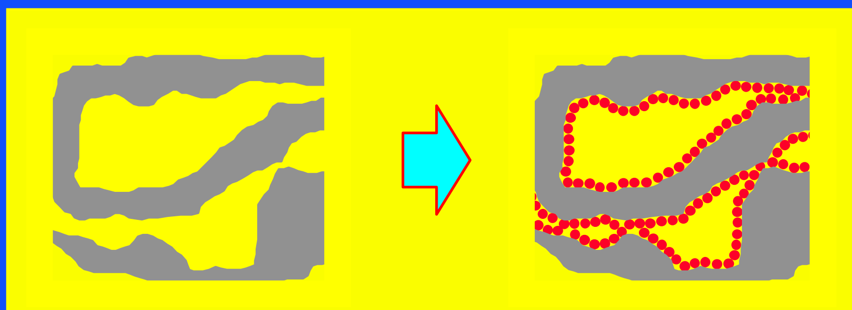
Synthesis of periodic mesoporous organosilicas



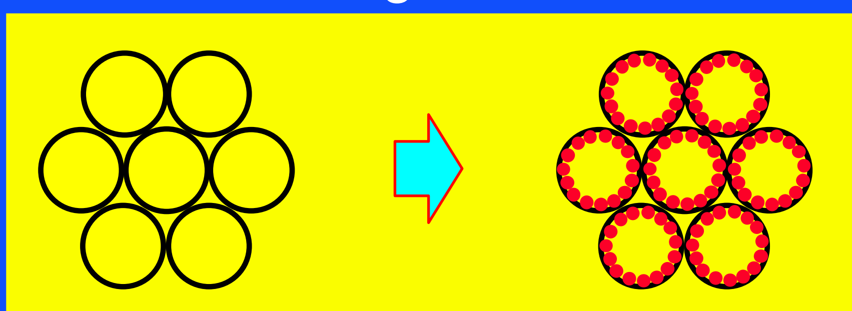
Hoffmann, Cornelius, Morell, Fröba, *Angew. Chem. Int. Ed.* 45 (2006) 3216

Grafted silicas: amorphous *versus* ordered

Grafting amorphous silica gel

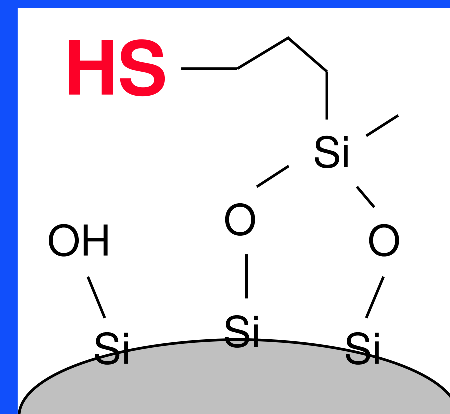


Grafting MCM-41



Easier access to
the binding sites !

Example of MPS



Uptake of Hg^{II} species:

100 % with MPS-MCM-41

incomplete accessibility
with amorphous MPS

Mesoporous silicas and electrochemistry

Several promising avenues:

- Ordered and open structure: effective and selective binding processes
- High porous volume: fast mass transport expected
- Host for reactants (catalysts, macromolecules, enzymes …)

Walcarius, *C.R. Chim.* 8 (2005) 693

One Problem: these solids are electronic insulators !

Two main methodological approaches to prepare silica-modified electrodes

Dispersion of silica in the bulk of a composite matrix

Deposition of a silica film on a solid electrode surface

Outline

Electrochemical characterization of materials reactivity

- Adsorption isotherms with the aid of organosilica modified electrodes
- Rate of access to the binding sites

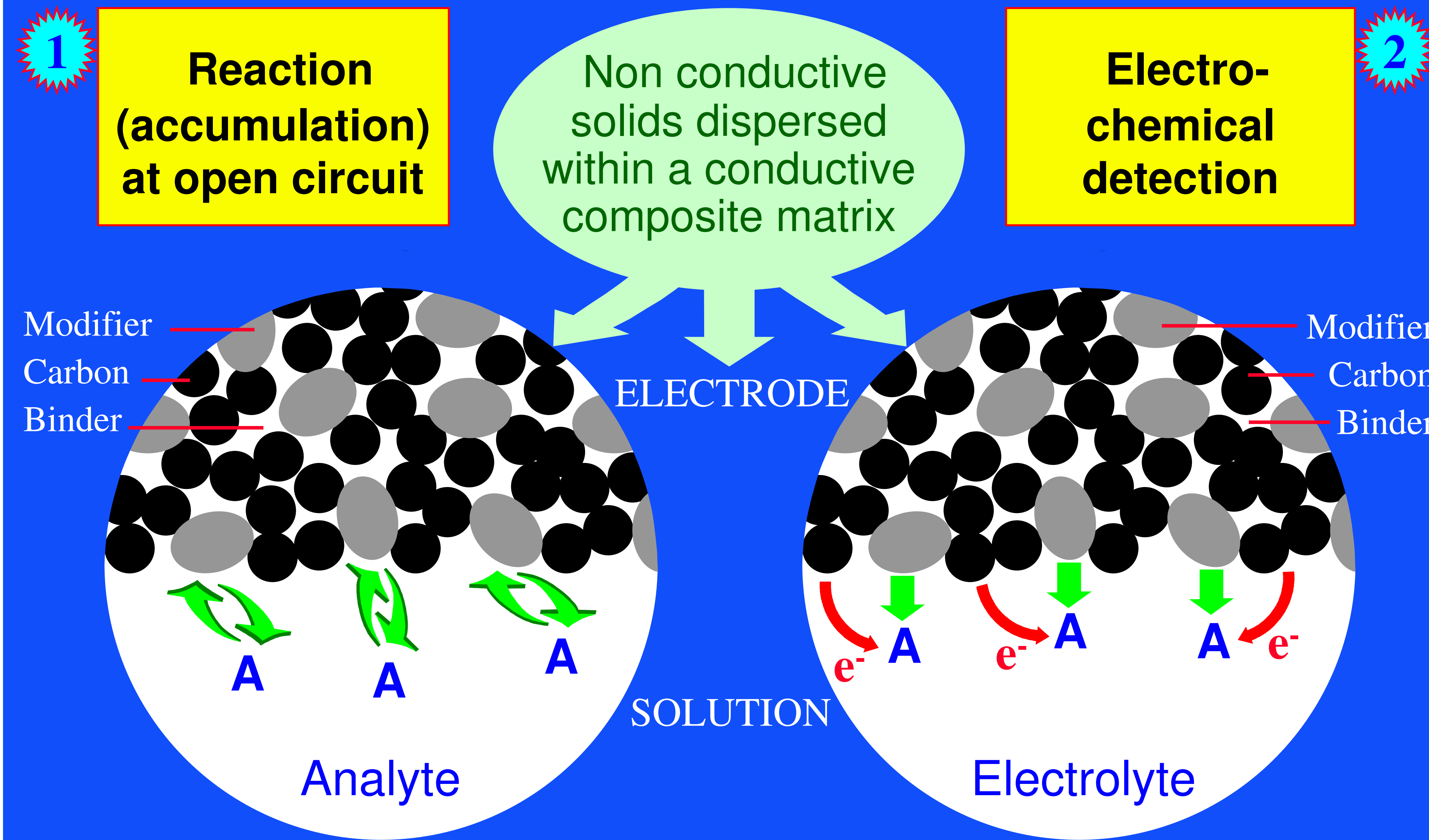
Interest of mesoporous organosilica in electroanalysis

(Hg(II) or Cu(II) sensing)

Electro-assisted generation of (organo)silica thin films

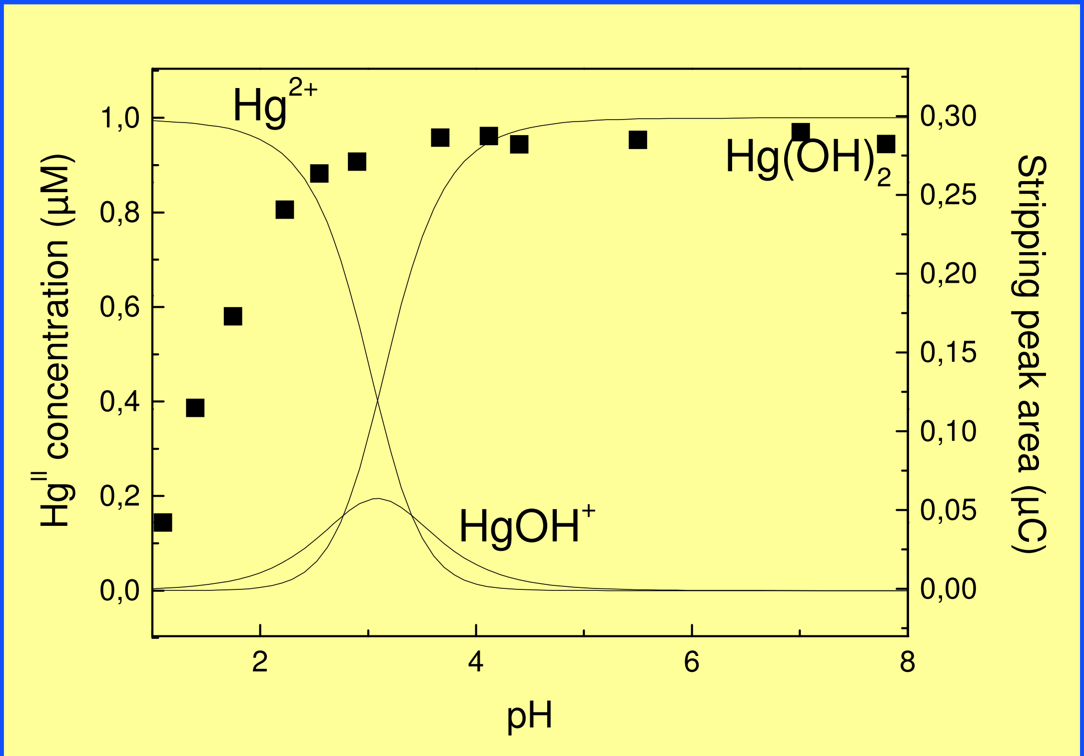
(Mesostructured <u>and</u> oriented silica films)

Accumulation-detection at MCPEs



Electrochemical monitoring of Hg^{II} binding on APS as a function of pH

10^{-6} M Hg^{II} in the absence of Cl^-



Superimposition with a diagram depicting the distribution of the hydrolysis products of mercury

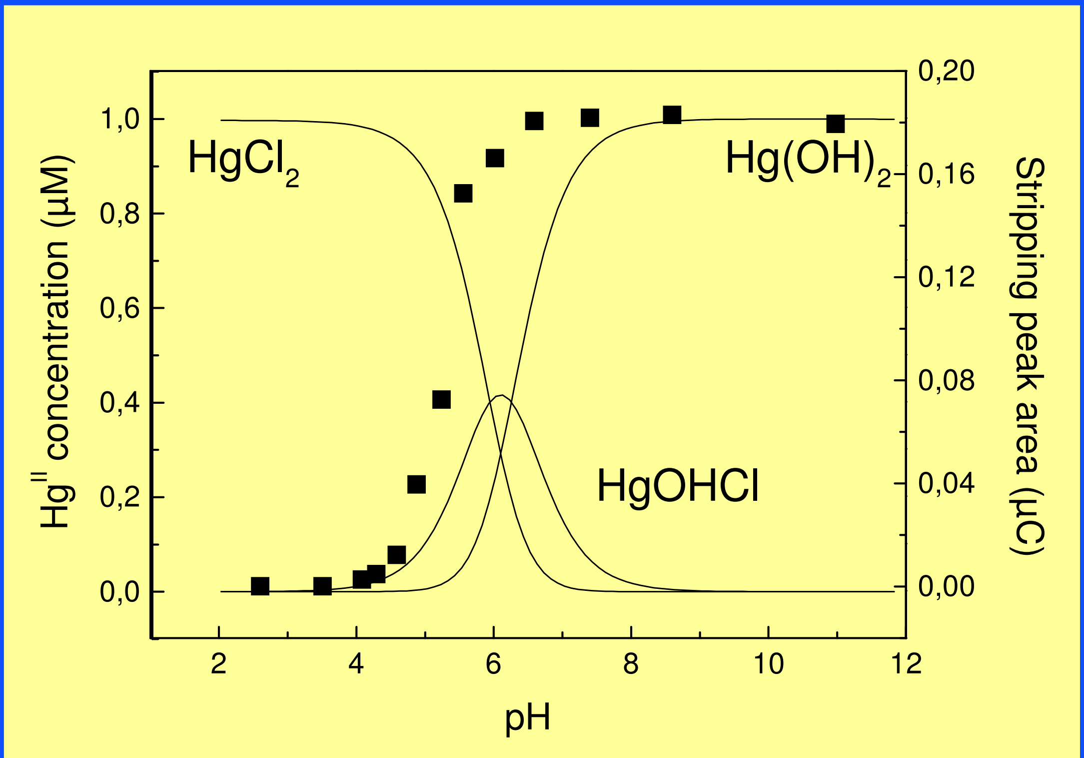
All the Hg^{II} species are liable to interact with APS

High ligand concentration in the materials induces non negligible amounts of amine groups, even at low pH

Walcarius et al., *Anal. Chim. Acta* 508 (2004) 87

Electrochemical monitoring of Hg^{II} binding on APS as a function of pH

10^{-6} M Hg^{II} in the presence of 10^{-4} M Cl^-



Superimposition with a diagram depicting the distribution of the hydrolysis products of mercury

The only adsorbed species are $Hg(OH)_2$ and HgOHCl

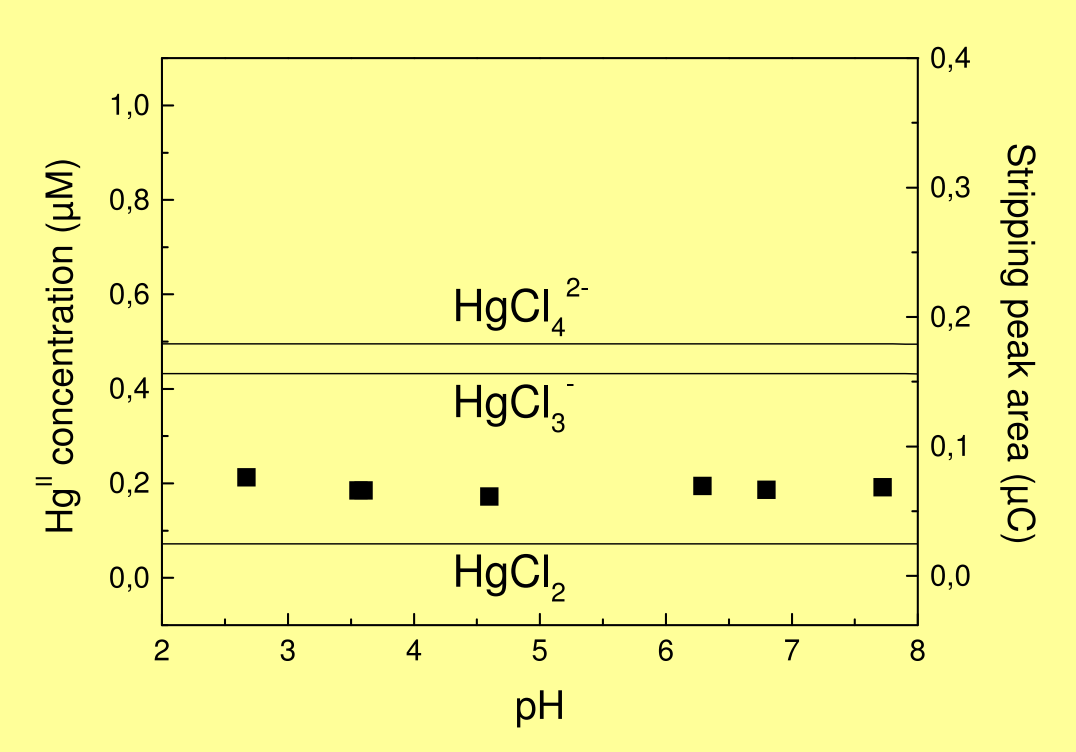
$HgCl_2$ is too stable to allow formation of a Hg^{II}-amine complex

Walcarius et al., *Anal. Chim. Acta* 508 (2004) 87

Electrochemical monitoring of Hg^{II} binding on APS as a function of pH

3/3

10^{-6} M Hg^{II} in the presence of 0.5 M Cl^-



Protonated amine groups ($R\text{-}NH_3^+Cl^-$) are liable to accumulate the negatively-charged chloro-complexes of Hg^{II} by ion exchange

Reaction is less quantitative than complexation because of competing action of Cl^- species

Walcarius et al., *Anal. Chim. Acta* 508 (2004) 87

Monitoring Hg^{II} binding on MPS

- Independent on pH (up to 10)
- Independent on Cl^- concentration

Access to the most common forms of inorganic mercury(II)

$Hg(OH)_2$ by complexation on APS

$HgCl_3^-$ and $HgCl_4^{2-}$ by electrostatic binding on protonated APS

$Hg(OH)_2 + HgCl_2 + HgCl_3^- + HgCl_4^{2-}$ by complexation on MPS

$HgCl_2$ by difference between APS and MPS

Preconcentration at modified electrodes

Rate-determining step: diffusion of analytes

organic-inorganic hybrids

<u>Preconcentration</u>:
diffusion to the binding sites in the porous matrix

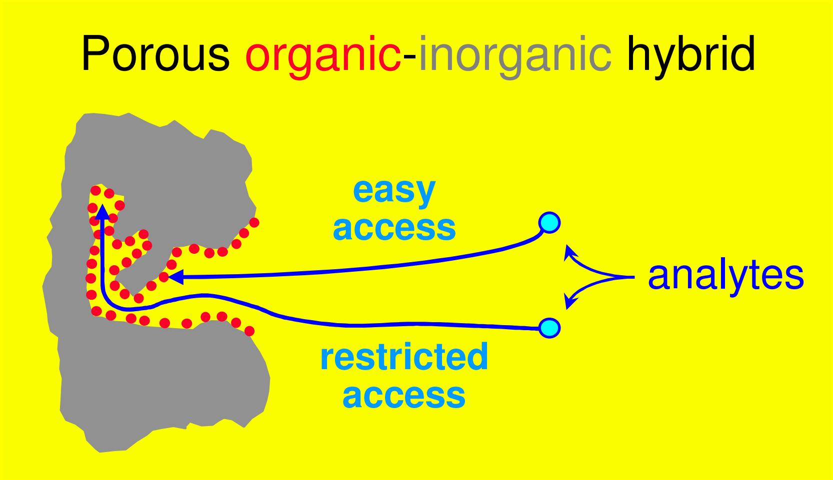
<u>Detection</u>:
diffusion out of the solid, to the electrode surface

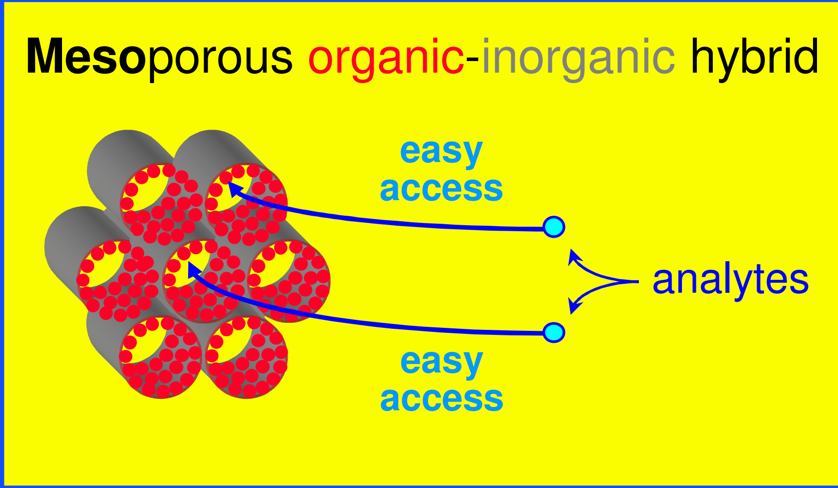
Electrochemical detection subsequent to open-circuit accumulation:
need for improving diffusion processes to get high sensitivity

Interest of ordered mesoporous silica

Rate of access to the binding sites

Problematic: mass transfer in porous medium





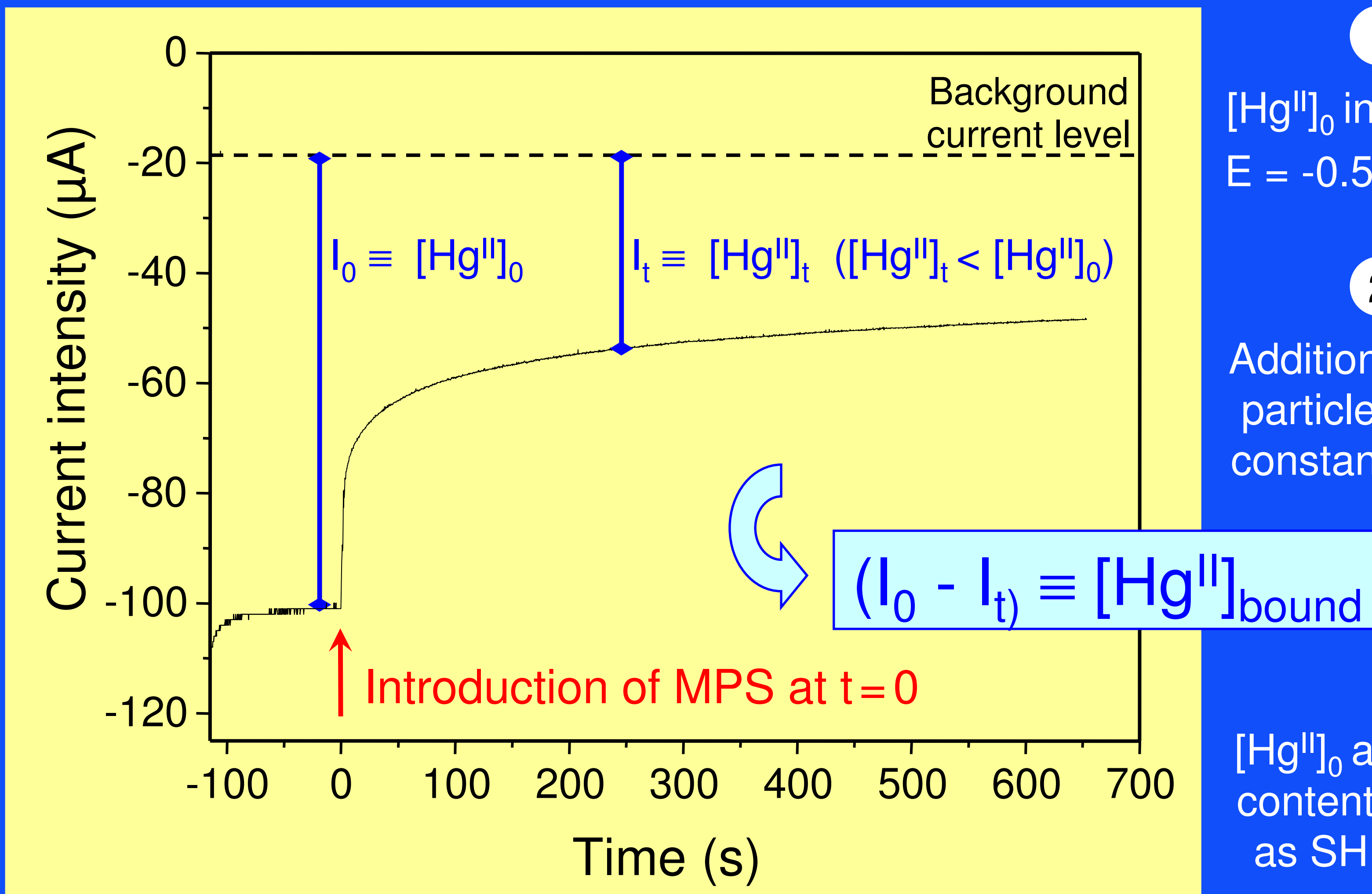
Monitoring the speed of access to the binding sites

Diffusion: usually fast (analysis by intermittent sampling: banished)

Need: fast in situ method likely to monitor continuously the consumption of the analyte from the external solution

General principle for kinetic studies

Steady state amperometry at rotating disk electrode



1

$[Hg^{II}]_0$ in solution

$E = -0.5\ V_{(Ag/AgCl)}$

2

Addition of MPS particles under constant stirring

$[Hg^{II}]_0$ and MPS content chosen as SH:Hg = 1

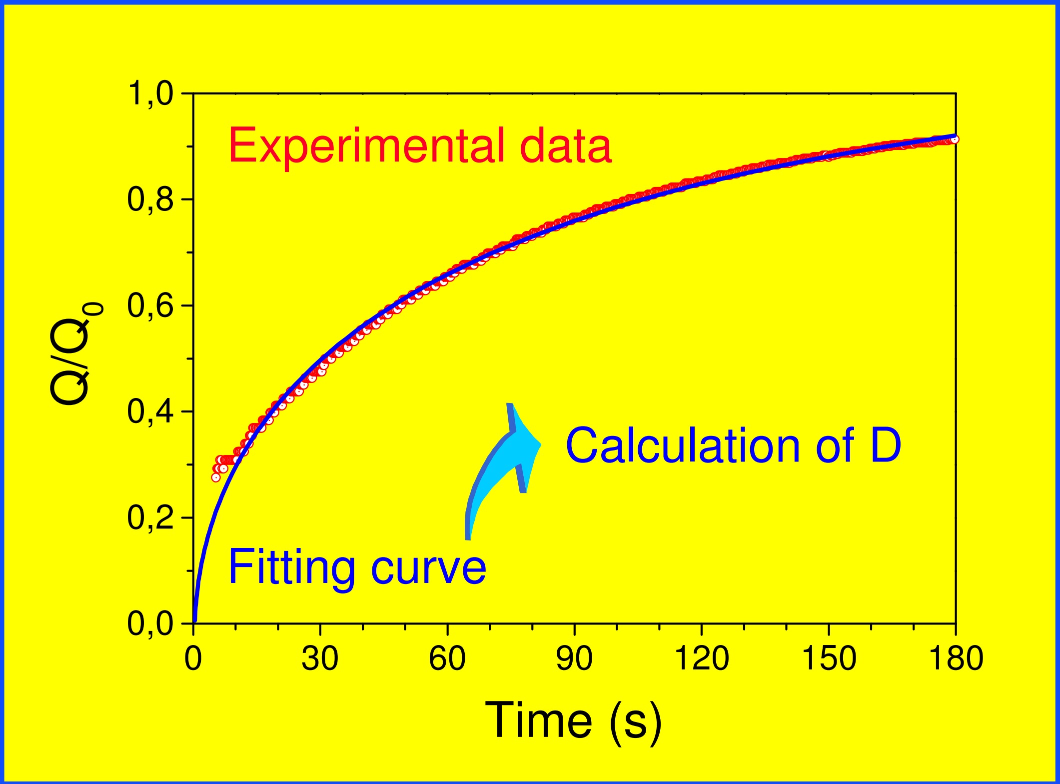
Kinetic data treatment

Data presentation:

Q/Q_0 curves

Q = fixed amount at time "t"

Q_0 = maximum capacity (fixed amount at t = ∞)



Data treatment:

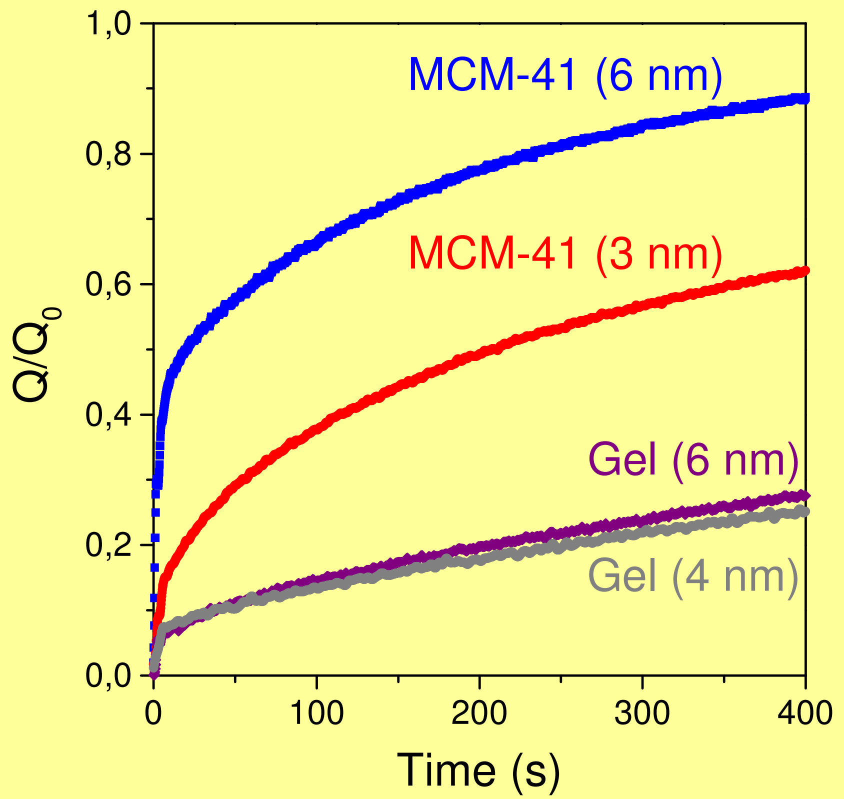
Fitting data according to a spherical diffusion model

$$\frac{Q}{Q_0} = 6\left(\frac{Dt}{a^2}\right)^{0,5} * \left\{\pi^{-0,5} + 2\sum_{n=1}^{\infty}(-1)^n \operatorname{ierfc}\left(\frac{n*a}{\sqrt{Dt}}\right)\right\} - 3\left(\frac{Dt}{a^2}\right)$$

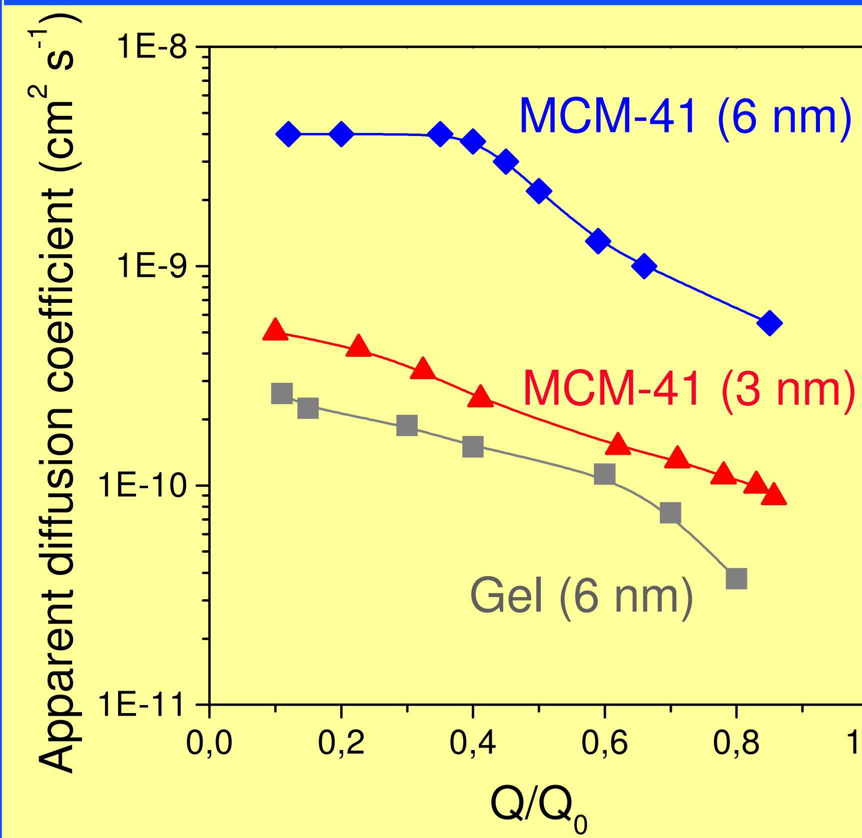
D = apparent diffusion coefficient ($cm^2\ s^{-1}$) ; a = particle radius (cm)

Hg^{II} in MPS: amorphous *versus* ordered

Experimental data points



Apparent diffusion coefficients

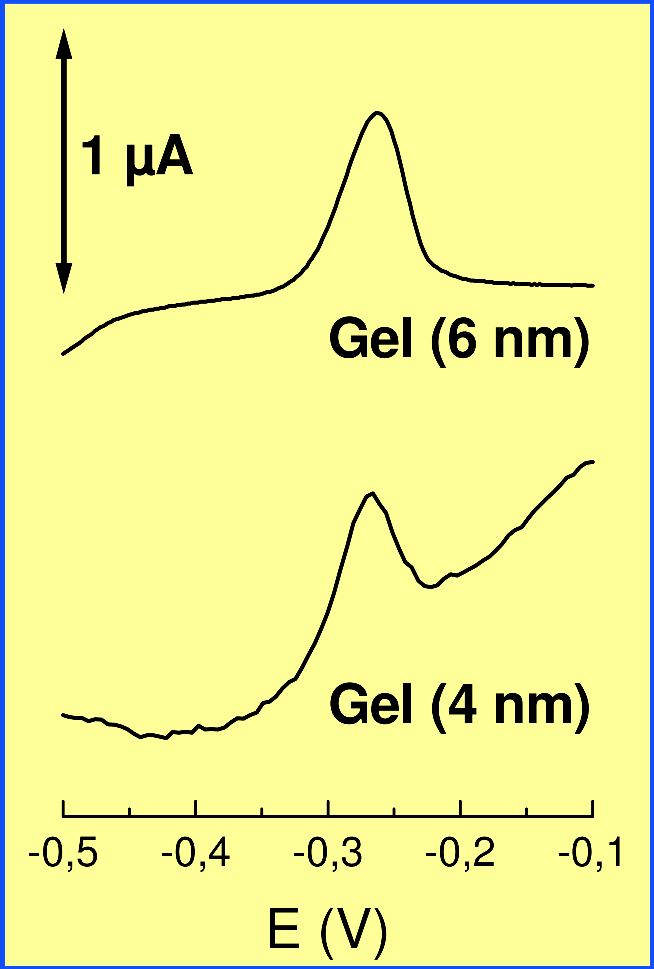


Faster mass transfer rates in ordered mesoporous adsorbents

D_{app} values tend to decrease when reaching the maximum capacity

Walcarius et al., *Chem. Mater.* 15 (2003) 2161

Preconcentration analysis of Hg^{II} at MPS-modified carbon paste electrodes

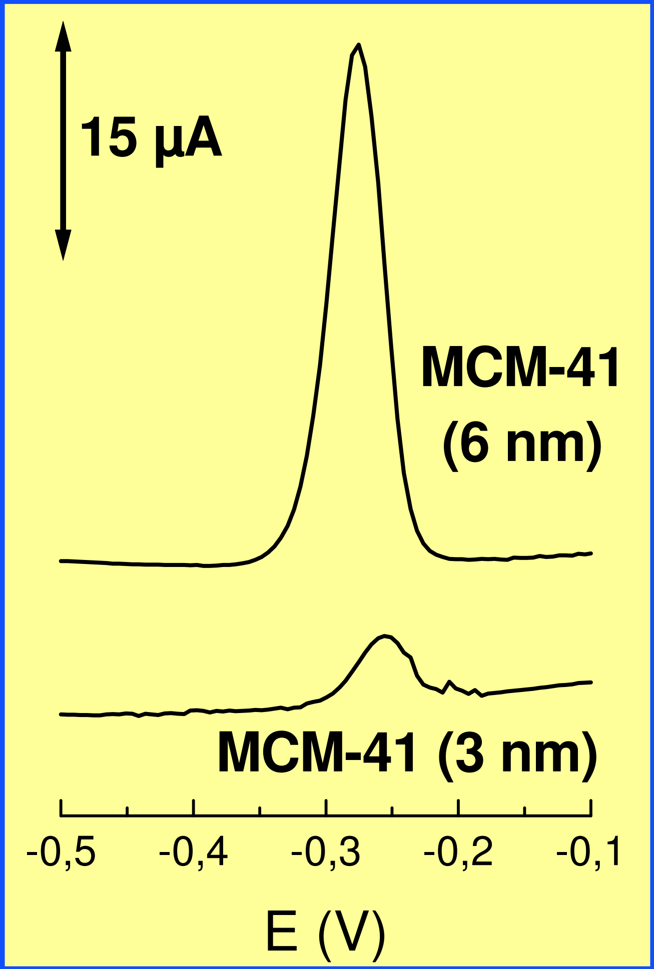


10^{-6} M Hg^{II}

2 min acc.

Detection by ASDPV

Walcarius et al. *Electroanalysis* 15 (2003) 414



Clear advantage for ordered materials over amorphous solids

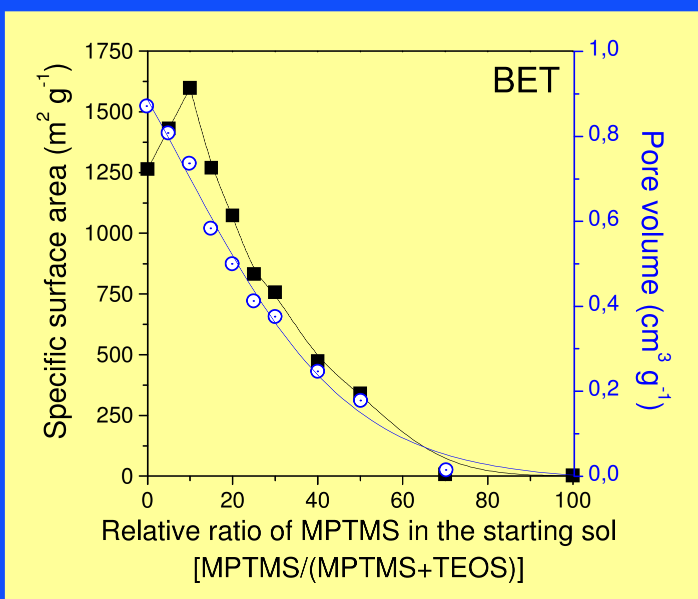
Thiol-functionalized mesoporous silicas obtained by the co-condensation route

Limitation of the grafting process

- Amount of functional groups restricted by the specific surface area
- Heterogeneous distribution of the organo-functional groups

Interest … and drawback of the co-condensation route

Example: TEOS + MPTMS (+ CTAB)

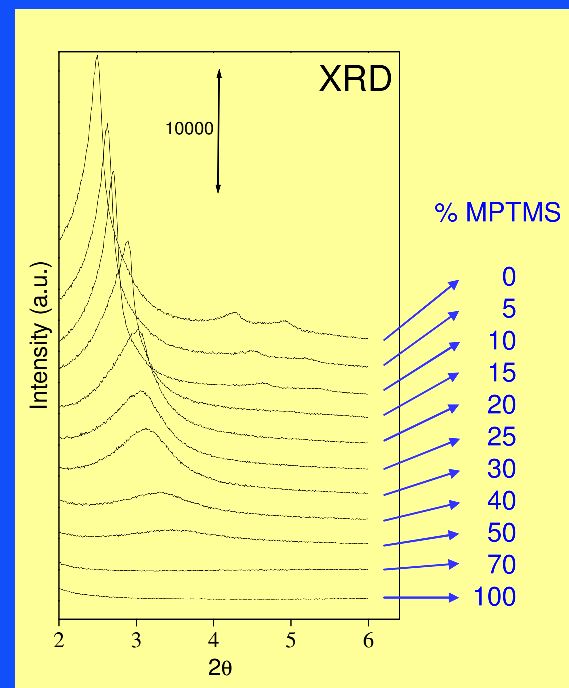


As MPTMS ↗ :

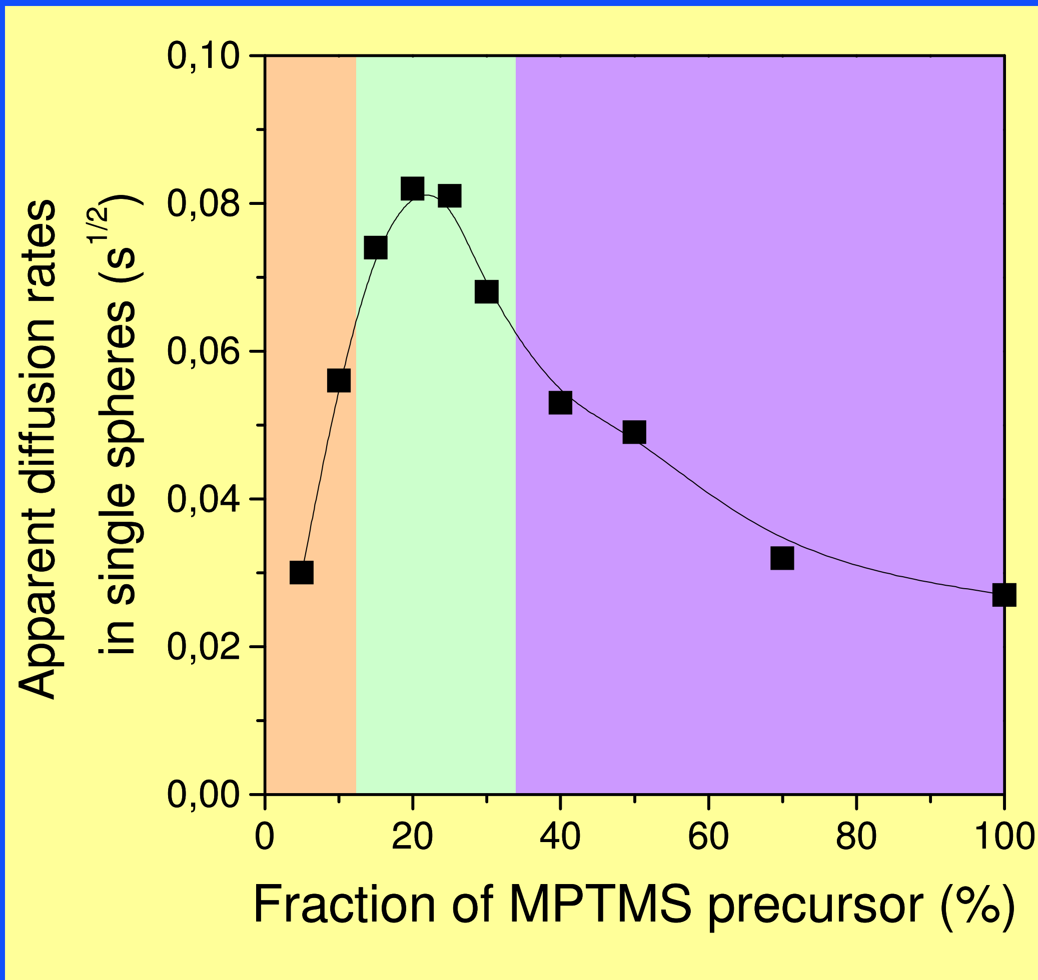
density of functional groups ↗

level of ordering ↘

porosity ↘

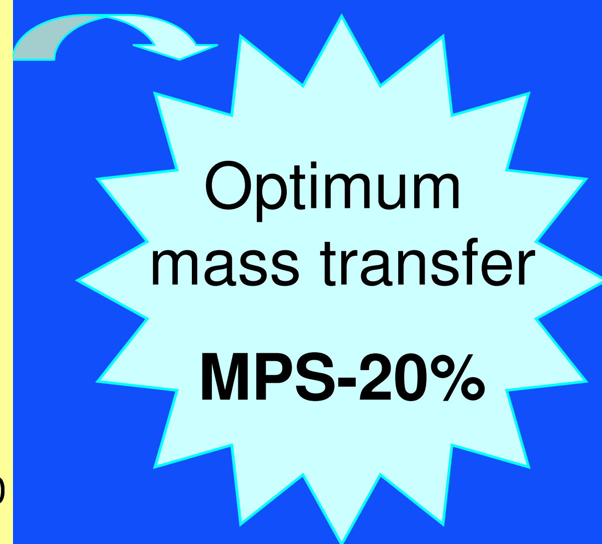


Access rates of Hg^{II} in thiol-functionalized mesoporous silicas obtained by the co-condensation route



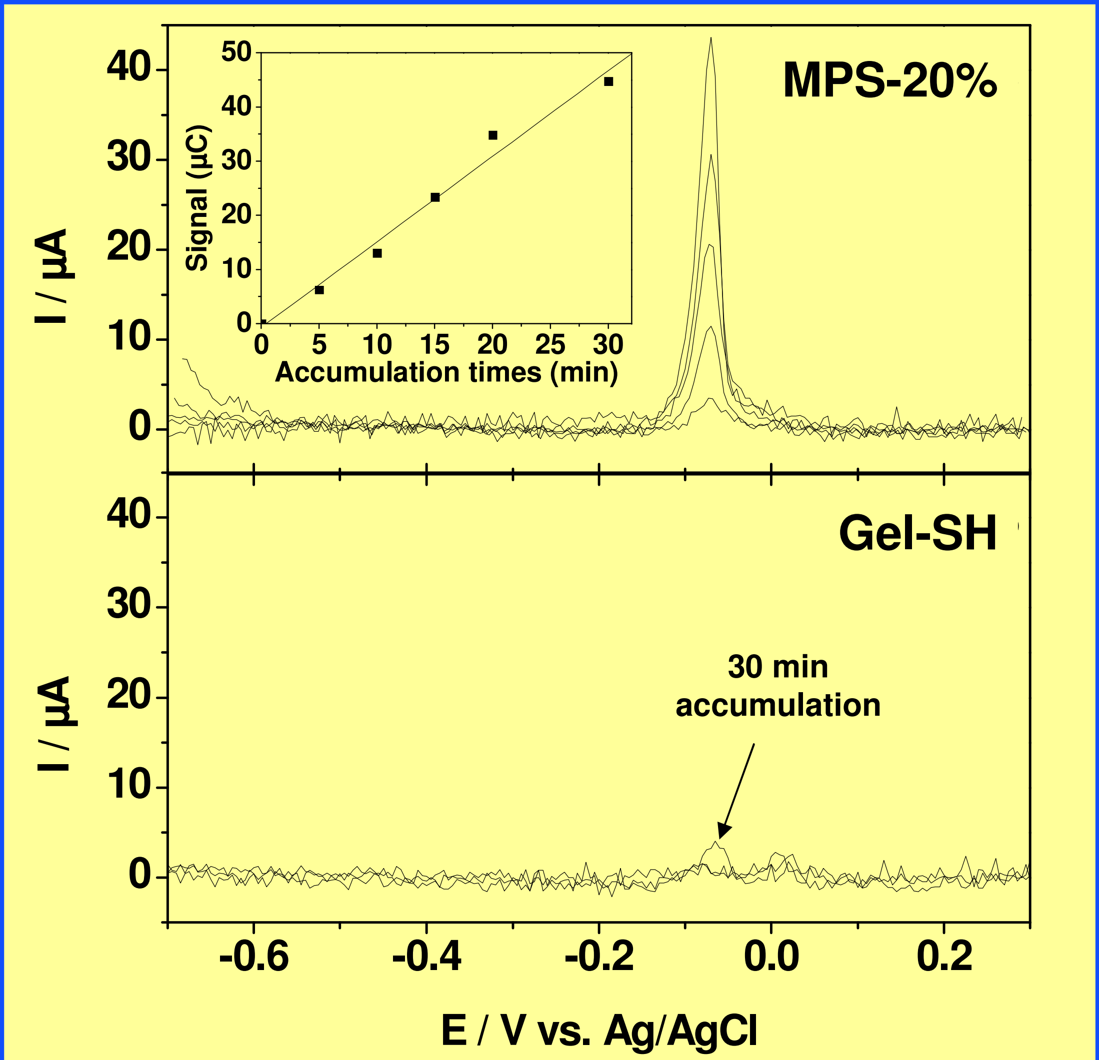
Synthesis of MPS-*x*% spheres

TEOS + *x* % MPTMS
(+ CTAB + NH_3)



Walcarius & Delacôte,
Chem. Mater. 15 (2003) 4181

Preconcentration analysis of Hg^{II} at MPS-modified carbon paste electrodes



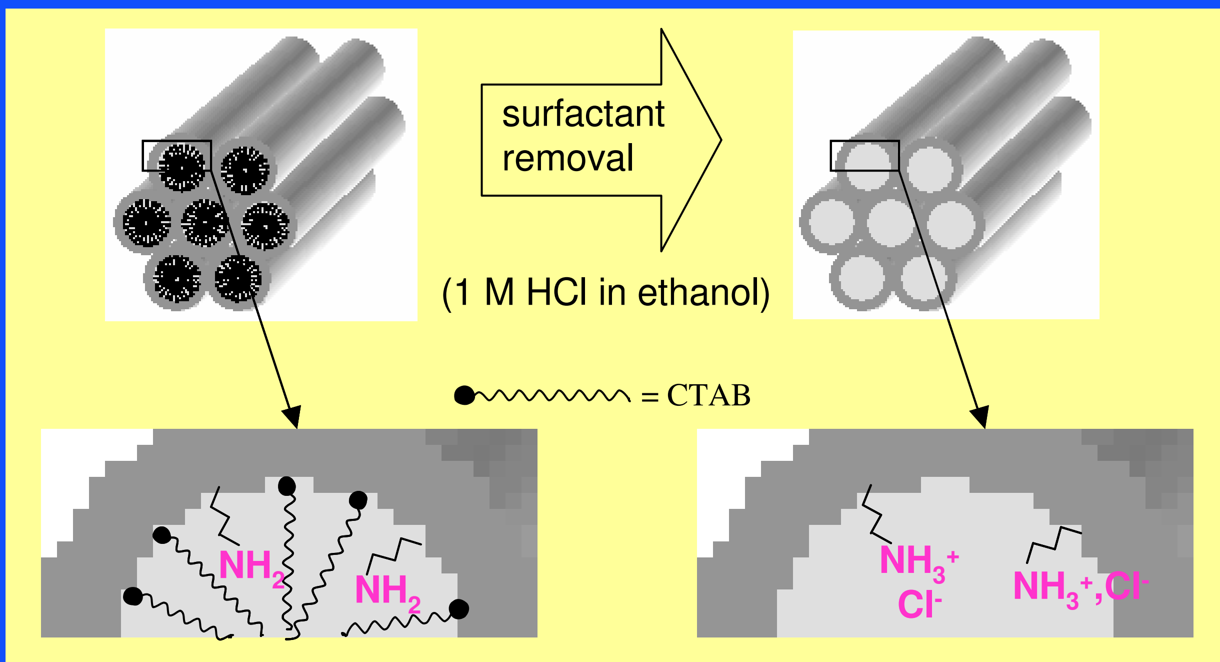
Effect of acc. time from 5×10^{-7} M Hg^{II}

Detection by ASDPV

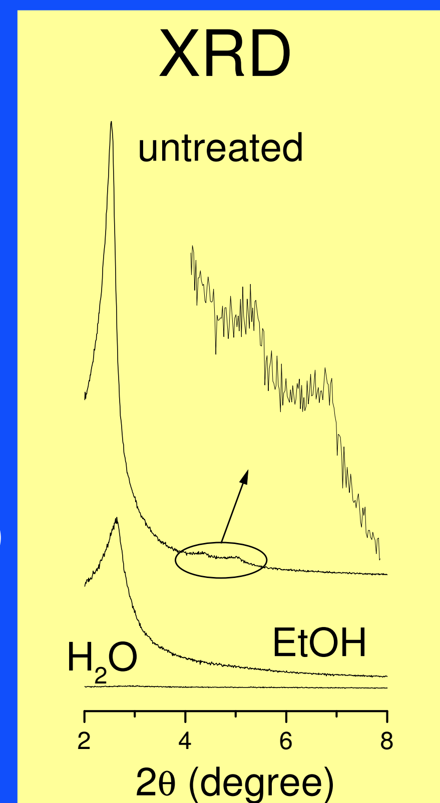
Sensitivity enhancement due to structural order

Etienne et al., in *Progress in Electrochemistry Research* (2005) pp. 145-184

Preconcentration of Cu^{II} at mesoporous APS obtained by co-condensation



Cu^{II} binding to ~~NH_2



~~NH_3^+ must be deprotonated !

OH^-

e^-

$$NH_3^+ \rightleftharpoons NH_2 + H^+$$

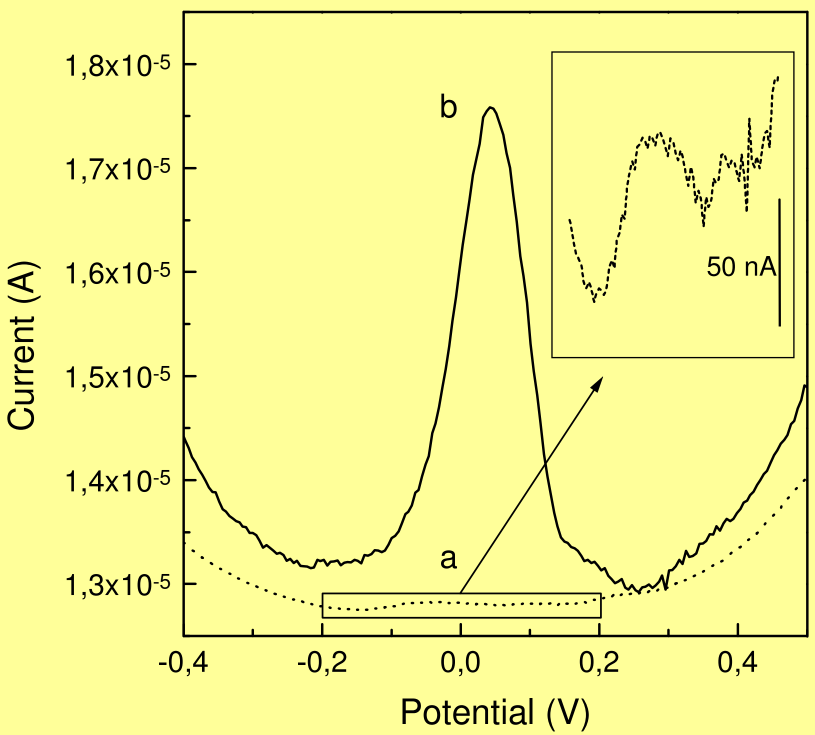
Elchem. shift

$$H^+ + e^- \rightarrow 1/2\ H_2\nearrow$$

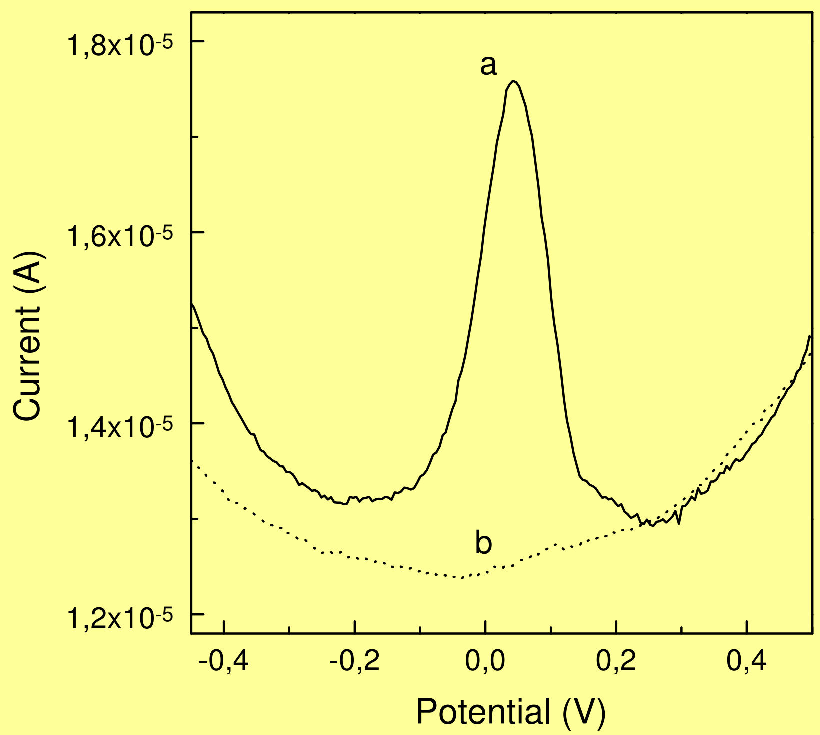
Preconcentration analysis of Cu^{II} at APS-modified carbon paste electrodes

Interest of the electrochemical deprotonation step

1 min acc. from 10 µM Cu^{2+}

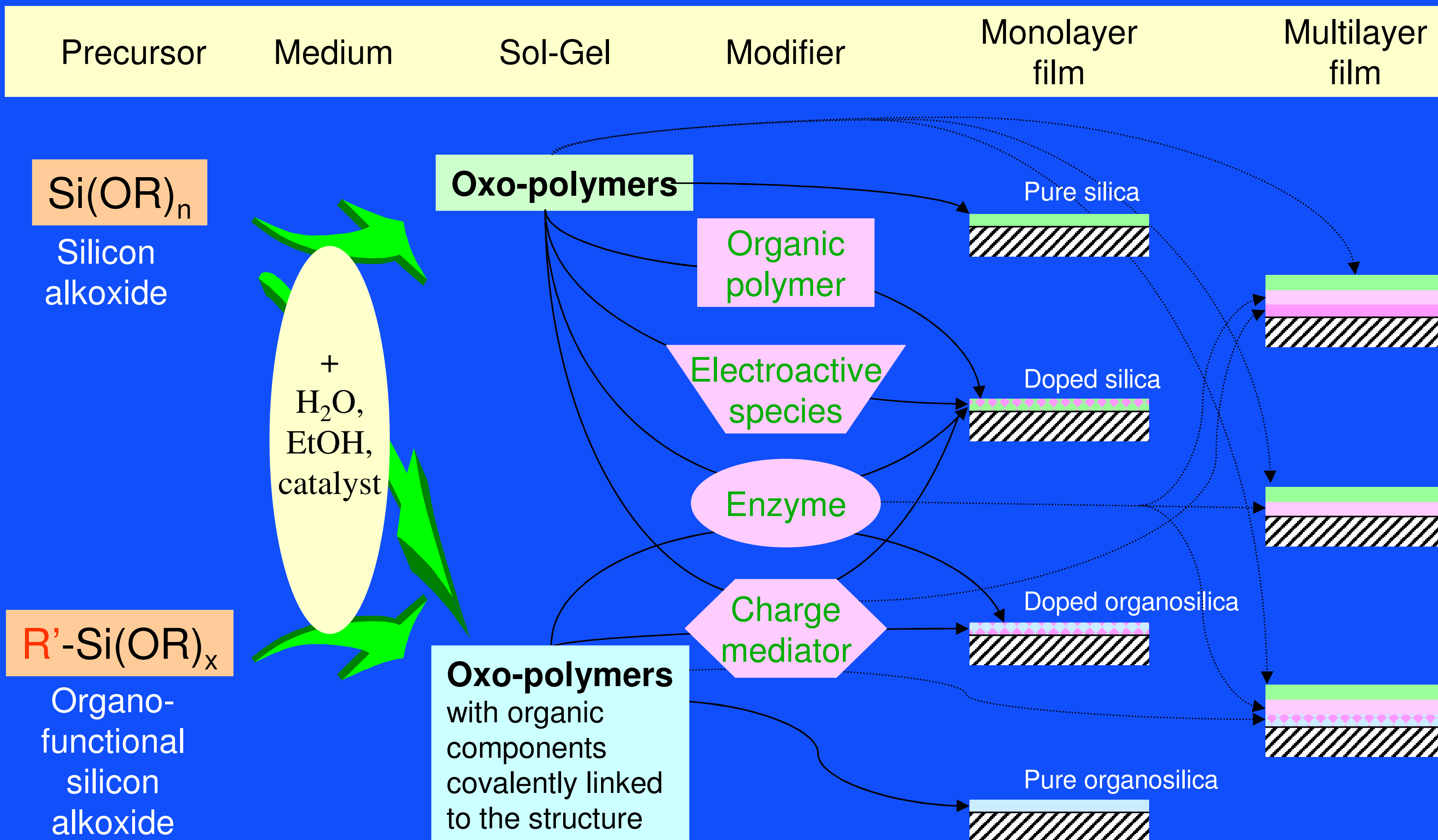


Easy regeneration



Sayen & Walcarius, *J. Electroanal. Chem.* 581 (2005) 70

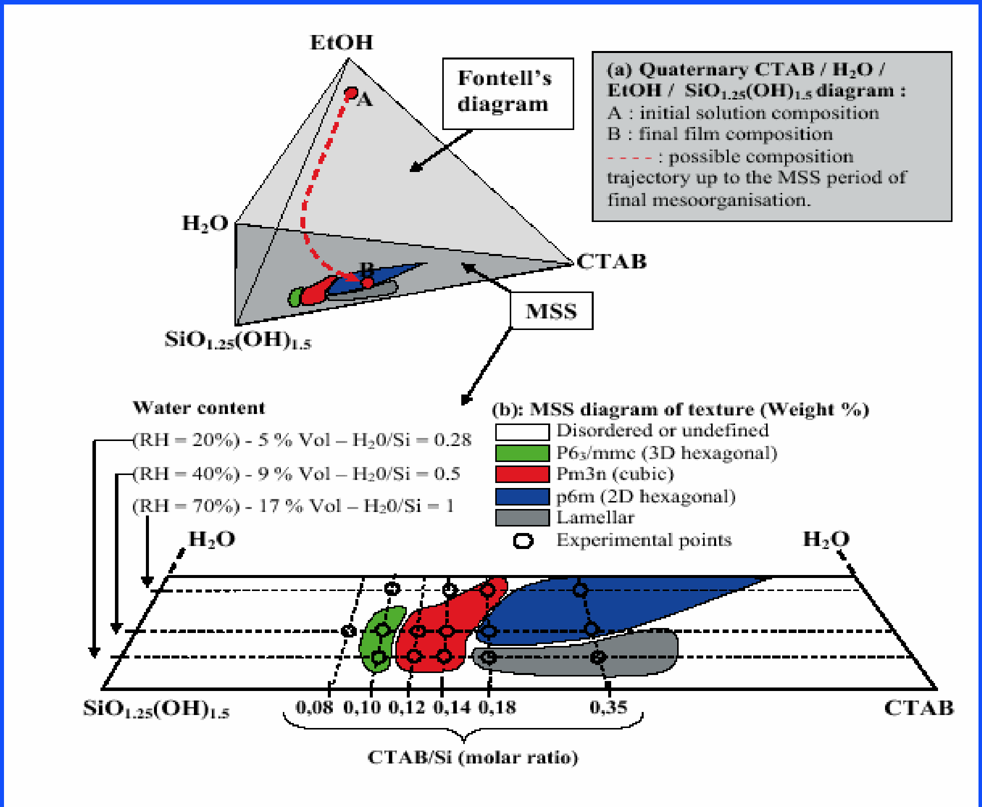
(organo)silica-sol-gel films on electrodes



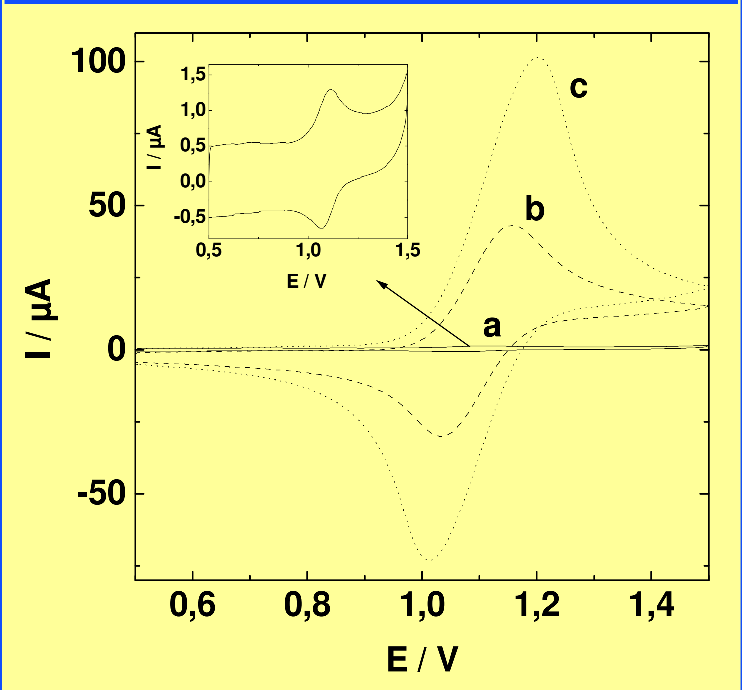
P. Audebert and A. Walcarius, in *Functional Hybrid Materials*, Eds. P. Gomez-Romero and C. Sanchez, Wiley-VCH, Weinheim (2004), Chap. 6, pp. 172-209

Mesostructured thin films on electrodes

Formation by Evaporation-Induced Self-Assembly (EISA)



Hexagonal 2-D and 3-D, cubic



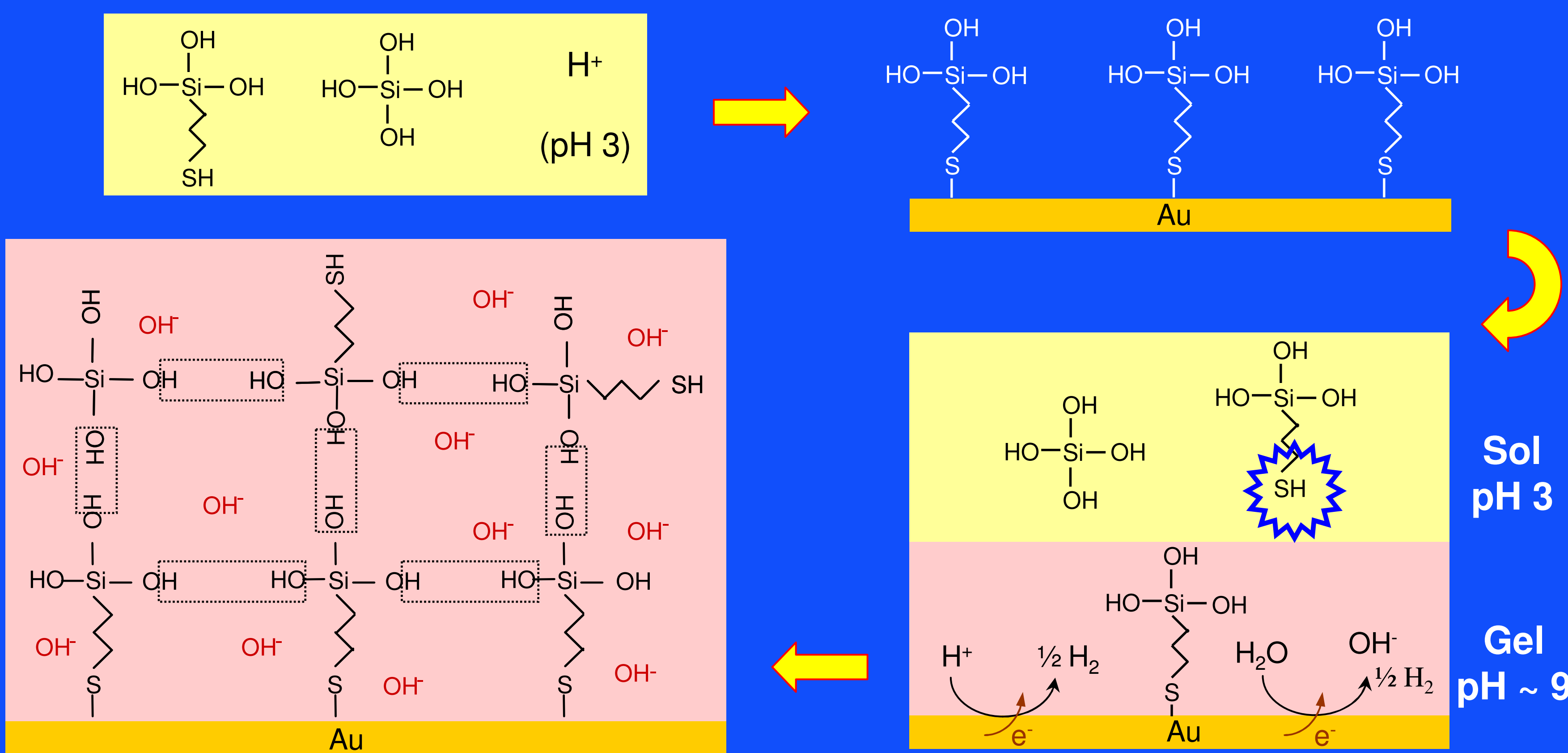
Next step: extension to functionalized films

M. Etienne, A. Quach, D. Grosso, L. Nicole, C. Sanchez, A. Walcarius, *Chem. Mater.* 19 (2007) 844

Electro-assisted generation of hybrid films

Formation of homogeneous organosilica films adhering well on electrode

Sol-gel process - self-assembly - local pH control by electrochemistry



S. Sayen, A. Walcarius, *Electrochem. Commun.* 5 (2003) 341

Oriented mesoporous silica thin films ?

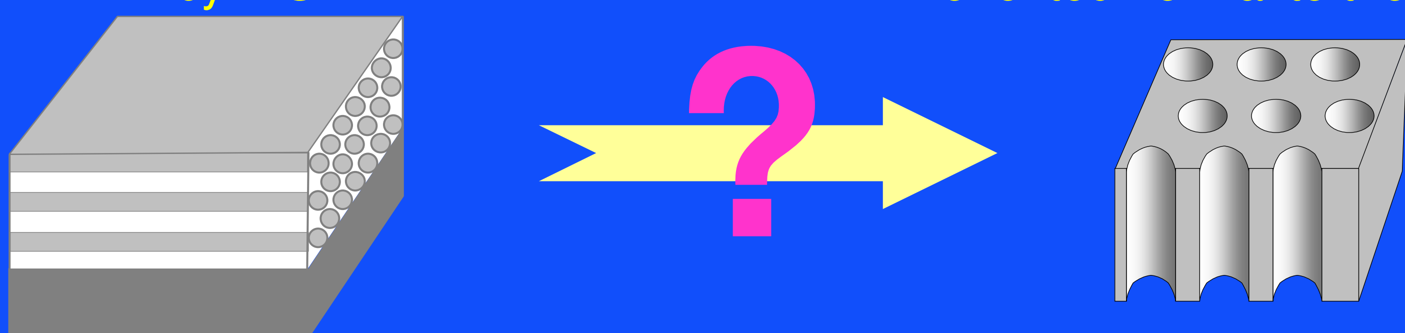
… A MAJOR CHALLENGE to date !!!

"A fundamental question is how nucleation and orientation can be controlled via chemical modification of the underlying surface and/or dimensional confinement of the self-assembly process"

C. J. Brinker & D. R. Dunphy
Morphological control of surfactant-templated metal oxide films
Curr. Opin. Coll. Interface Sci. 11 (2006) 126

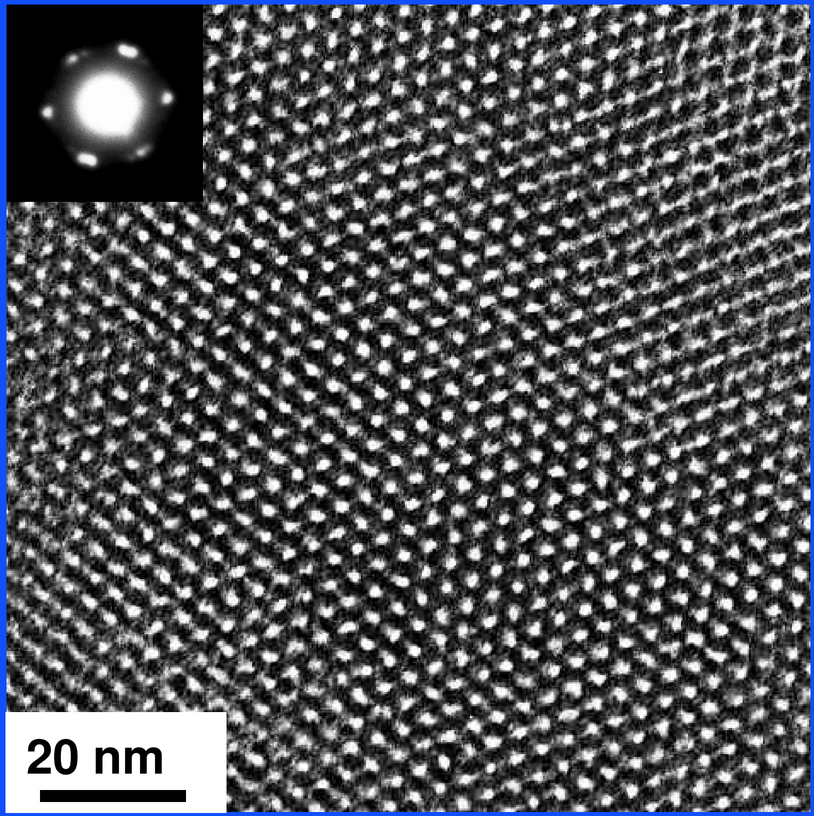
2D-Hex mesostructures by EISA

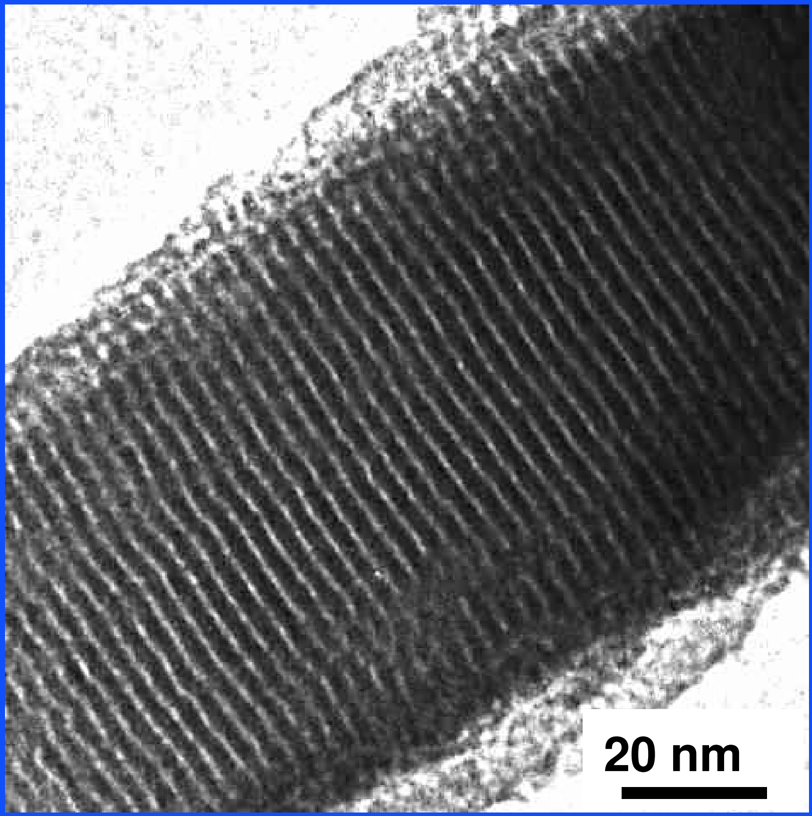
2D-Hex mesostructures oriented normal to the substrate



Oriented mesoporous silica film on electrode

Electrochemistry is likely to provide well-ordered mesoporous silica films



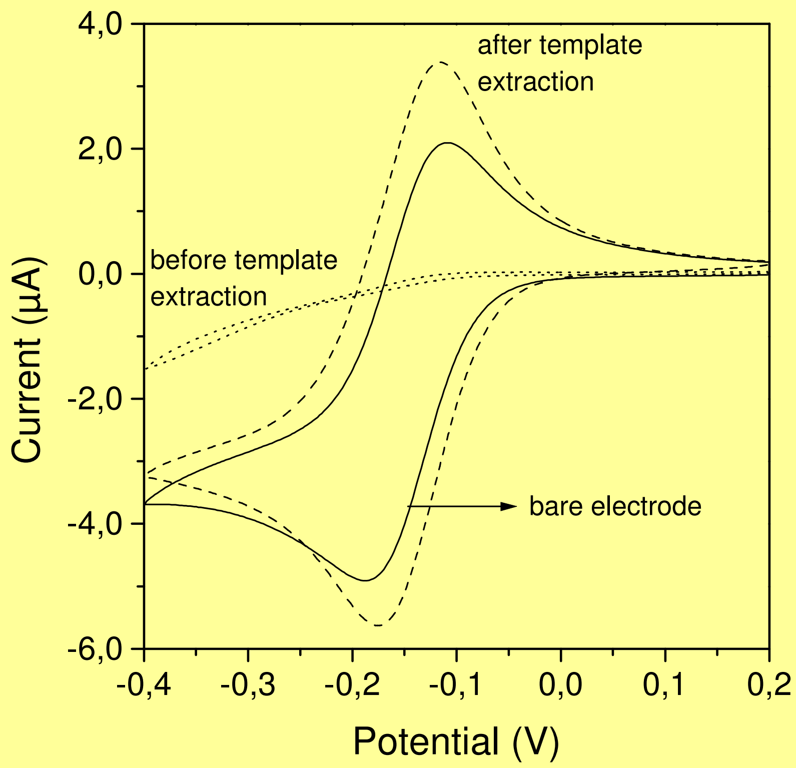


… with mesopore channels well-oriented perpendicular to the support !

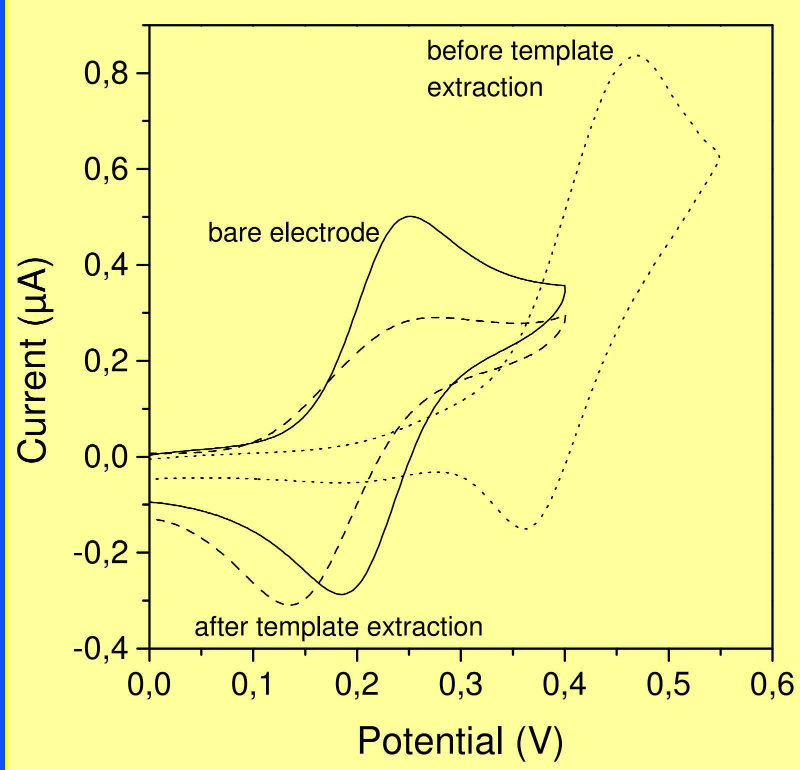
A. Walcarius, E. Sibottier, M. Etienne, J. Ghanbaja, *Nature Mater.* 6 (2007) 602

Cyclic voltammetry characterization

5 mM $Ru(NH_3)_6^{3+}$



0.5 mM ferrocene ethanol



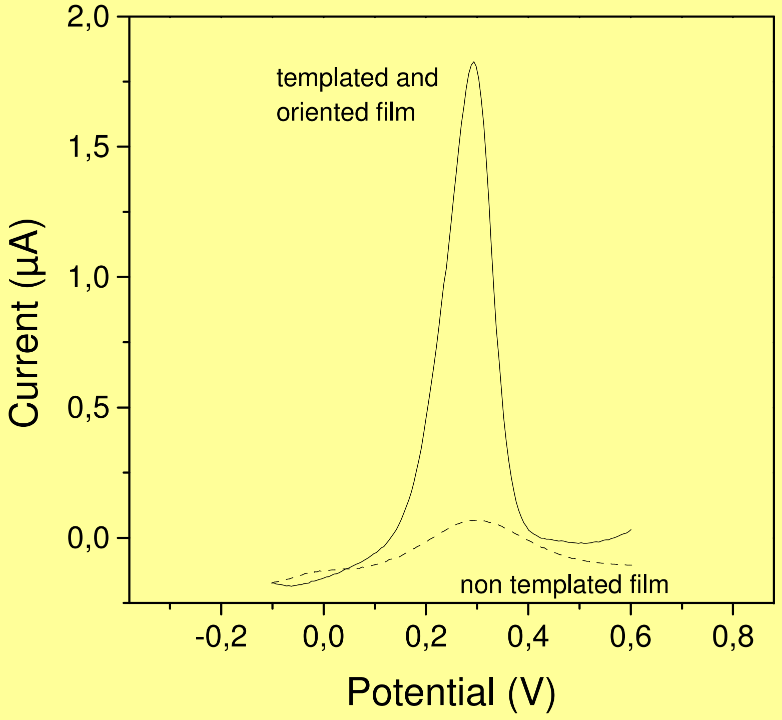
→ Easy access at electrode/film and film/solution interfaces

A. Walcarius, E. Sibottier, M. Etienne, J. Ghanbaja, *Nature Mater.* 6 (2007) 602

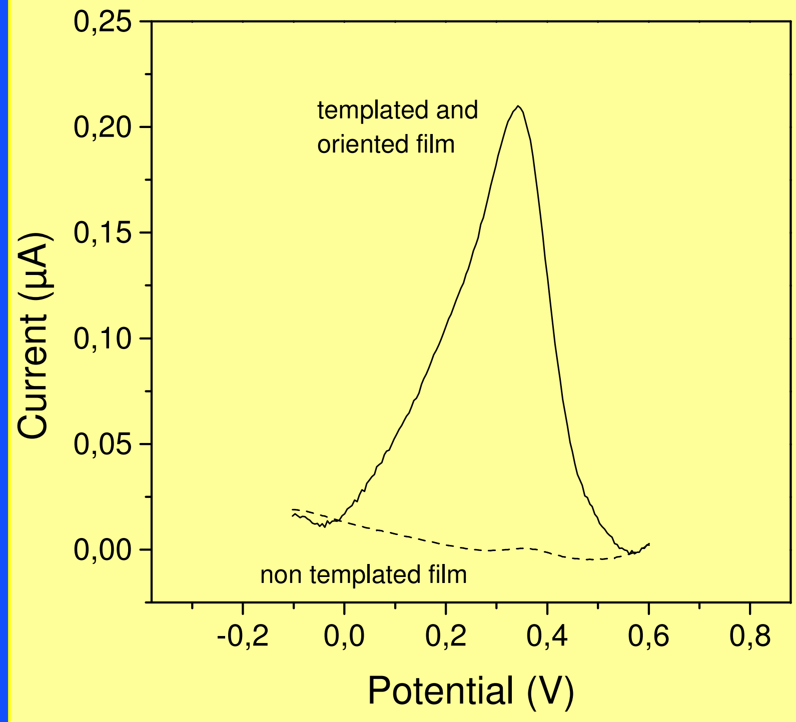
Preconcentration electroanalysis of Cu^{2+}

At amine-functionalized oriented mesoporous silica film on gold electrode

2 min acc. from 1 µM Cu^{2+}



15 min acc. from 0.01 µM Cu^{2+}



A. Walcarius, E. Sibottier, M. Etienne, J. Ghanbaja, *Nature Mater.* 6 (2007) 602

Conclusions

Combination of functionalized silica-based organic-inorganic hybrid materials with electrochemistry offers promising avenues from several point of views

Electrochemical methods are likely to provide useful information on the materials properties (complexation behavior as a function of pH, rates of mass transfer in porous environment)

The ordered mesoporous materials are attractive electrode modifiers to be applied in preconcentration electroanalysis (high sensitivity as a result of fast mass transfer rates)

Electrochemistry can be applied to the generation of ordered and oriented mesoporous silica thin films

Acknowledgements

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