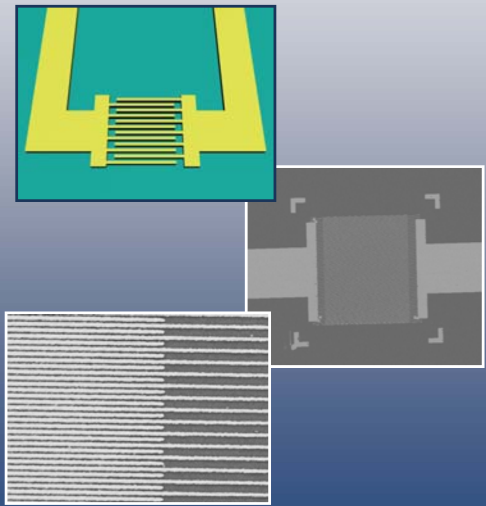
Interdigitated NanoElectrodes for sensing: fabrication and characterization



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NILSIS nanobiomed

CNM - Institute of Barcelona:

Centro Nacional de Microelectrónica IMB

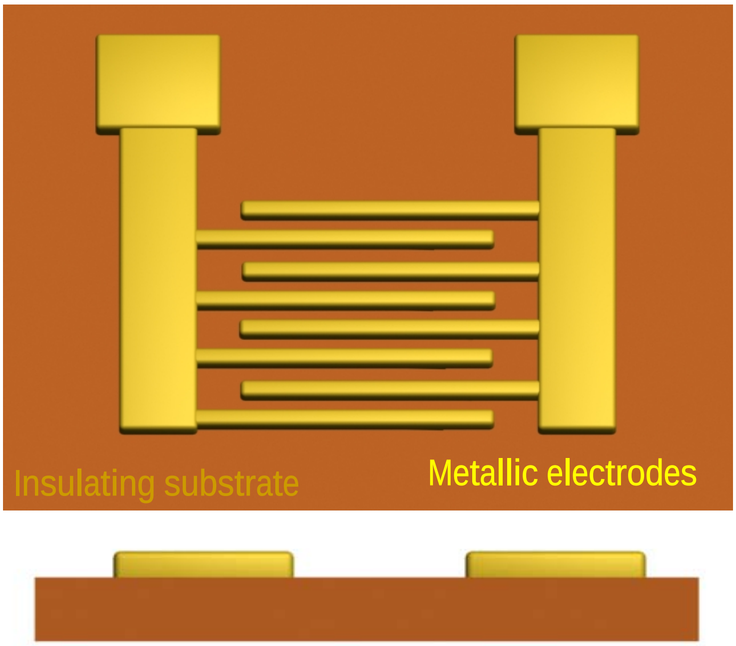
Multidisciplinar: collaboration between groups
-> chemistry + biology + nanofabrication

Fabrication and characterization of NanoBioSensors

Interdigitated Electrodes (IDEs)

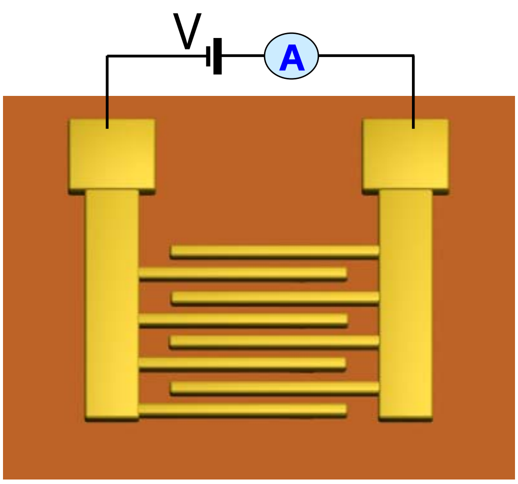
Biosensors, electrochemical sensors, nanoparticles detection

1. IDEs: Introduction
2. Fabrication
3. Characterization
   a. Voltamperometry, I(V)
   b. Impedances, $\vec{Z}(f)$
   c. Nanoparticles

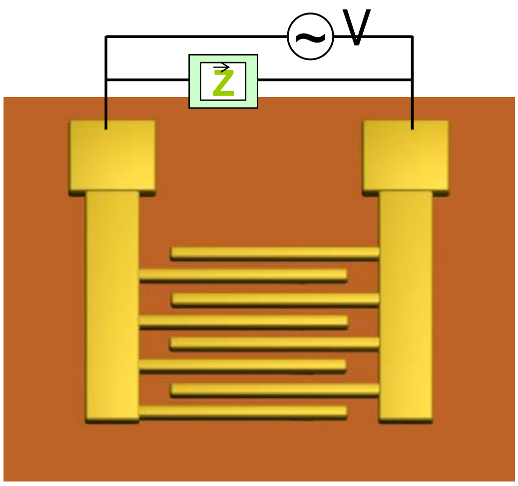


Using IDEs for Sensing

1. Voltamperometry: measurement of electrochemical current coming from red/ox reactions in the electrodes.

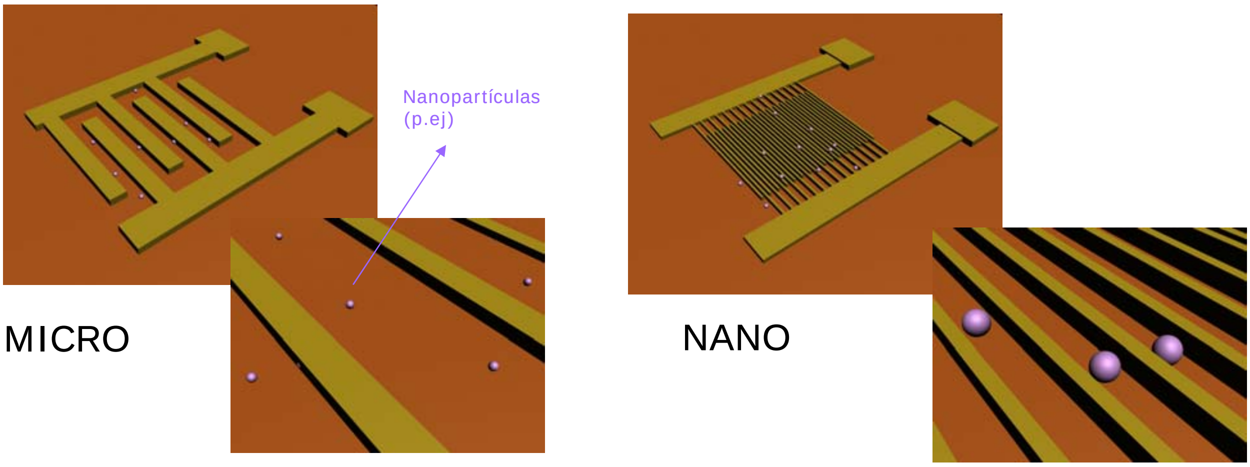


2. Impedimetric Spectroscopy: measurement of the resistivity and capacitance of the solution, as a function of the frequency.



Why nano IDEs for sensing

- For the detection and quantification of nano entities (i.e. virus, proteins, nanoparticles…) the sensitivity increases when the size of the electrode is similar to the size of the objetc.



Fabrication

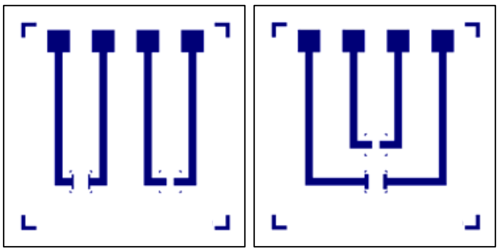
Design:

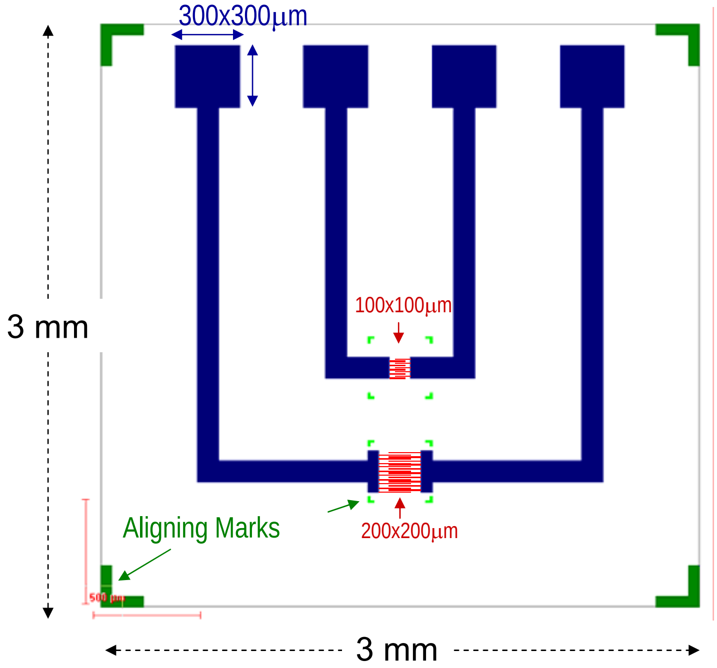
-Combination of MICRO and NANO fabrication.

- Aligning marks added, to facilitate the electron beam lithography

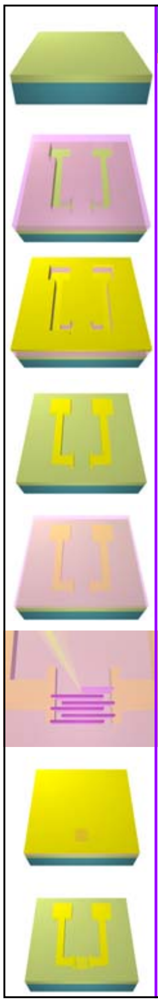
-Contacts were designed with standard size, so the samples can be bounded to a PCB.

Two different geometries

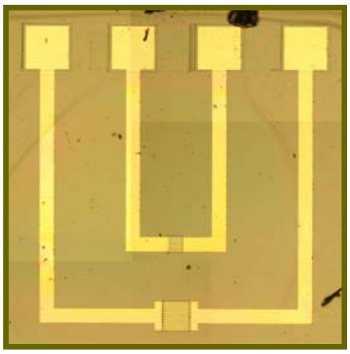


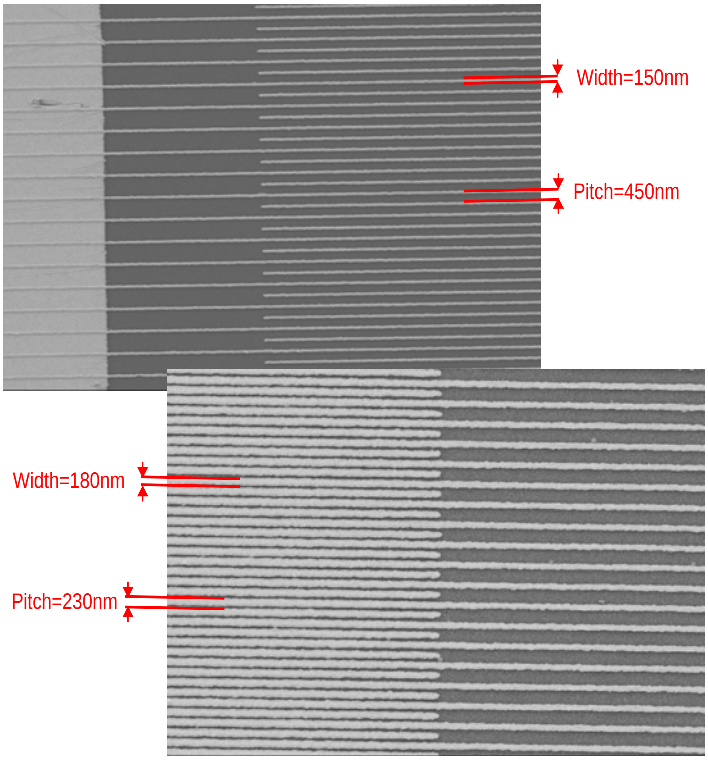


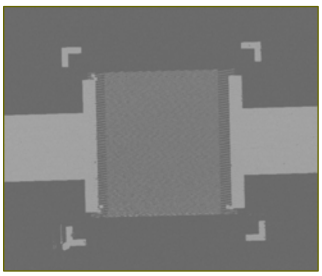
1. Optical lithography
2. EBL



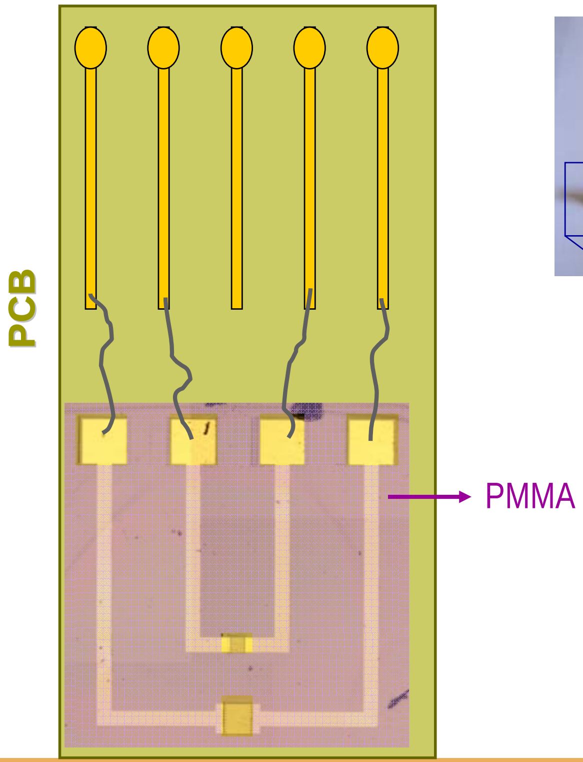
Fabrication: RESULTS

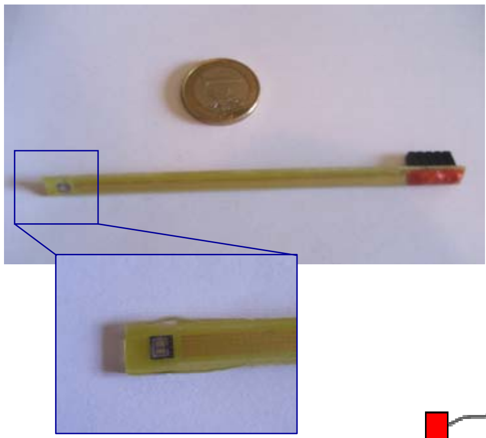


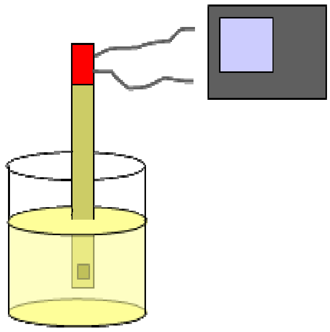




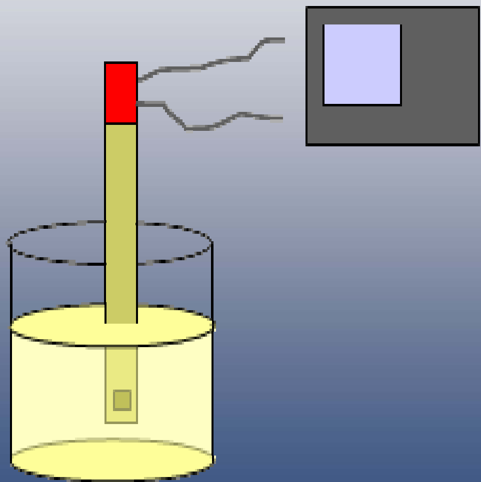
Fabrication: Packaging



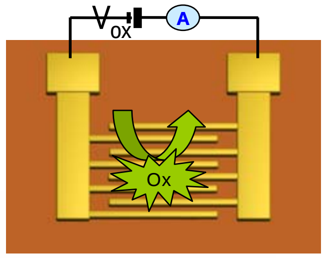




Characterization



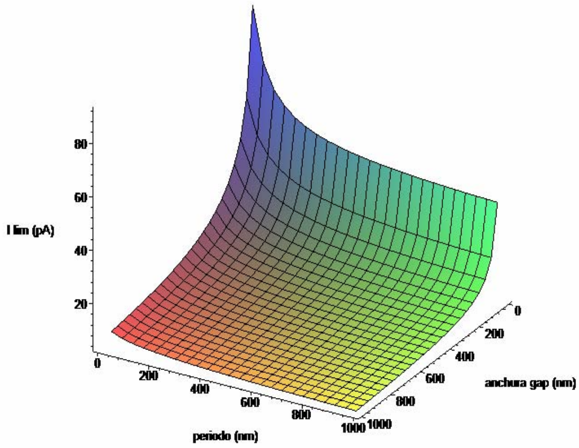
Voltamperometry



$$I_{\lim} = mbnFc^{*}D\left\{0{,}637\ \ln\left(2{,}55\frac{w_g + w}{w_g}\right) - 0{,}19\left(\frac{w_g}{w_g + w}\right)^2\right\}$$

$$0{,}05\frac{w^2}{D} \le t_{\lim} \le 14\frac{w^2}{D}$$

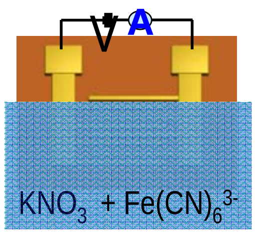
m = number of digits
b = length of the digits
n = number of e^- involved in the red/ox process
F = Faraday constant
c^* = concentration of red/ox species
D = difussion coefficient of the redox species
w_g= width of the “gap” between electrodes
w = width of the electrodes



The detection increases if: m», b», w«, w»w_g → Nanoelectrodes

K. Aoki, M. Morita, O. Niwa, H. Tabei. *J. Electroanal. Chem*, 256 (1988) 269

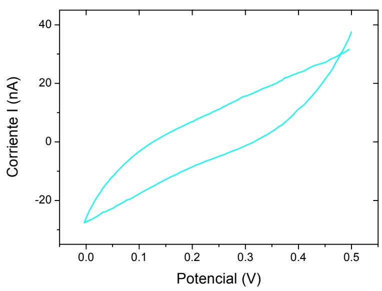
Voltammograms



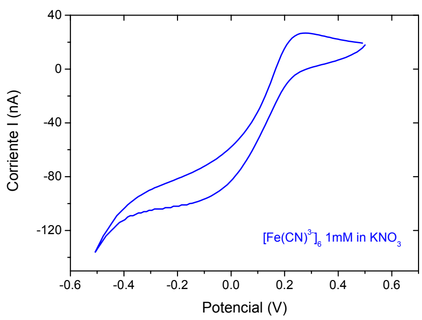
First tests: reduction of ferricianure

$$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-},\ E_0=+0.35V$$

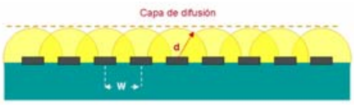
KNO_3 (not active)



Ferricianure



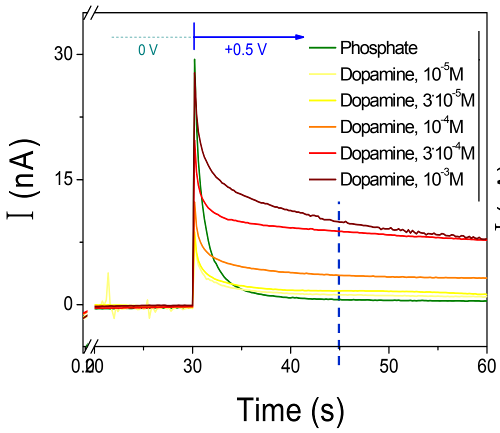
Ultra-micro vs. micro electrode



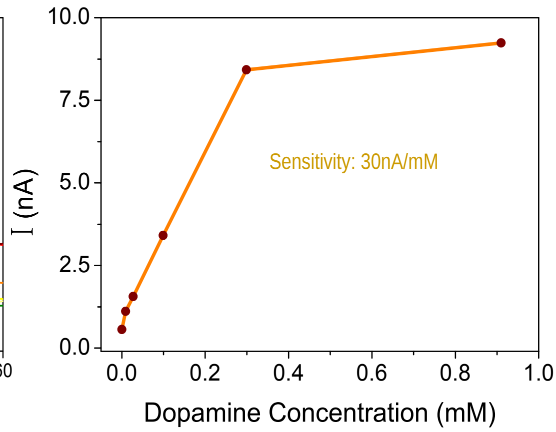
Chronoamperometry -> CALIBRATION OF THE SENSOR

Fix potential. Additions of active species of known concentration and volume.

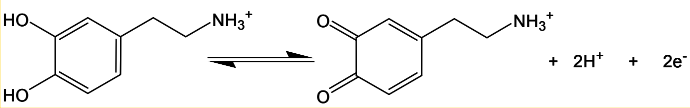
Chronoamperometry



Calibration (I at t>45s)

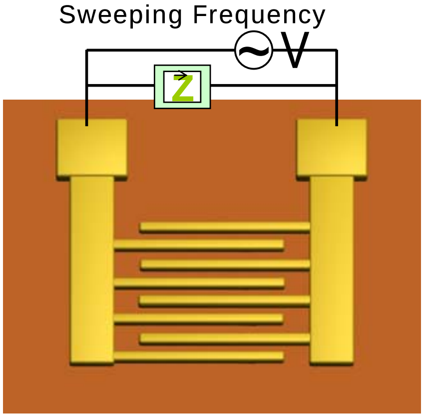


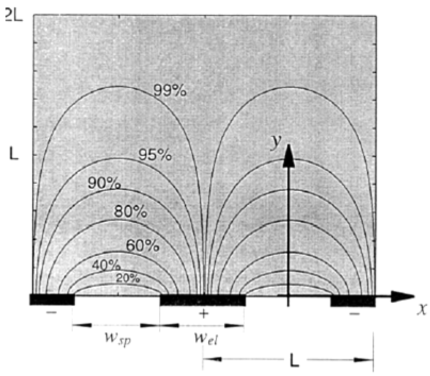
Dopamine in Phosphate (Ph=7.4)



After calibration, the electrode can be used to determine the concentration of unknown solutions.

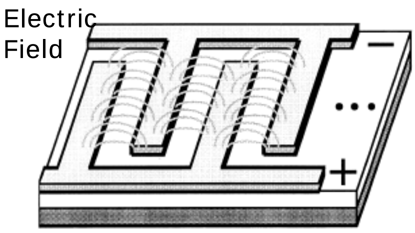
Impedance Spectroscopy





95% of the current comes from a height below 2L.

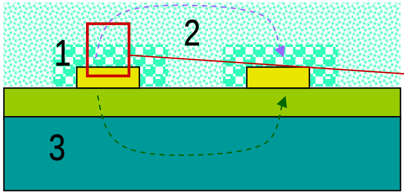
Nanoelectrodes (L<<)



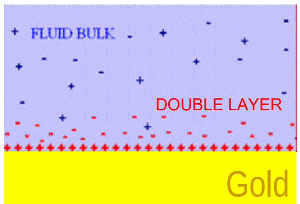
-Changes in the conductivity and the capacitance of the solution can be detected.

-Nanoparticles (or nano-objetcs) can be detected.

Electric Model

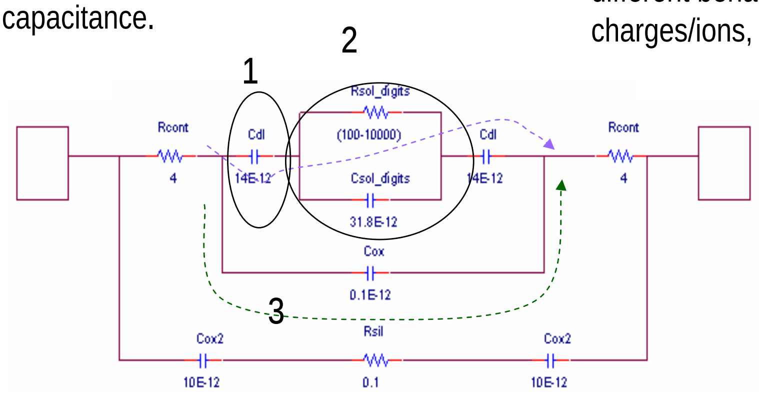


1 .- DOBLE LAYER: the surface of the electrode is charged -> opposite sign charges (ions) are attracted/induced -> "dobule layer capacitance"



The thickness of the doble layer depends on the concentration of ions in the solution

3 .- SUBSTRATE: Eventhough it is an insulator, it also creates a "parasitic" capacitance.

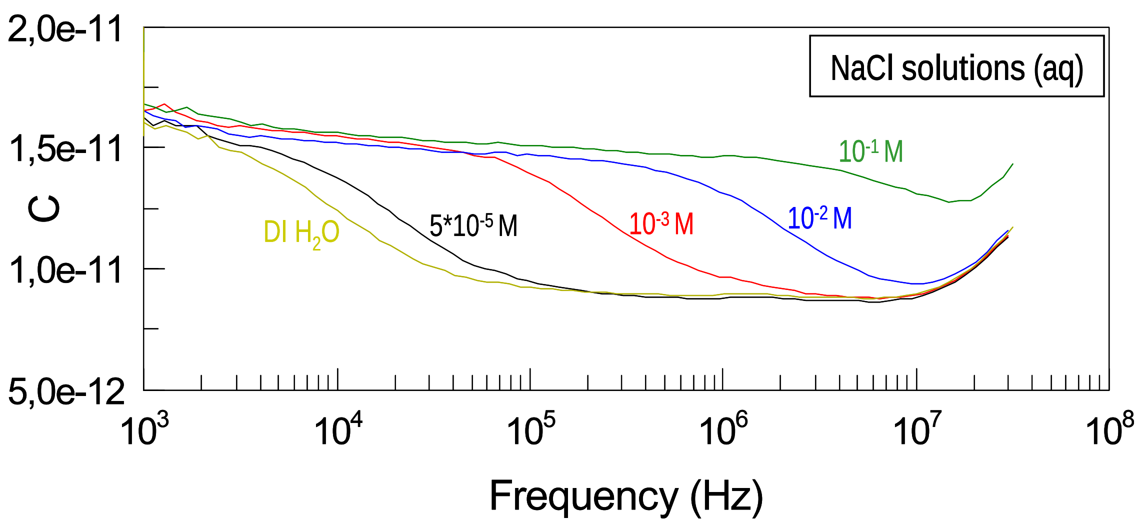


2 .- DISOLUCIÓN: Each disolution or media has a different behaviour, associated to the quantity of charges/ions, their movility in the solution, its nature, etc. [C y R del medio]

- High frequency: solution
- Low Frequency: doble layer
- High resistivity medias: substrate

Dependence on the conductivity

Aqueous Solutions of NaCl, with different concentrations (i.e., the number of ions is changed -> the resistivity of the media varies)

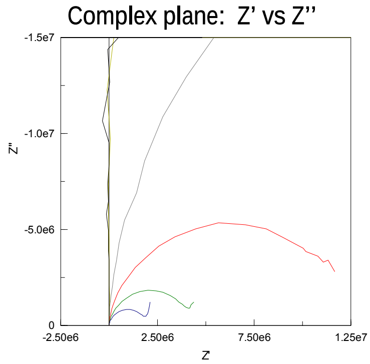


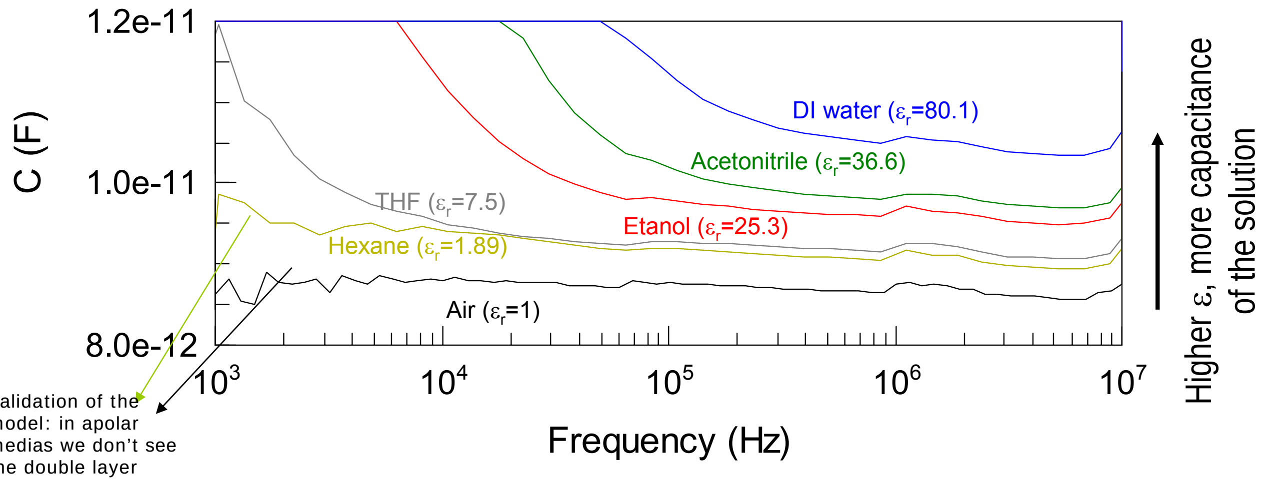
More ions -> "better" doble layer -> we keep on seeing it even for high frequencies

Dependence on ε_r

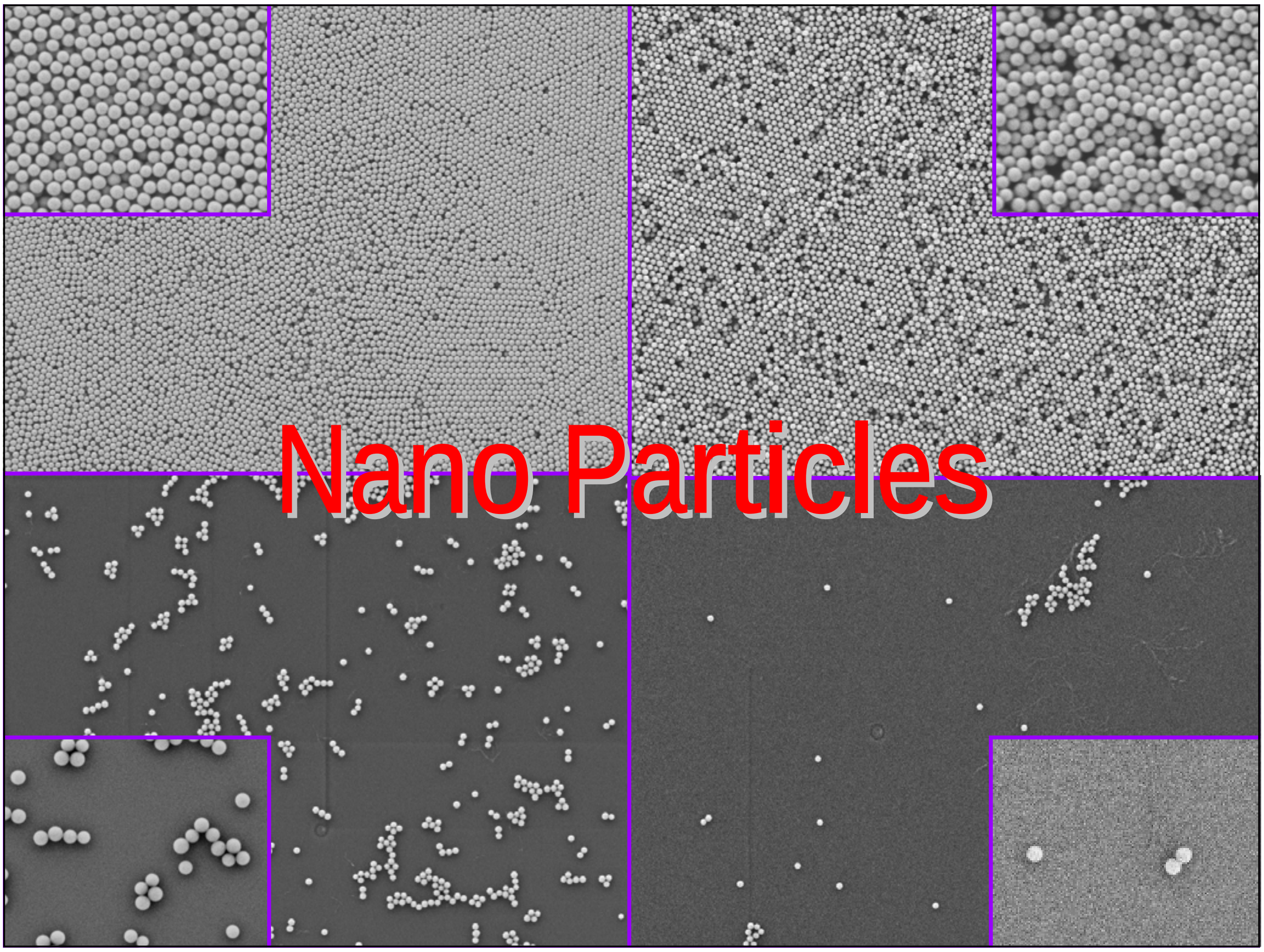
Measurements in different liquids with different permitivity (i.e., the capacity of charge storage is different).

$$C = \epsilon_0 \epsilon_r \frac{A}{d}$$

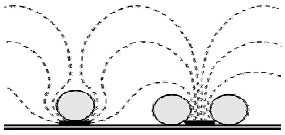


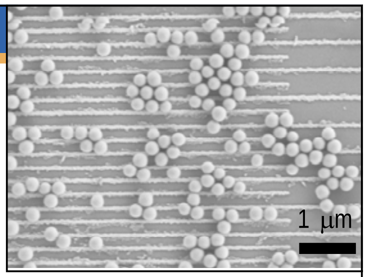


Validation of the model: in apolar medias we don't see the double layer



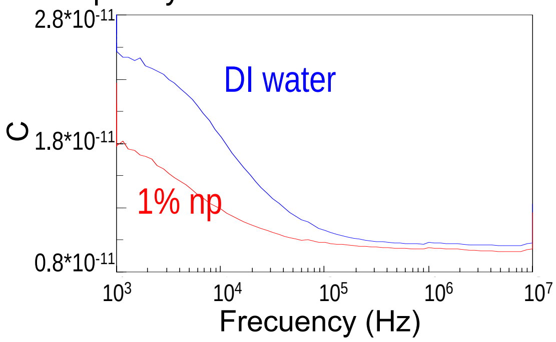
Latex Nanoparticles (ϕ=300nm)





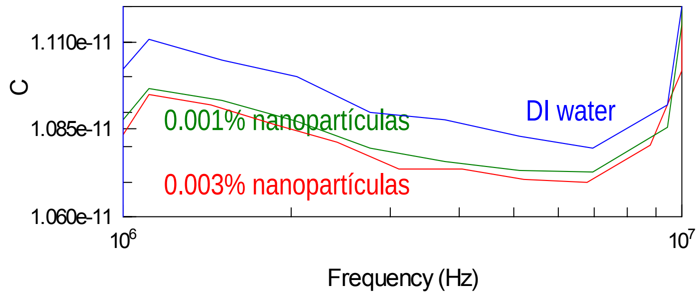
High concentration

In the case of a high quantity of nanoparticles on the surface, the capacity decreases, mainly for low frequency.



Low concentration

For low concentrations of nanoparticles, the capacity at high frequency decreases. As it is shown in the graph, very low changes can be detected.



Conclusions

-We have **designed and fabricated gold nanoelectrodes** onto an insolating substrate (SiO_2) by a combination of micro and nanofabrication.

-**Electrochemical current measurements** have demonstrated the good performance of the sensor. Furthermore, chronoamperometric measurements allow the calibration of the device.

-**Impedance spectroscopy** measurements have also shown the good performance of the sensor. The response varies for different solutions, changing the conductivity or the permitivity of the media..

-Preliminary results of the **detection of nanoparticles** have been shown.