

Bottom-up approach for the elaboration of nanocomposite
model structures
based on organically capped platinum nanoparticles
electrocatalyst

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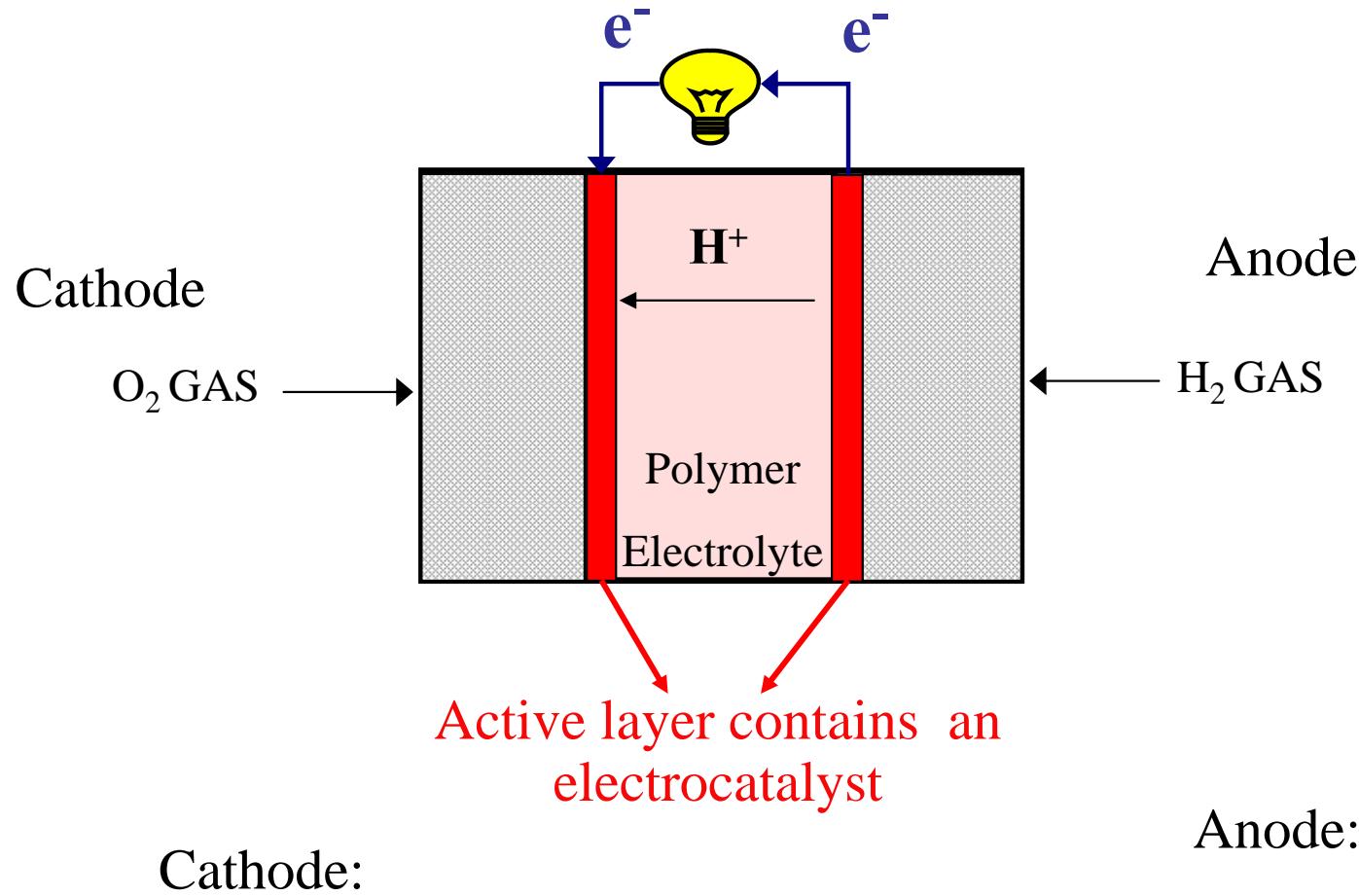
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DSM/DRECAM/SPAM-LFP Groupe Edifices-Nanométriques

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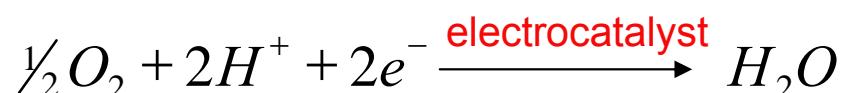
INTRODUCTION

PEMFC and electrocatalyst

→ Polymer Exchange Membrane Fuel Cell is an electrochemical device...



Cathode:



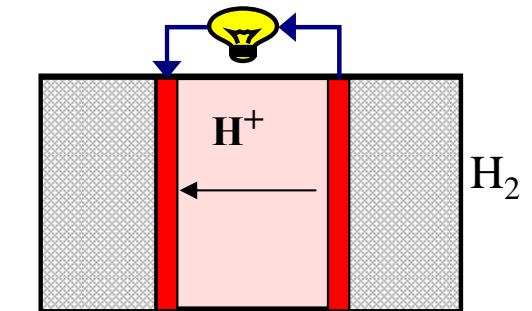
Anode:



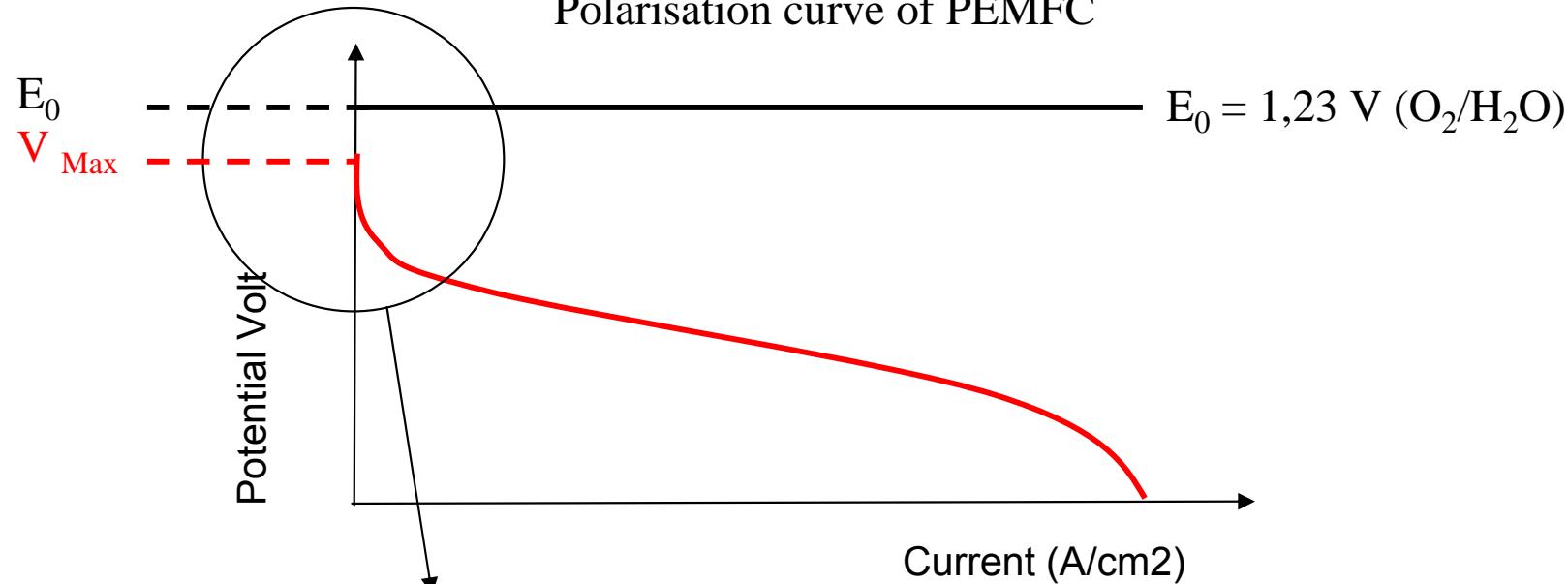
INTRODUCTION

PEMFC and electrocatalyst

→ Platinum as electrocatalyst



Polarisation curve of PEMFC



$E_0 - V_{Max}$ « Activation over-potential »
(essentially at cathode)



Platinum exhibits the lowest over-potential

Using platinum cannot be bypassed for PEMFC development, but it is rare and expensive...

INTRODUCTION

Platinum as electrocatalyst

→ Optimization of platinum loading is a challenge...and requires model electrodes

→ Control the platinum loading over a wide range

→ Control the polydispersity of nanoparticles (shape and size)

→ Control the manipulation of catalyst



Bottom up approach offers such possibilities :

- Solution chemistry from molecular precursors affords **capped or stabilized platinum nanoparticles** with low polydispersity which can be handled in solution

INTRODUCTION

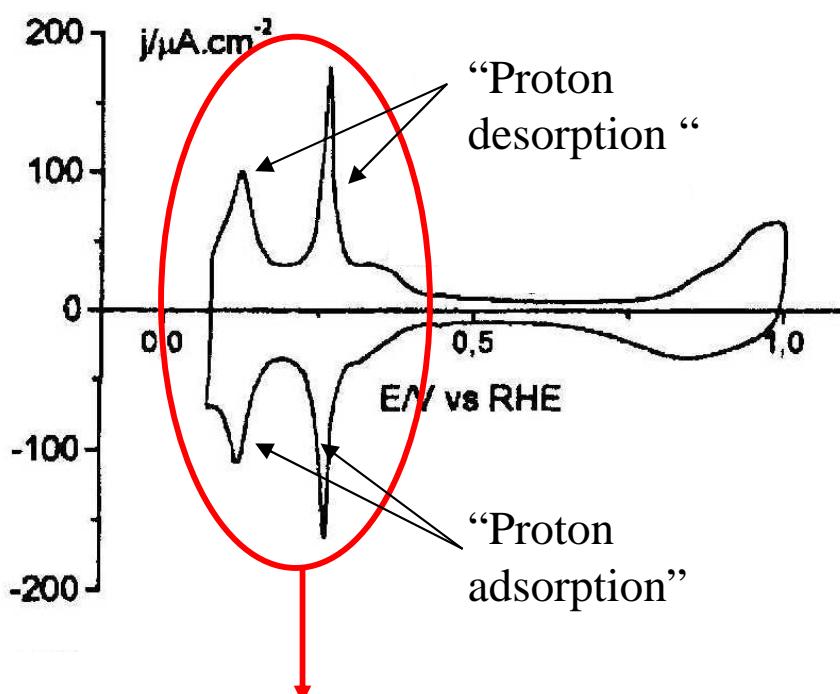
Capped or stabilized Platinum as electrocatalyst

- The capping or stabilizing agent conflicts with electrochemical characterization

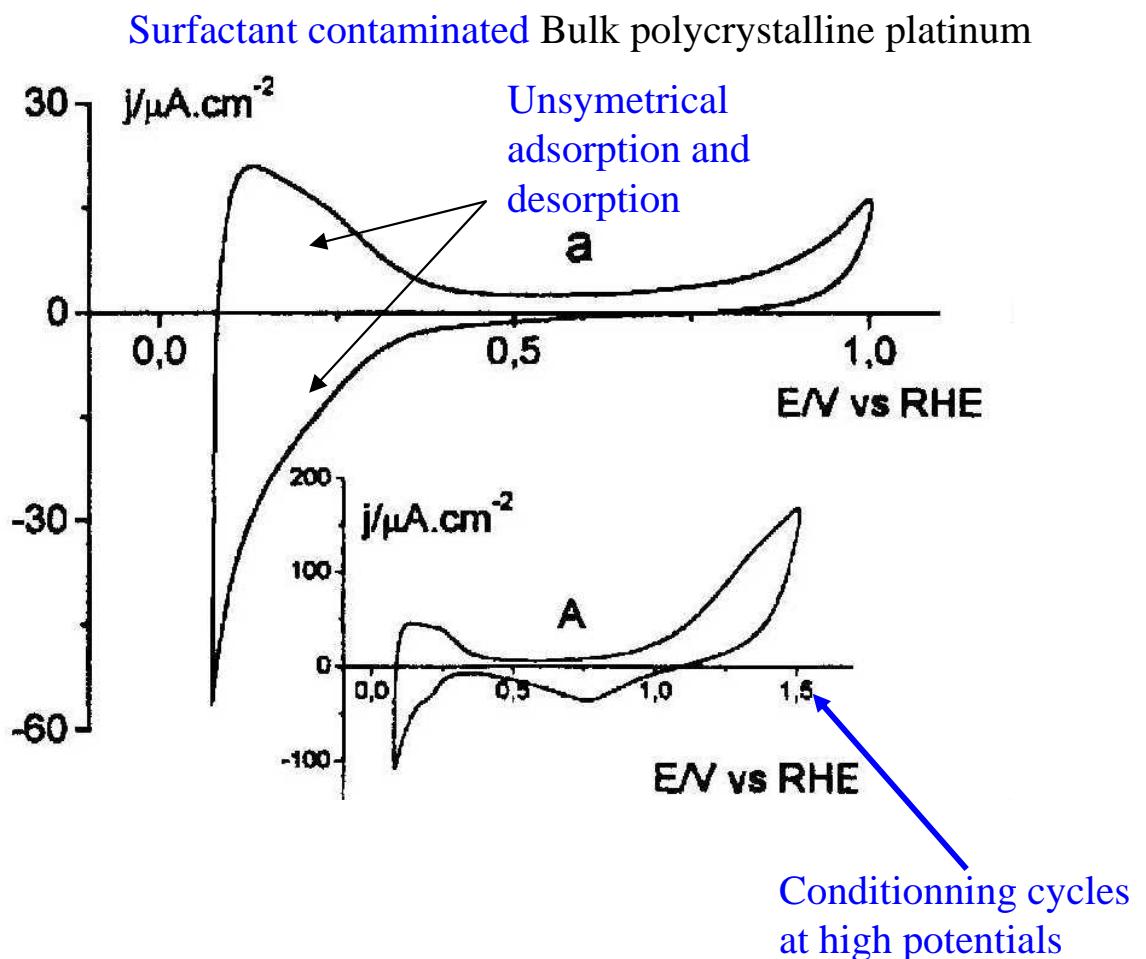
Hydrogen under potential deposition (upd) :

H_2SO_4 1 M, 100 mV/s

“Clean” Bulk polycrystalline platinum



Coulombic charge used to estimate an “electroactive surface area”

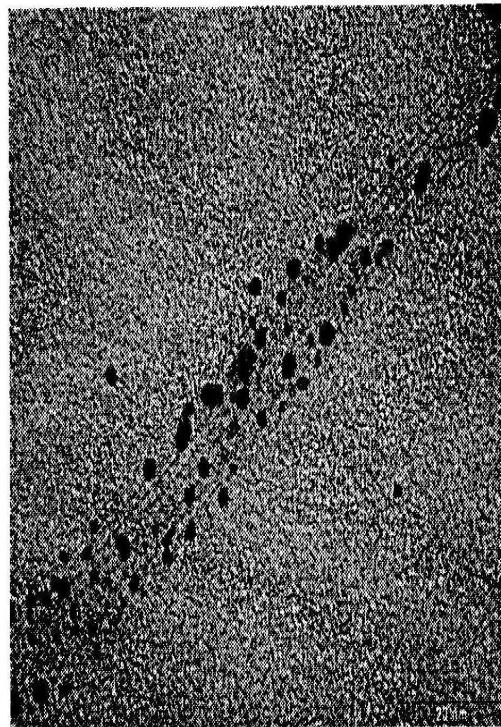


INTRODUCTION

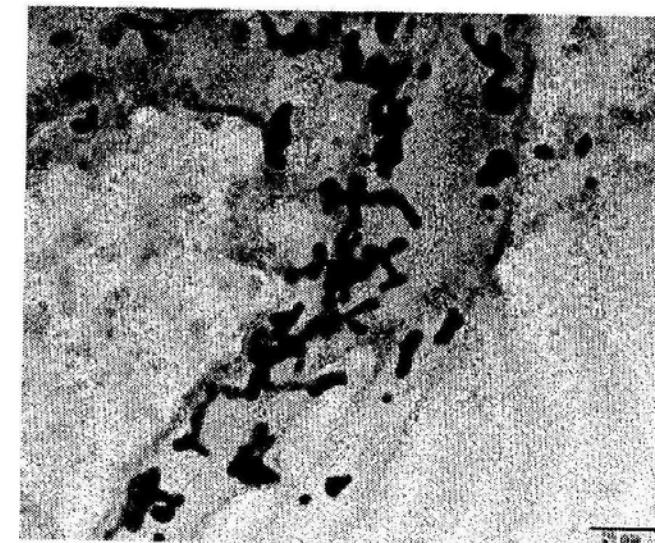
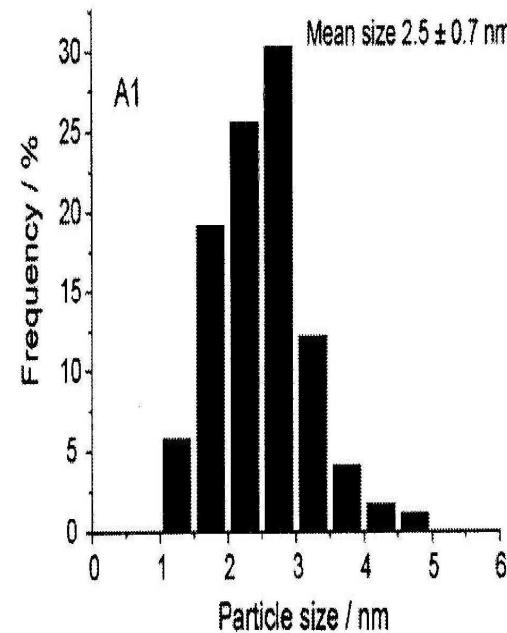
Capped or stabilized Platinum as electrocatalyst

- Cycling at high potential strongly disturbs nanoparticle feature

Electrochemical oxidation treatments :



Raw sample



Cycled sample

Strongly disturb nanoparticle features !

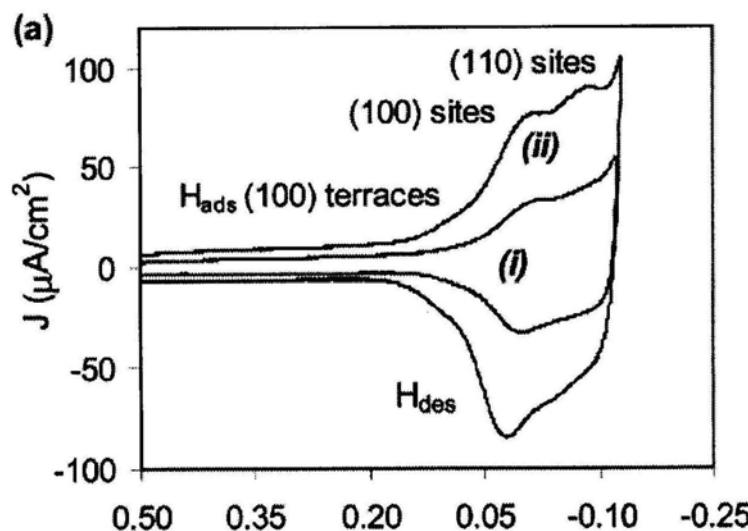
Removing capping/stabilizing agent while keeping the nanoparticle core surface realistic ?

INTRODUCTION

Capped or stabilized Platinum as electrocatalyst

- Control of platinum nanoparticle features versus electrochemical activity characterization

Hydrogen underpotential deposition may be observed while a stabilizing agent is used...
(polyacrylate-capped nanoparticles)

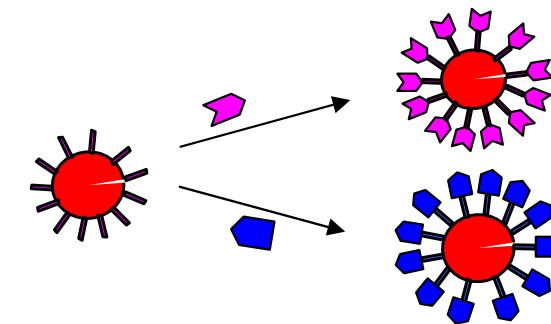


For electrocatalysts few information concerning:

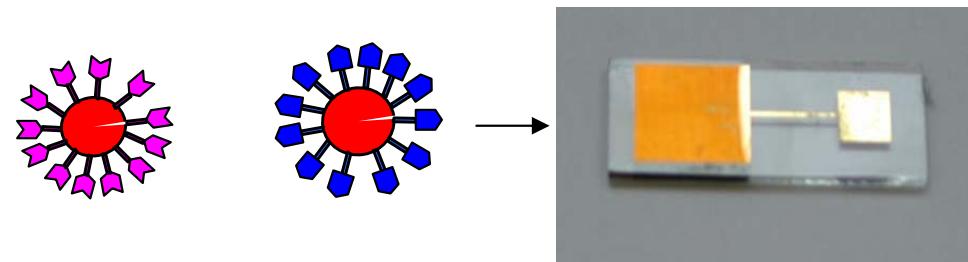
- the relation between the feature of capping/stabilizing agent and the electrochemical behaviour
- the influence of the nature of the interaction between capping/stabilizing agent and the nanoparticle surface on the electrochemical behaviour...

Bottom-up approach for the elaboration of nanocomposite model structures based organically capped platinum nanoparticles electrocatalyst

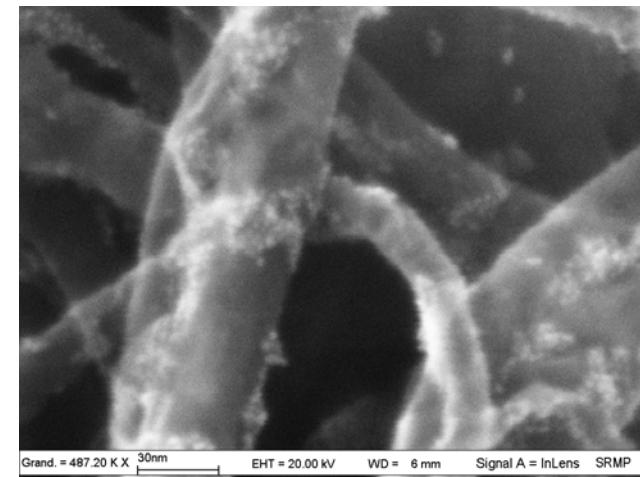
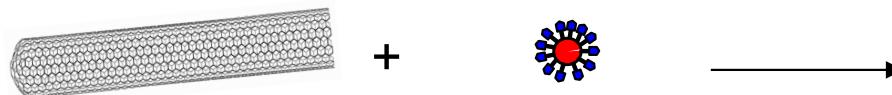
1 – Organically capped platinum nanoparticles



2 - Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles



3- nanocomposite based on organically capped platinum nanoparticles and carbon nanotubes



4 -Conclusion

PART 1: SYNTHESIS AND CHARACTERIZATION OF NANO-OBJECTS

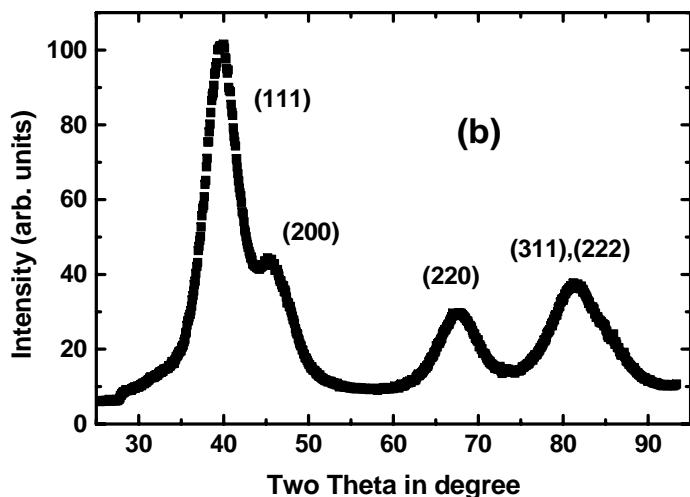
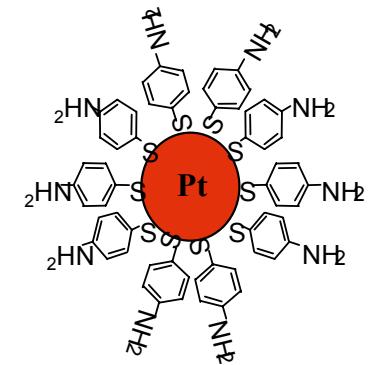
Organically capped platinum nanoparticles

→ 4-mercaptoproline functionalized platinum nanoparticles

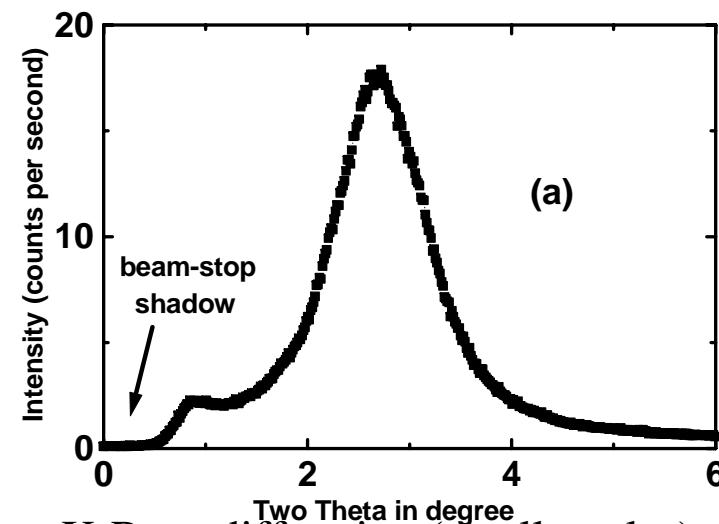
Isolated solid powder: 15 % organic content

Proposed a chemical formula: $\text{Pt}_{265}(-\text{S}-\text{C}_6\text{H}_4-\text{NH}_2)_{80}$

Averaged molar weight : ~60 000 g/mole



X-ray diffraction (wide angles)
FCC Structure
Core diameter (scherrer) ~2 nm



X-Rays diffraction (small angles)
Low size polydispersity
(defined averaged interparticle distance)

PART 1: SYNTHESIS AND CHARACTERIZATION OF NANO-OBJECTS

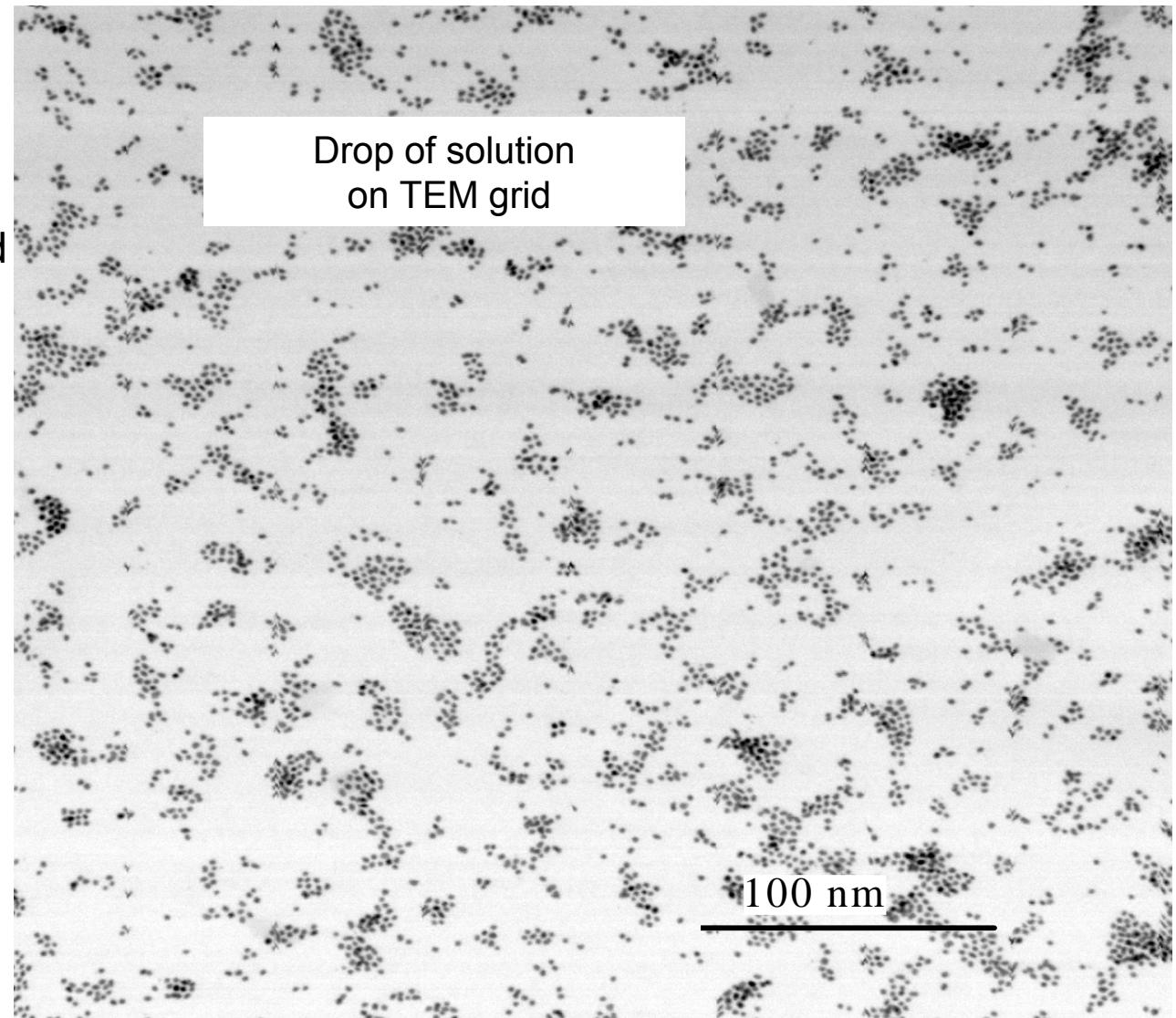
Organically capped platinum nanoparticles

→ Capping molecules allow spontaneous solubilisation as individual nanoparticles



Solution of controlled concentration

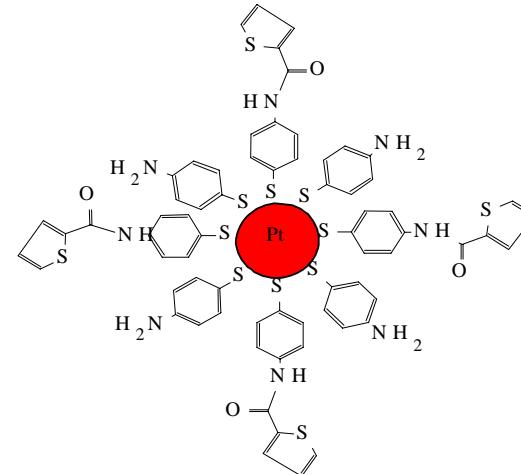
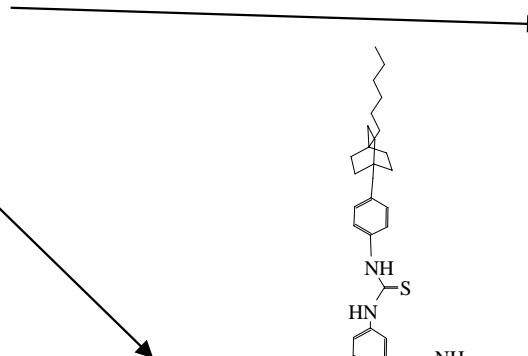
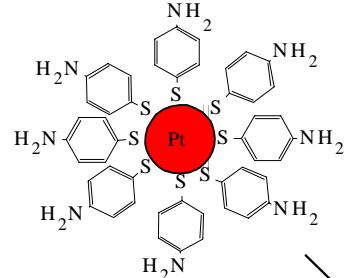
Individualized
objects →



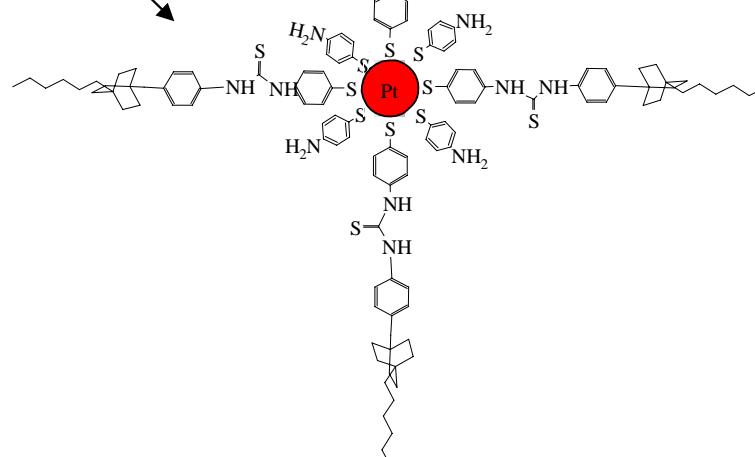
PART 1: SYNTHESIS AND CHARACTERIZATION OF NANO-OBJECTS

Making different bricks from by modification through « over-grafting » reactions

Mother brick



Derivatized/overgrafted nanoparticles

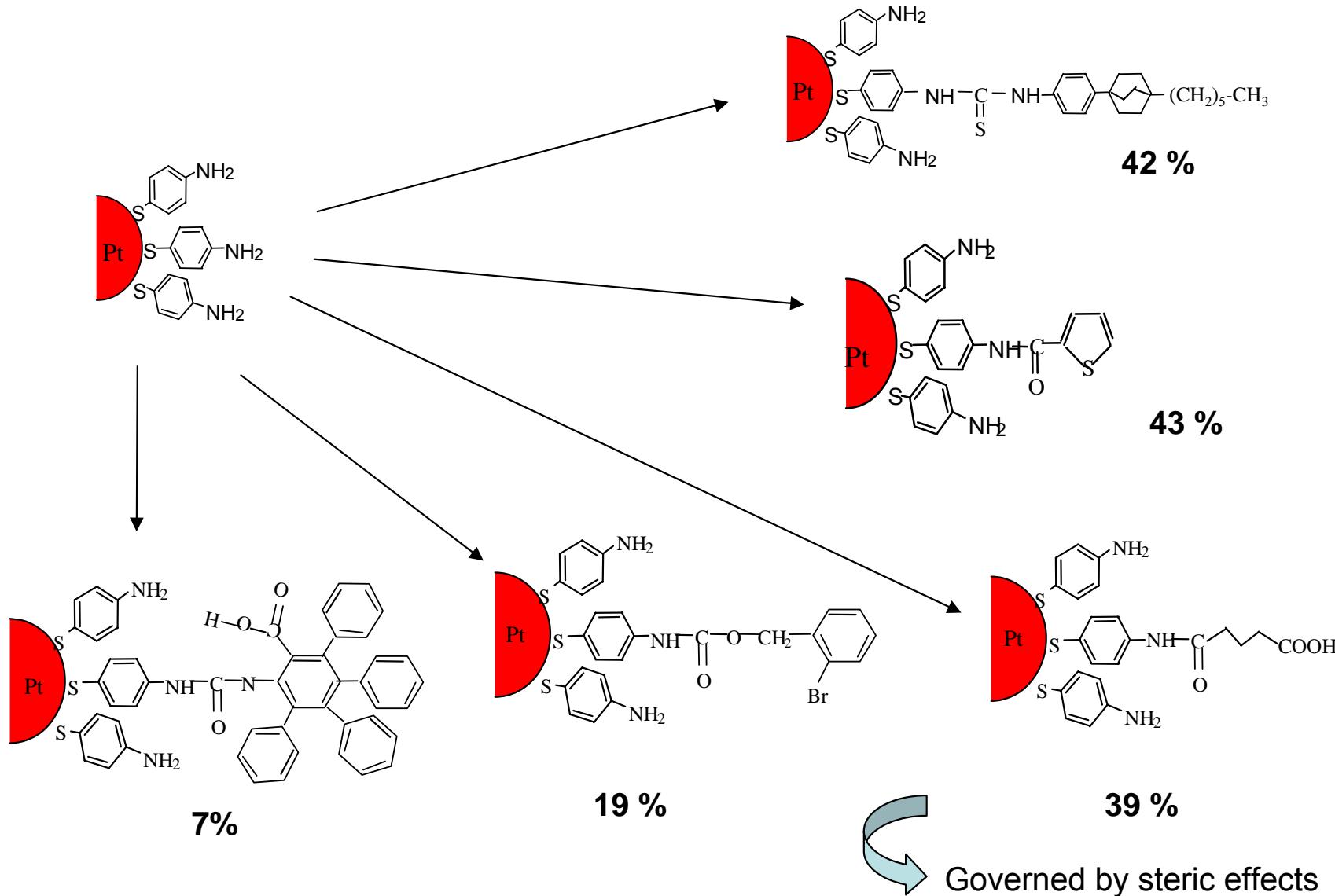


- Control of nanoscale environment of platinum core
- Long term stability of stock solutions

PART 1: SYNTHESIS AND CHARACTERIZATION OF NANO-OBJECTS

Characterizing partial over grafting

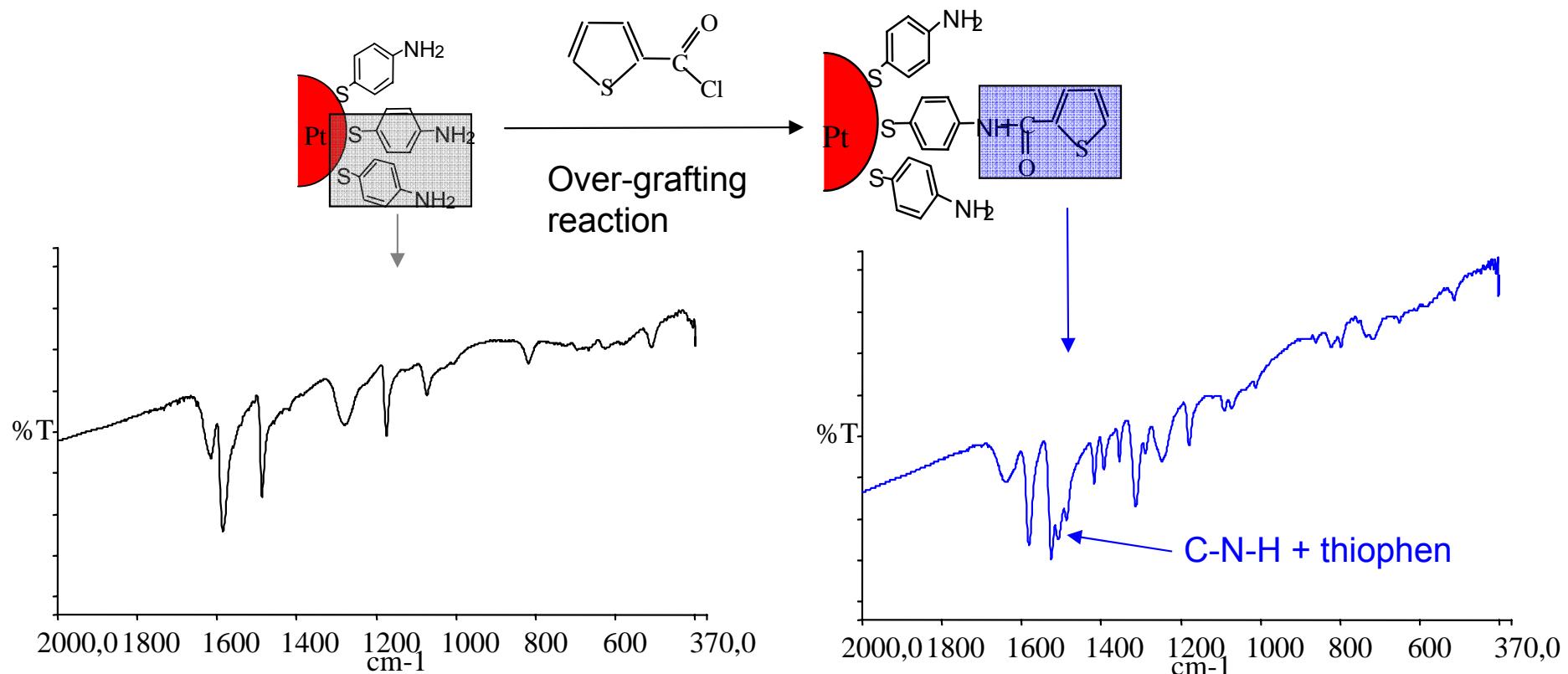
→ Over-grafting ratio (% of reacted amine functions) :



PART 1: SYNTHESIS AND CHARACTERIZATION OF NANO-OBJECTS

Characterizing over grafting

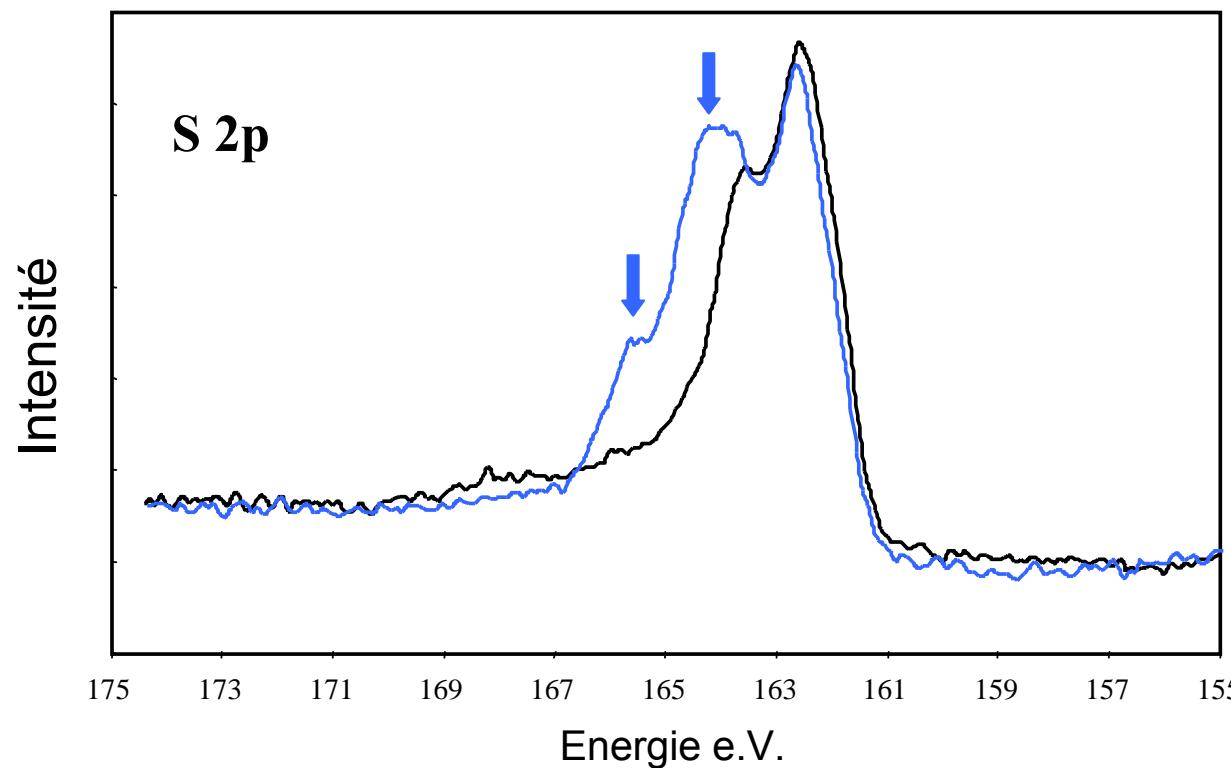
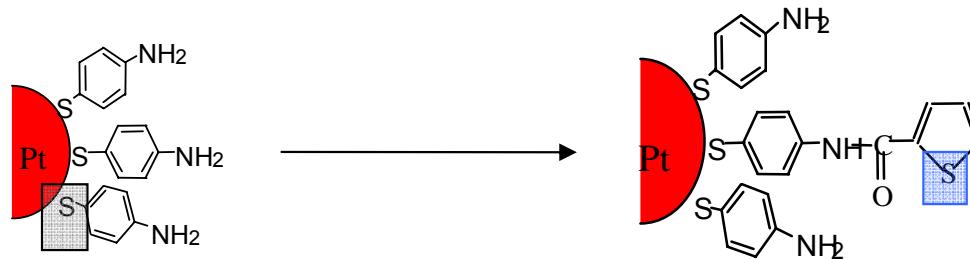
- Infrared spectroscopy:



PART 1: SYNTHESIS AND CHARACTERIZATION OF NANO-OBJECTS

Characterizing over grafting

→ X-ray photo-electron spectroscopy (XPS)

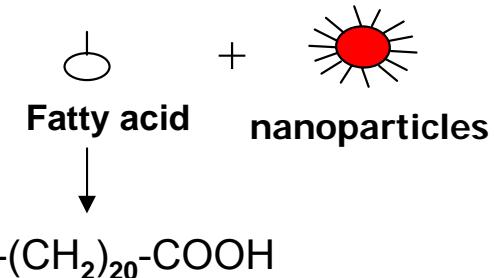
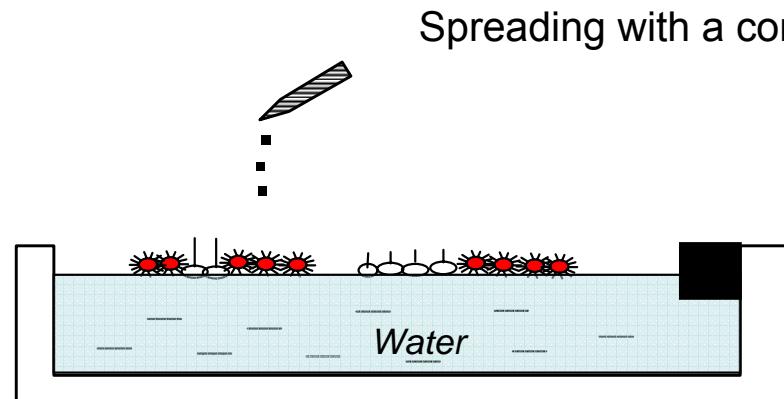


Part 2: Elaboration and properties of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

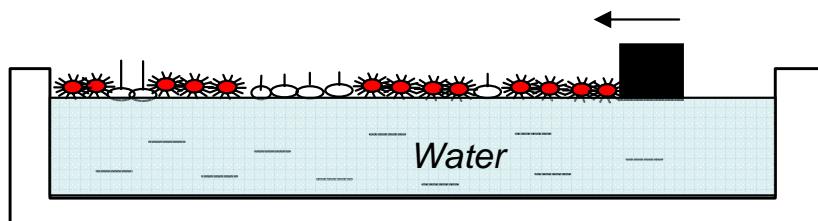
Elaboration and features of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

→ Langmuir-Blodgett procedure

1- Spreading



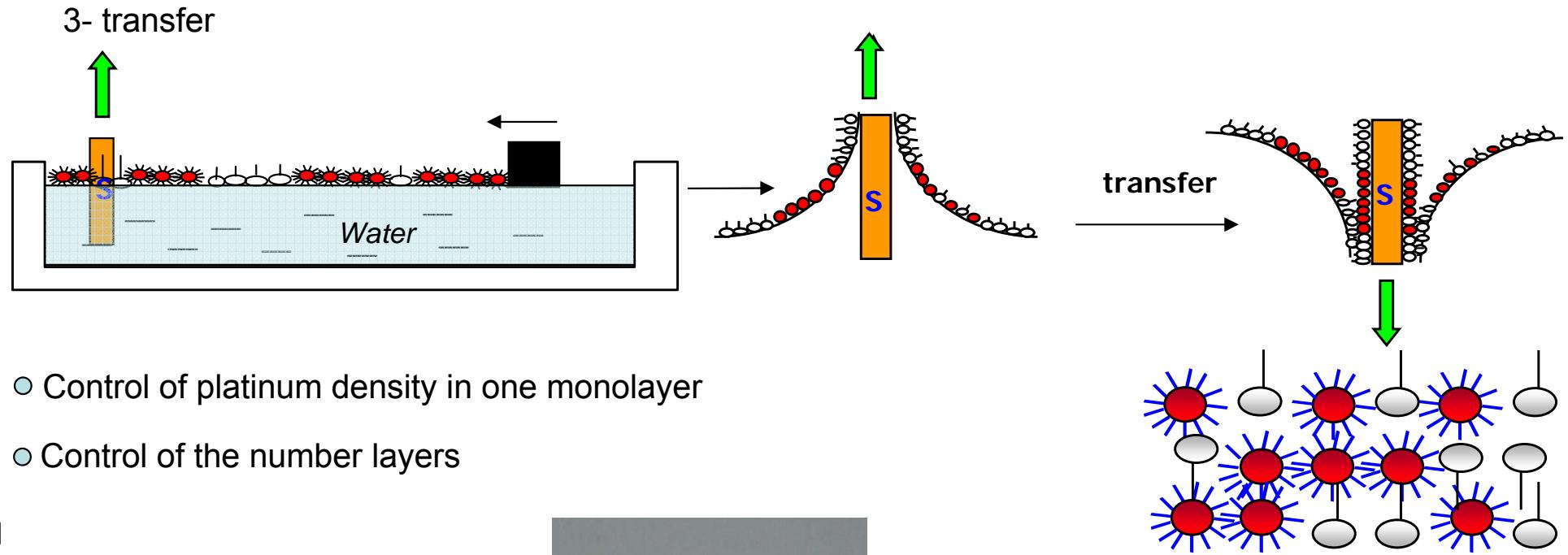
2- Compression at controlled surface pressure: mixed film formation



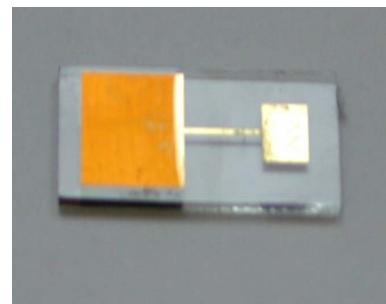
Note: contrôle of platinum density 2 $\mu\text{g}/\text{cm}^2$ to 0.2 $\mu\text{g}/\text{cm}^2$

Part 2: Elaboration and properties of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

Elaboration and features of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles



Two ways to control platinum density on the solid substrate



Note :
fatty acid can be eliminated
after film deposition

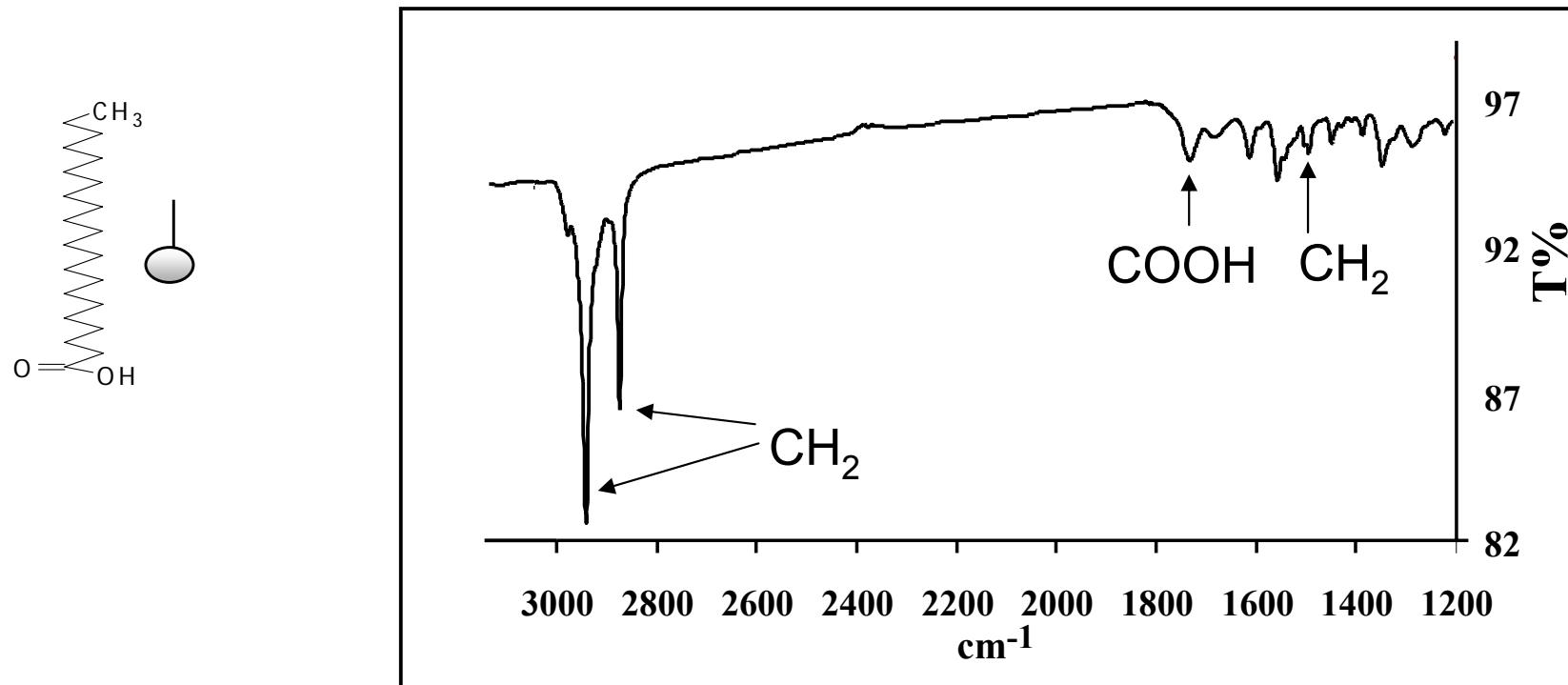
H. Perez, R. M. Lisboa de Sousa, J-P. Pradeau and P-A. Albouy
Chem. Mat 13 (5) (2001) 1512-1517

H. Perez, V. Noël, S. Cavaliere, A. Etcheberry, P-A. Albouy
Chem. Mat 13 (5) (2001) 1512-1517

PART 2: ELABORATION AND CHARACTERIZATION OF SOLID STATE NANOSTRUCTURES FROM PREFORMED NANO-OBJETS

Characterization of Langmuir-Blodgett films

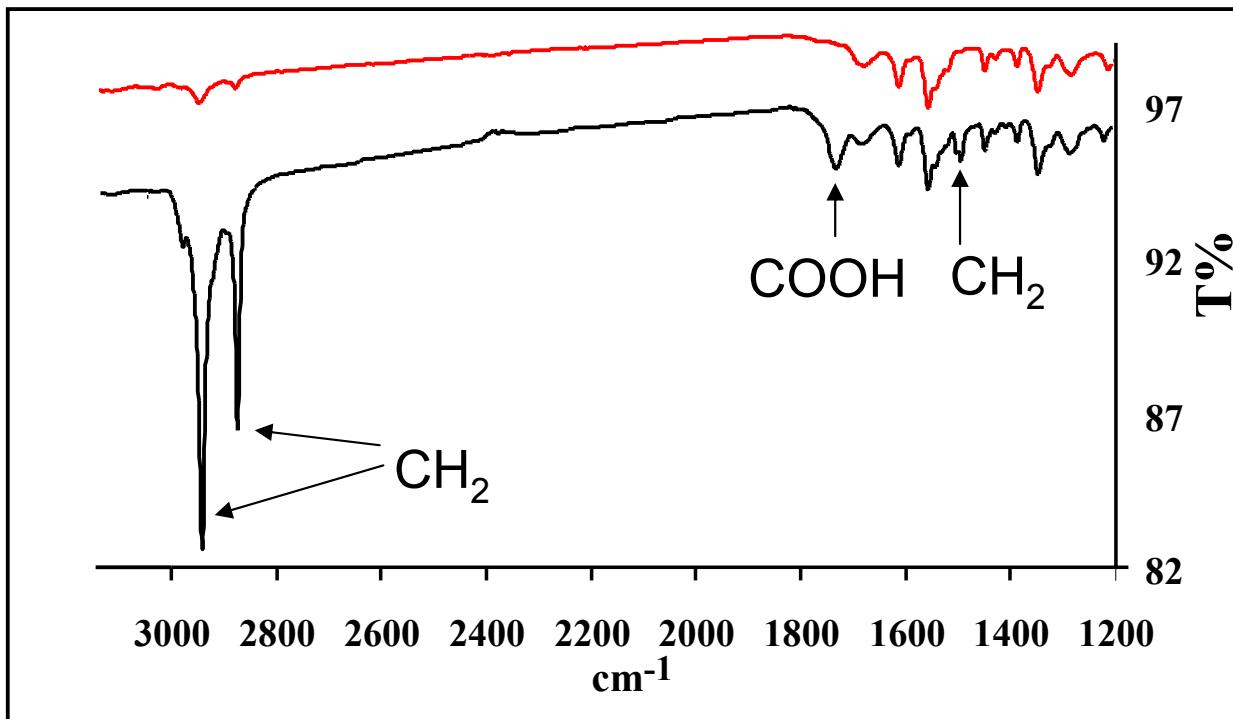
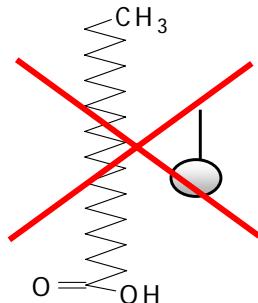
→ Infrared spectroscopy



PART 2: ELABORATION AND CHARACTERIZATION OF SOLID STATE NANOSTRUCTURES FROM PREFORMED NANO-OBJETS

Characterization of Langmuir-Blodgett films

→ Infrared spectroscopy



Evidence of fatty acid removal by washing procedure (skeletonization)

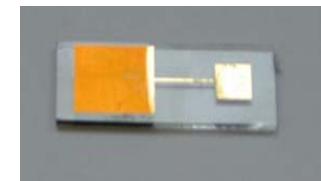
Part 2: Elaboration and properties of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

Behaviour towards a classical probe

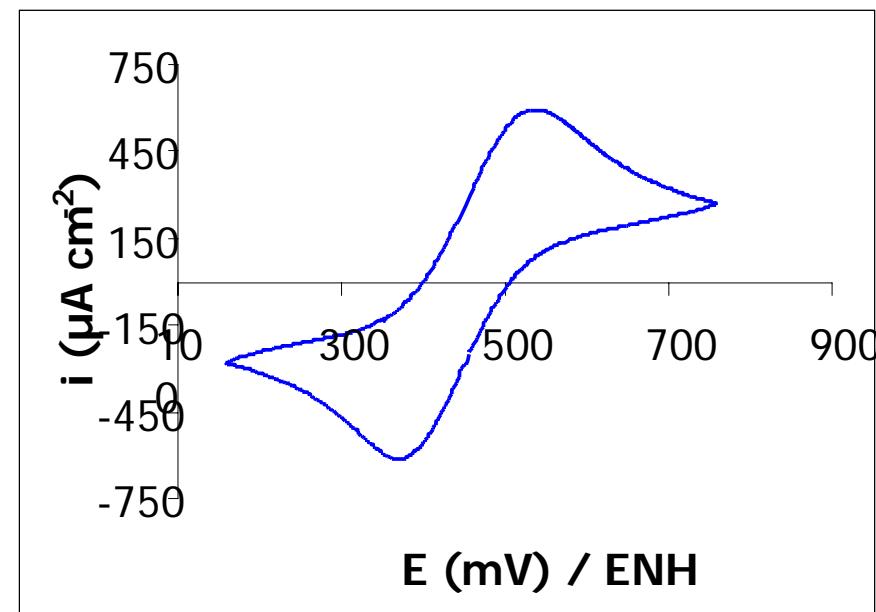
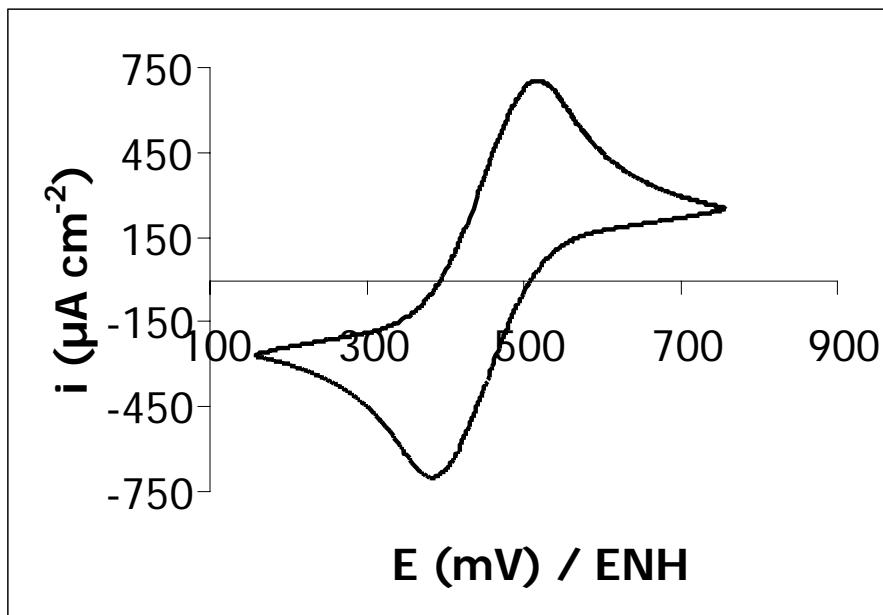
→ $[\text{FeCN}_6]^{3-/4-}$ redox probe

5 mM $[\text{FeCN}_6]^{3-/4-}$ in 0.1 M Na_2SO_4 @ 20 mV s⁻¹

Bare gold electrode



5 layers Pt 1 / fatty acid (50/50)

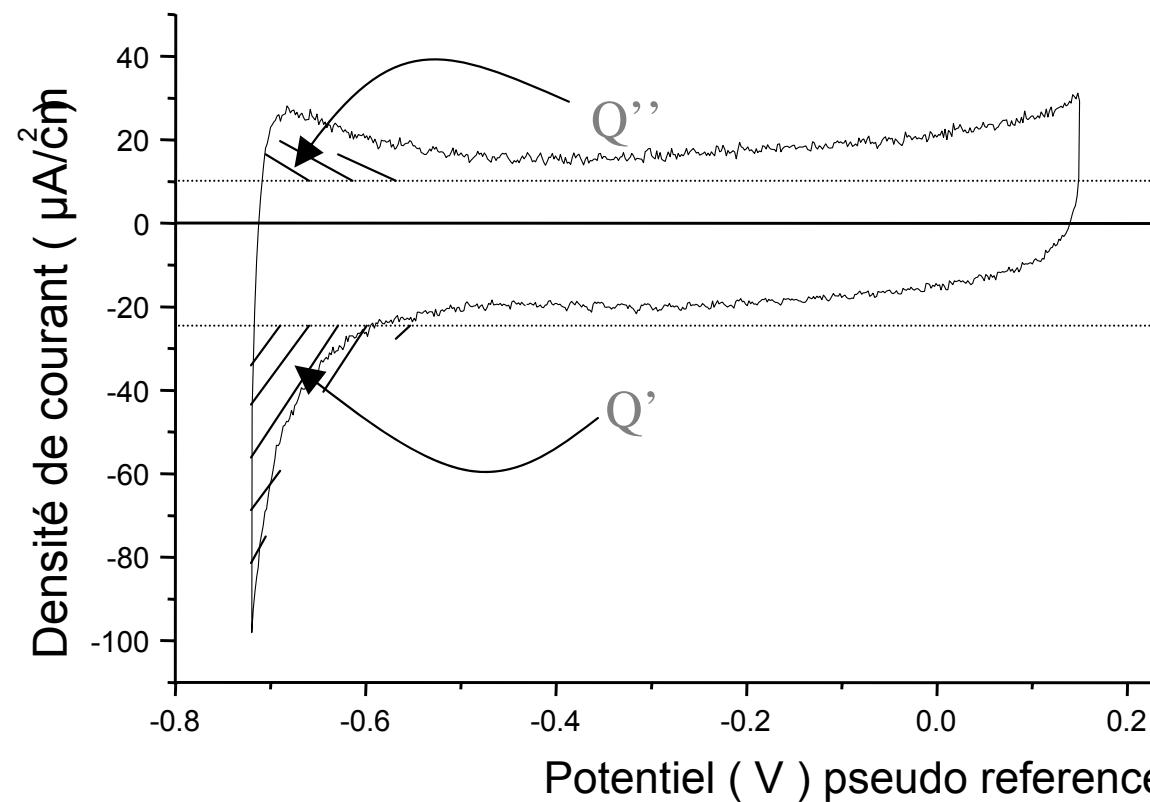


$[\text{FeCN}_6]^{3-/4-}$ behaves as quasi reversible system with Pt 1

Part 2: Elaboration and properties of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

Hydrogen under potentiel deposition (upd)

Thiol capped platinum nanoparticles exhibits H upd feature of « contaminated » surface

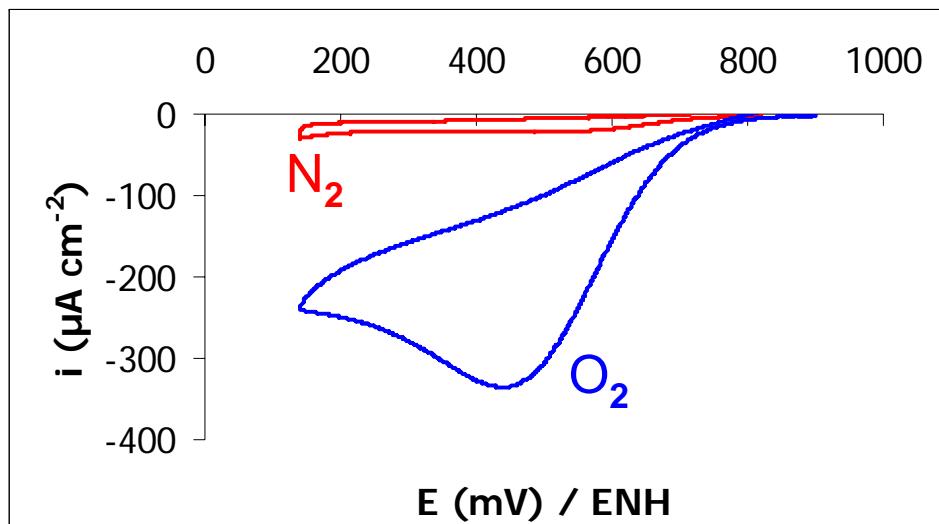


- $Q' \neq Q''$
- Low electroactive surfaces...

Part 2: Elaboration and properties of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

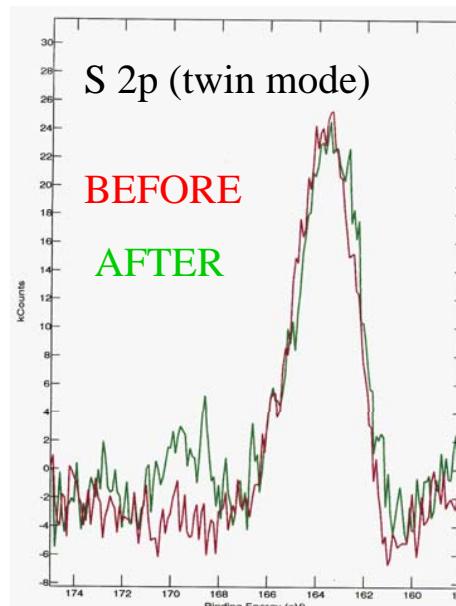
Oxygen reduction

→ Nanoparticles exhibit a direct significant response to oxygen reduction

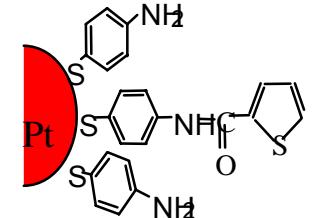


HClO_4 1 mol L⁻¹, 20 mV s⁻¹

Cavaliere S. Raynal, F. Etcheberry A., Herlem M., Perez H.
Electrochim. Solid State Let. 7 (10): A358-A360 2004



before cycling	after cycling
$\text{Pt } 4f/\text{S } 2p$ $S \text{ 2p } 161-166 \text{ eV}$	3.77 4.04
$\text{Pt } 4f/\text{Au } 4f$	0.15 0.16



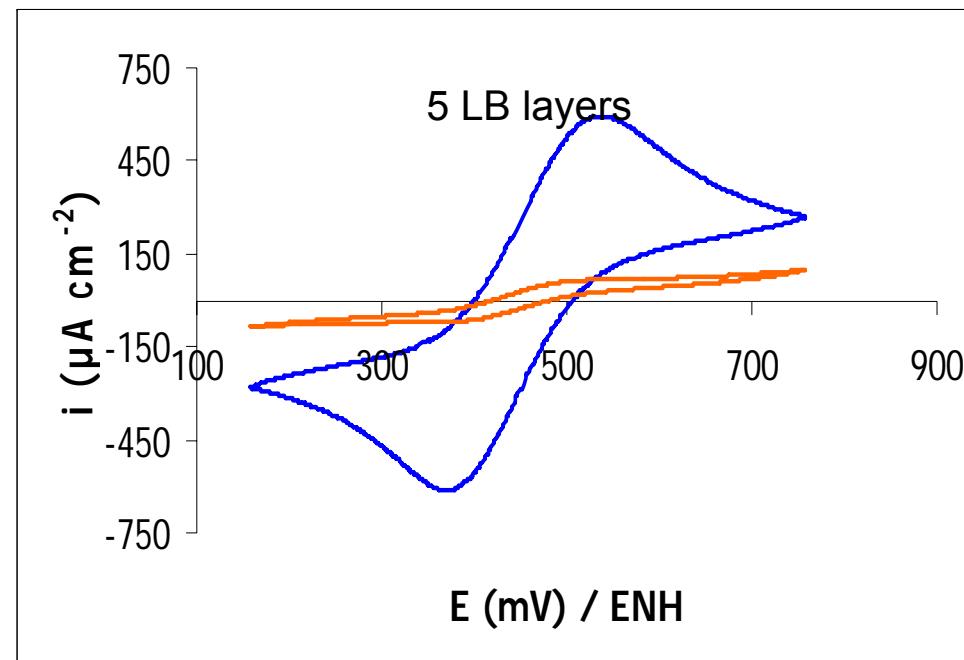
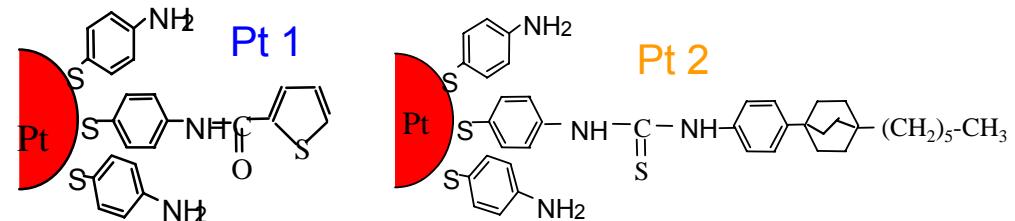
Prolonged cycling keep the organic crown essentially unchanged

Part 2: Elaboration and properties of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

Electrochemical behaviour: effect of organic crown in mixed films

→ $[\text{FeCN}_6]^{3-/4-}$ redox probe

5 mM $[\text{FeCN}_6]^{3-/4-}$ in 0.1 M Na_2SO_4 @ 20 mV s⁻¹

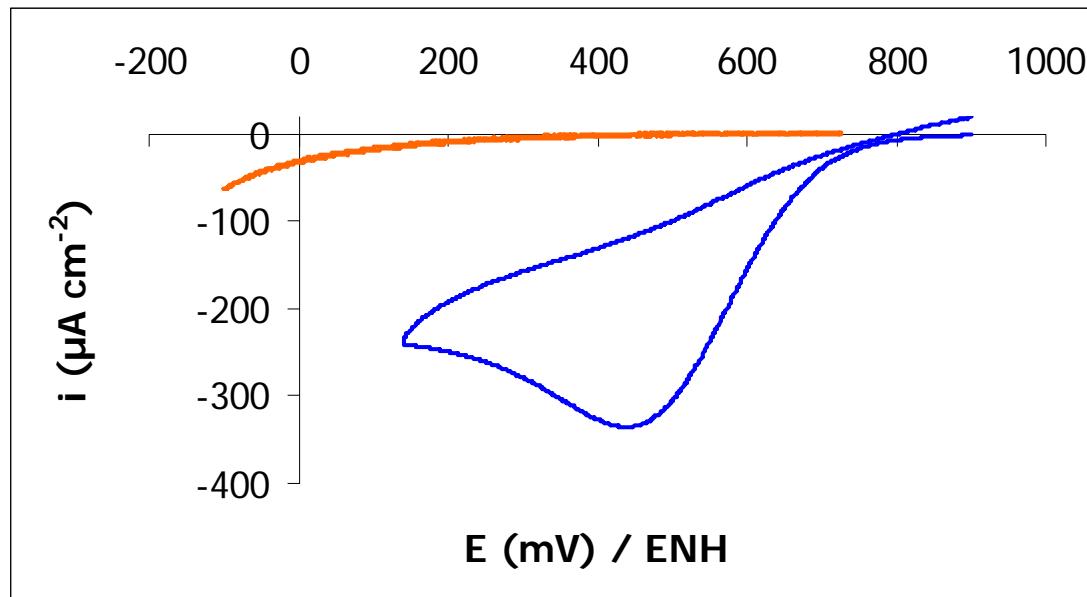
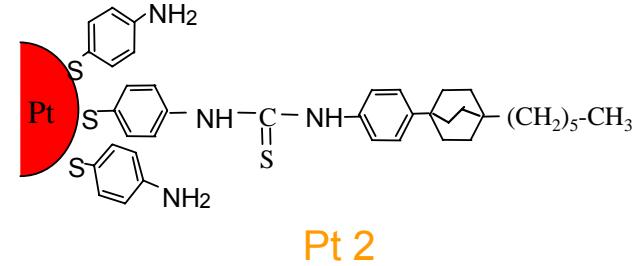
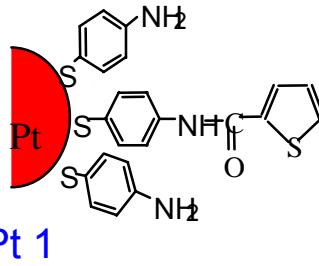


Electrochemical response is
blocked with Pt 2
(Residual response could be due to
pinholes)

Part 2: Elaboration and properties of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

Electrochemical behaviour: effect of organic crown in mixed films

→ Oxygen reduction



HClO_4 1 mol L⁻¹, 20 mV s⁻¹



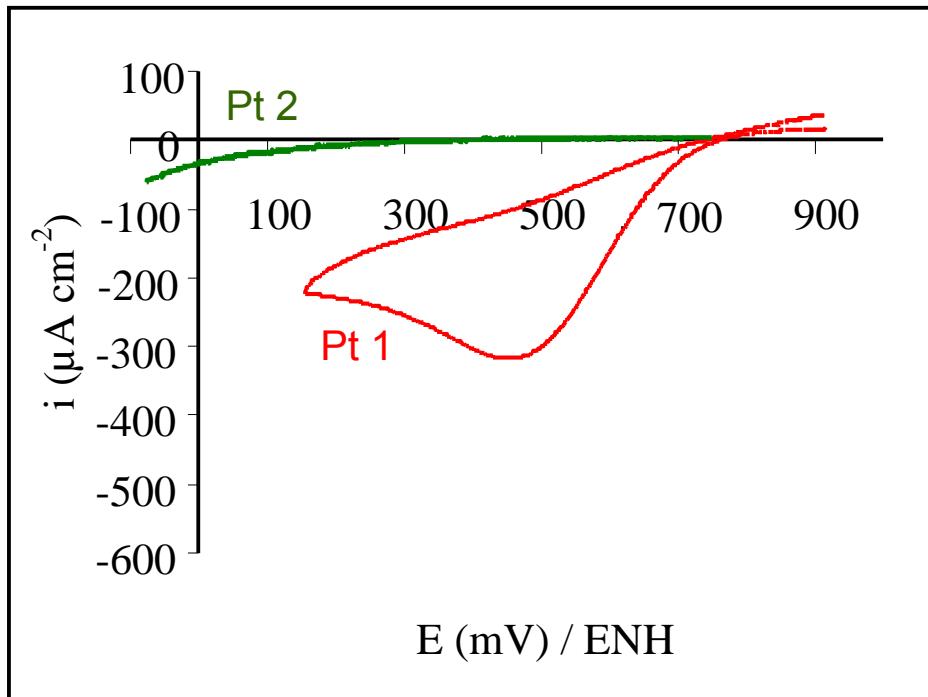
Effect of the fatty acid matrix ?

Pt 2 Exhibit no electrochemical activity towards oxygen reduction

Part 2: Elaboration and properties of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

Electrochemical behaviour: Effect of organic crown versus fatty acid elimination

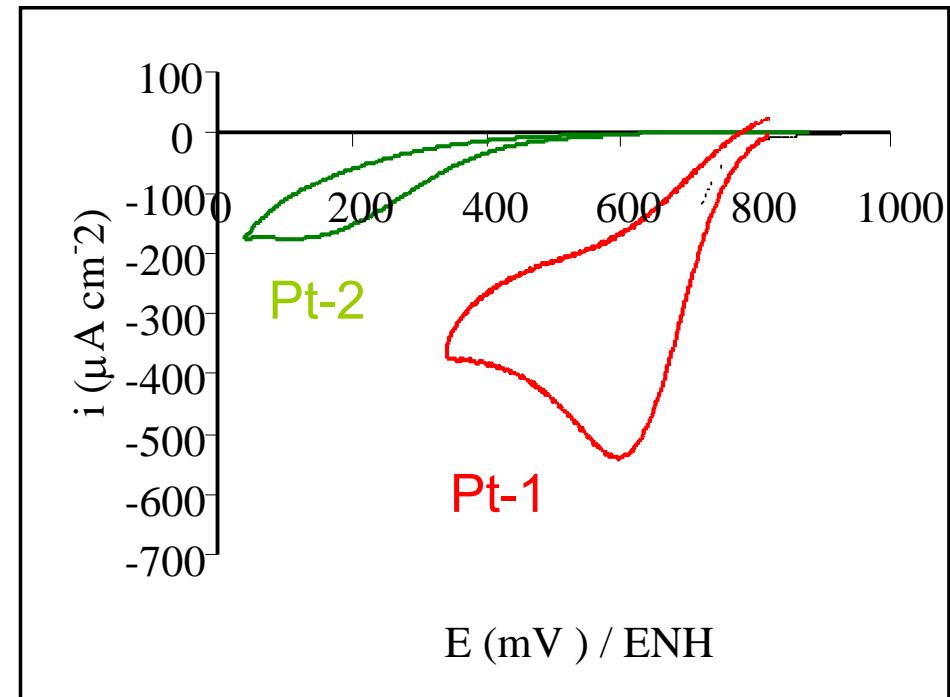
→ O₂ saturated 1 M HClO₄ @ 20 mV s⁻¹



Before whashing



effect nanoparticle environment:



After whashing

- Surrounding (fatty acid)
- Local (organic crown)

Part 2: Elaboration and properties of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

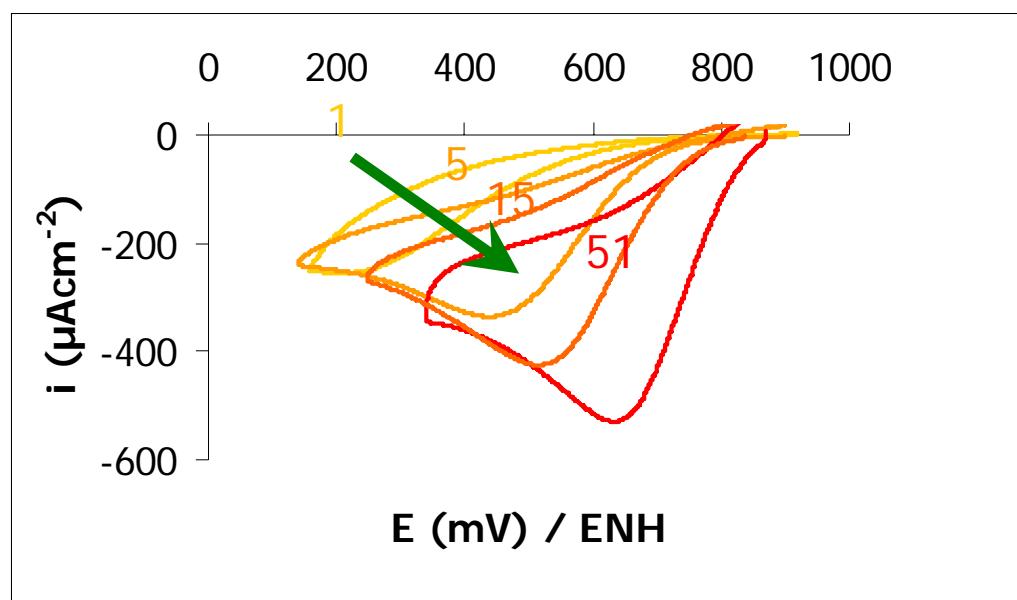
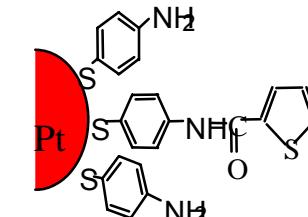
Electrochemical behaviour: Effect of platinum loading

→ O₂ reduction (mixed films)

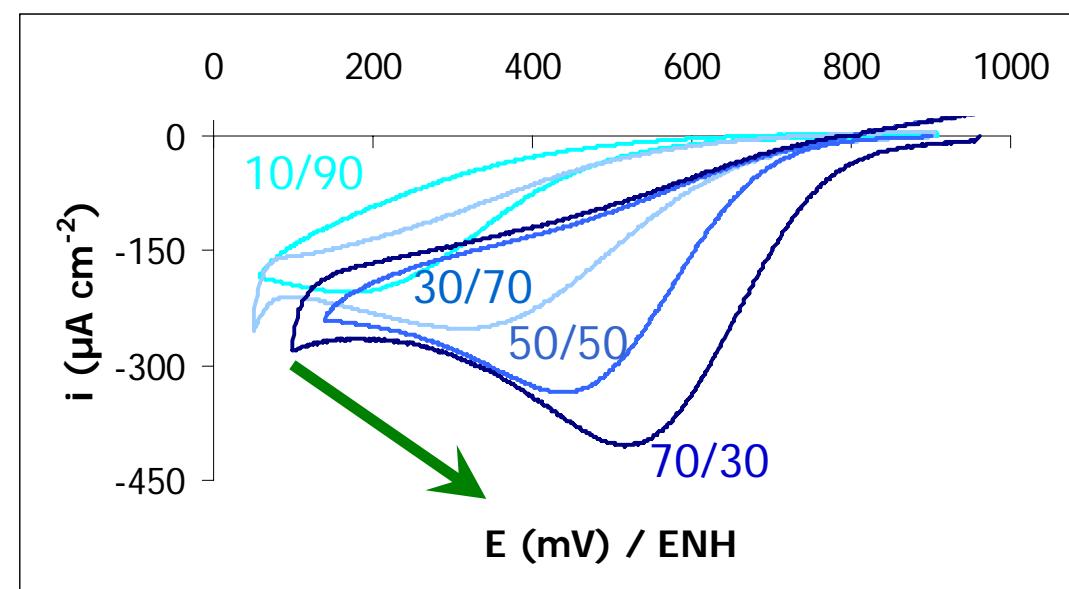
Two ways to modify platinum density

A
Fixed density in the layer
Increasing number of layers

B
Fixed number of layer
density in one monolayer $\sim 0.1 \text{ } \mu\text{g/cm}^2$ to $\sim 0.8 \text{ } \mu\text{g/cm}^2$



O₂ saturated 1 M HClO₄ @ 20 mV s⁻¹



O₂ saturated 1 M HClO₄ @ 20 mV s⁻¹

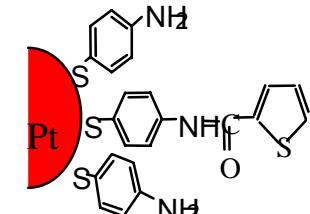


Both kinds of dilution lead to the same strong effect on current and potential

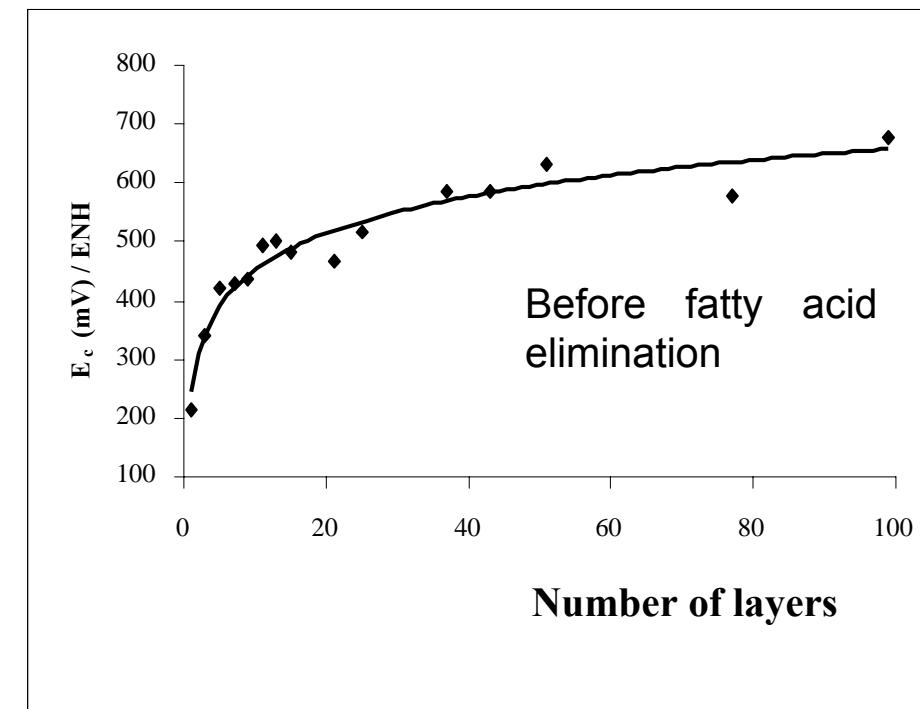
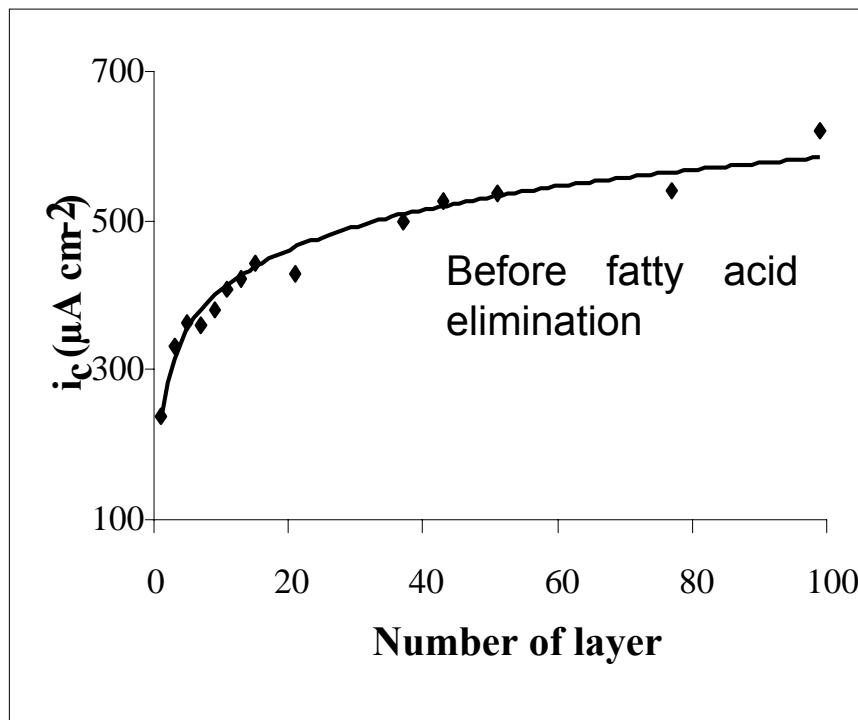
Part 2: Elaboration and properties of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

Electrochemical behaviour: Effect of platinum loading

→ Platinum density effect after fatty acid elimination (50/50 Pt-1/fatty acid ratio)



(O_2 saturated 1 M $HClO_4$ @ 20 mV s⁻¹)

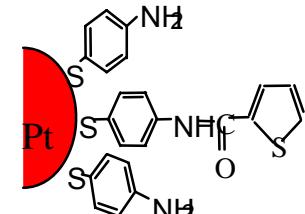


Slow improvement of electrochemical response

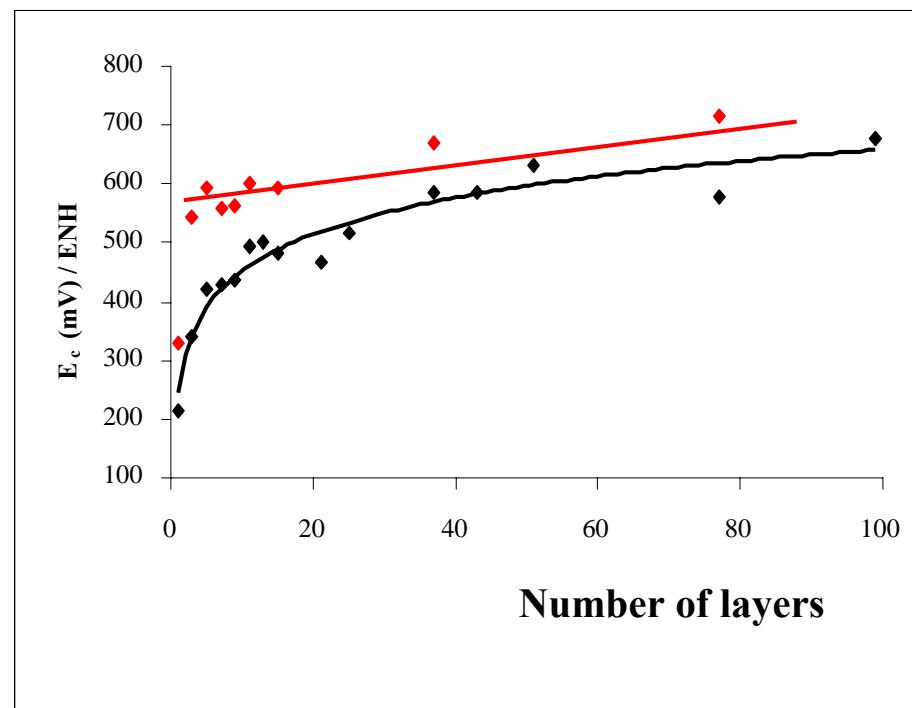
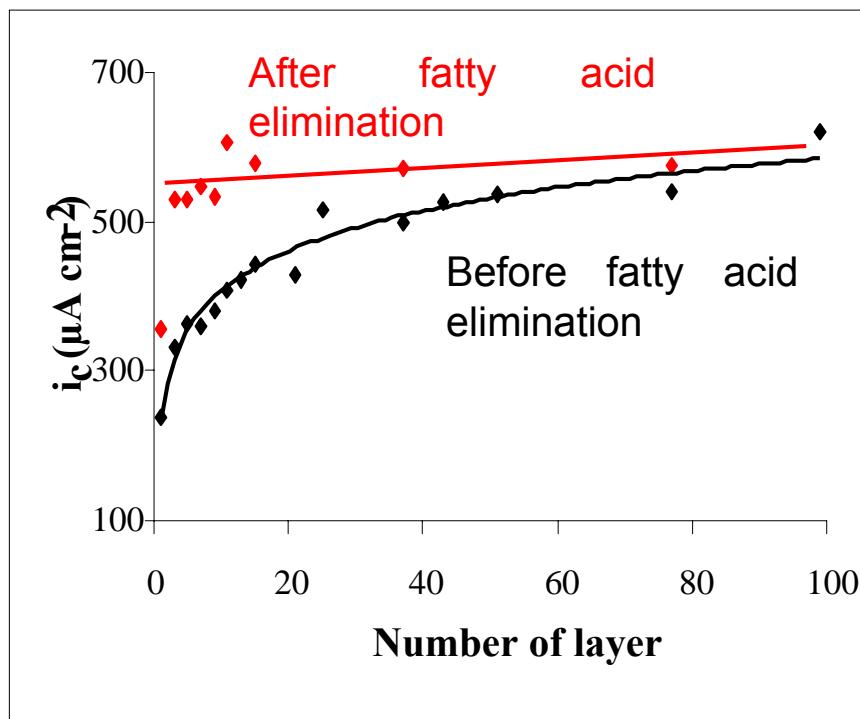
Part 2: Elaboration and properties of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

Electrochemical behaviour: Effect of platinum loading

→ Platinum density effect after fatty acid elimination (50/50 Pt-1/fatty acid ratio)



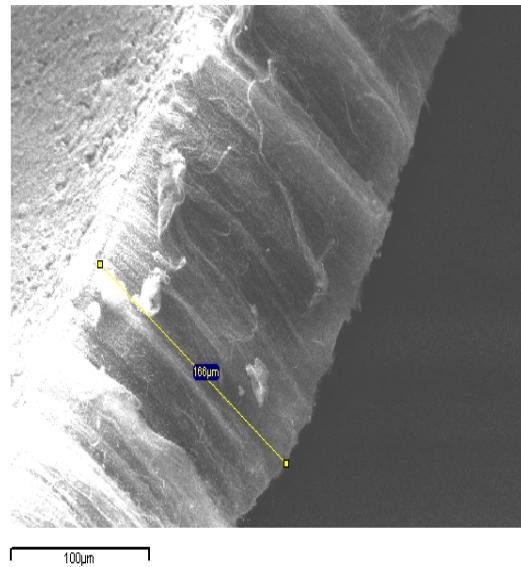
(O₂ saturated 1 M HClO₄ @ 20 mV s⁻¹)



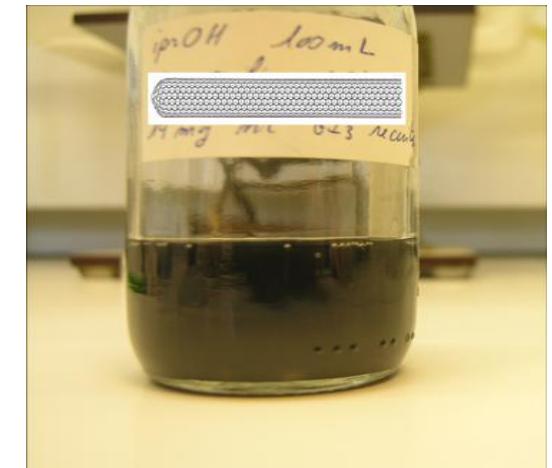
After fatty acid elimination one layer loading gives the same electrochemical response as several layers

Part 3: Elaboration and properties of nanocomposite based on organically capped platinum nanoparticles and carbon nanotubes

Main goal: To make model porous electrodes with controlled platinum loading and controlled nanoparticle feature which can be characterized ex-situ (three-electrode cell) and in fuel cells



Sonication



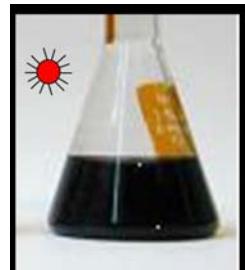
Nanotube liquid dispersion
of known concentration

M. Pinault, M. Mayne-L'Hermite, C. Reynaud,
O. Beyssac, J. N. Rouzaud and C. Clinard
Diamond and Related Materials 13 (2004) 1266–1269

B. Baret Ph-D Thesis 2008

Part 3: Elaboration and properties of nanocomposite based on organically capped platinum nanoparticles and carbon nanotubes

Association of platinum nanoparticles and carbon nanotube through Bottom-up approach :



+



NP Solution in
in solvent 1

NT Suspension NT
in solvent 2

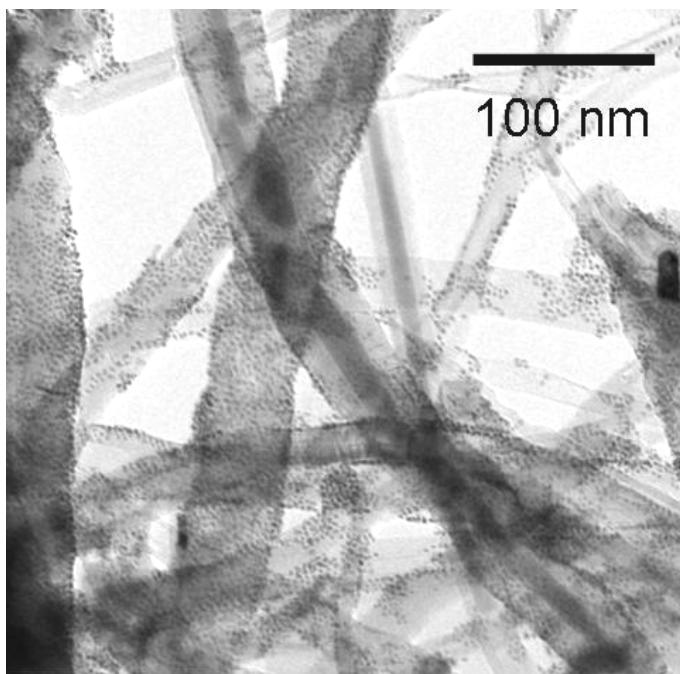
Mixture under stirring



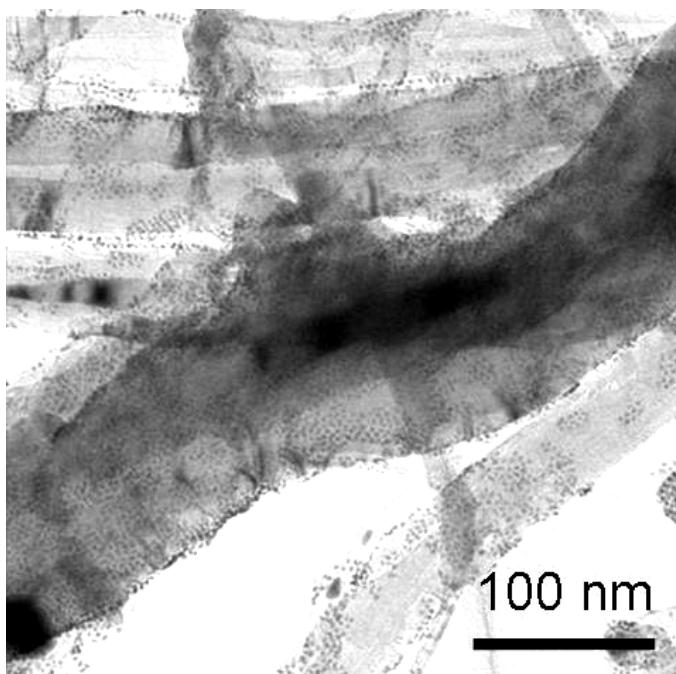
Control of relative amount allows nanocomposites liquid dispersion formation with controlled coverage of nanotube

Part 3: Elaboration and properties of nanocomposite based on organically capped platinum nanoparticles and carbon nanotubes

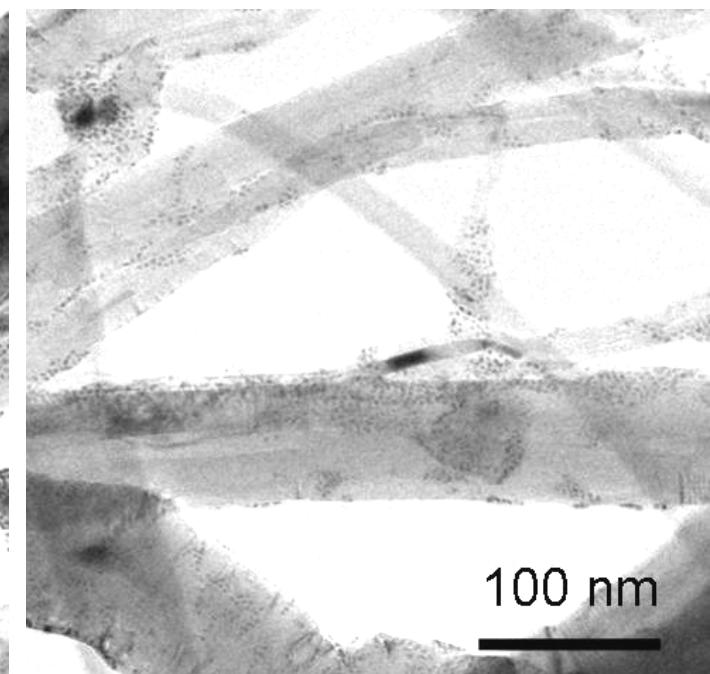
Charaterization of nanocomposite dispersions by Transmission Electron Microscopy



NP/NT=1/2



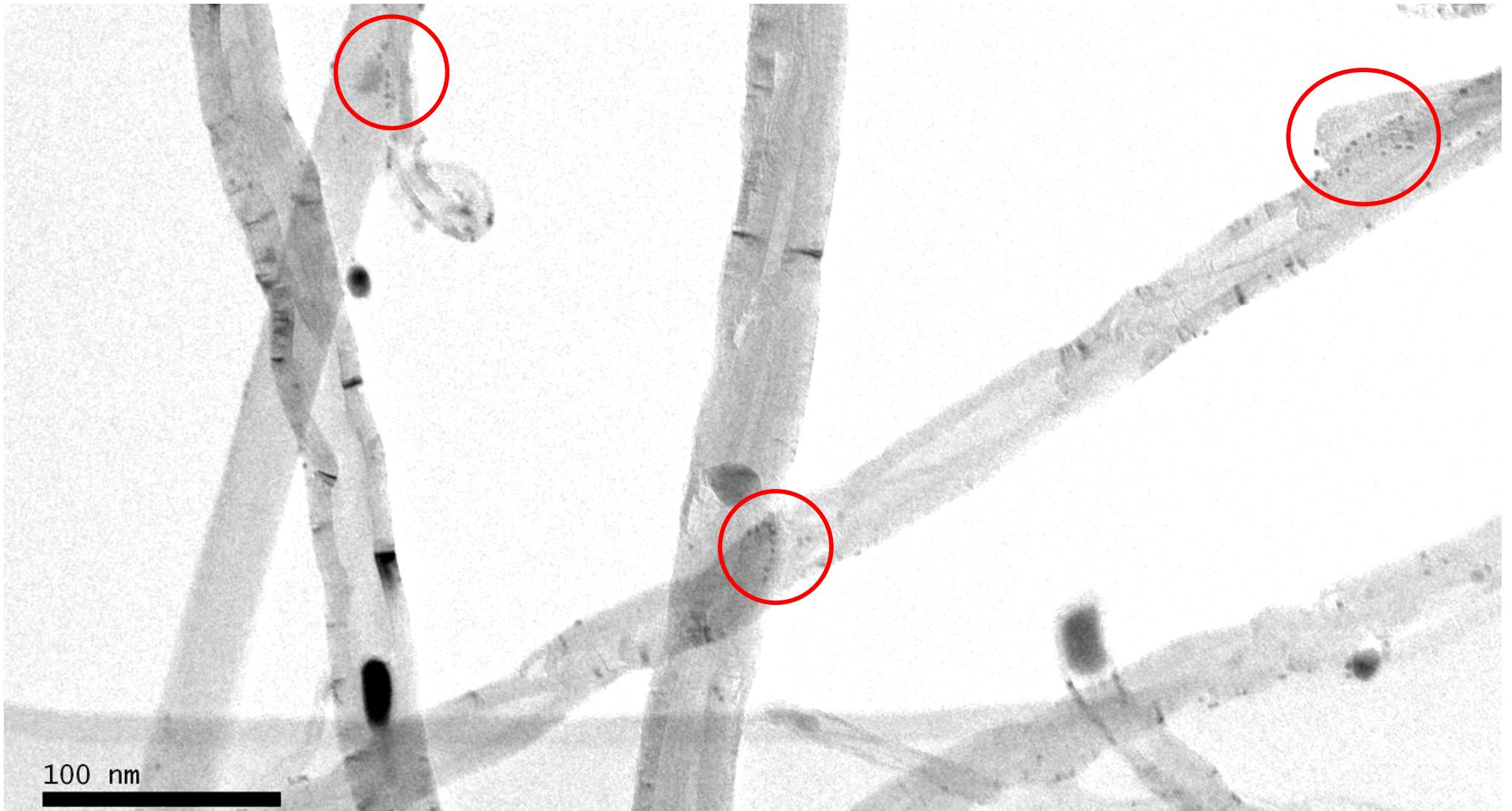
NP/NT=1/5



NP/NT=1/10

Part 3: Elaboration and properties of nanocomposite based on organically capped platinum nanoparticles and carbon nanotubes

Charaterization of nanocomposite dispersions by Transmission Electron Microscopy

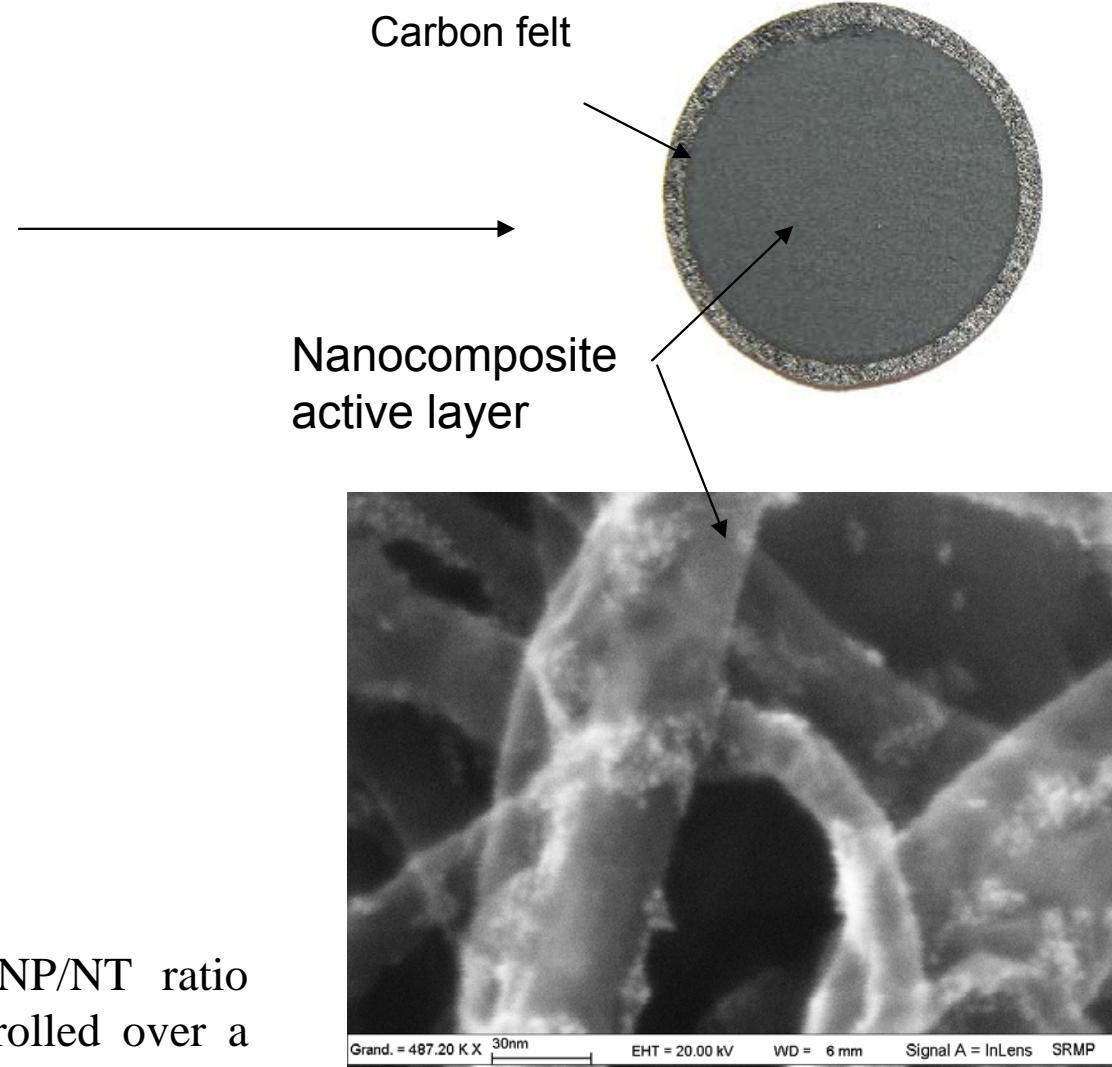
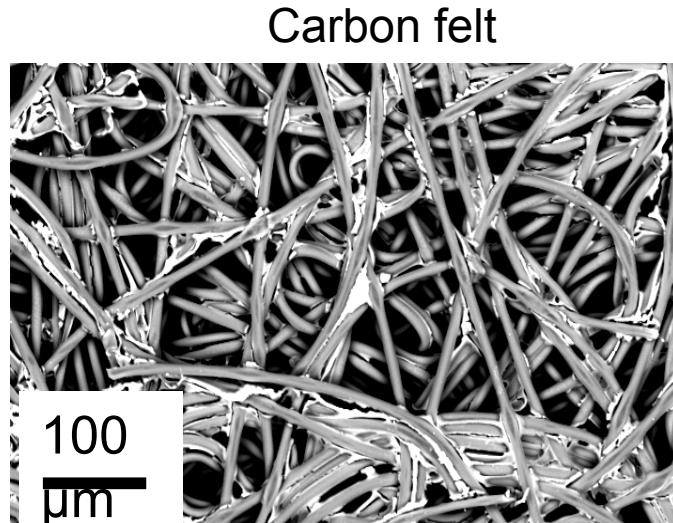


100 nm

NP/NT = 1/100

Part 3: Elaboration and properties of nanocomposite based on organically capped platinum nanoparticles and carbon nanotubes

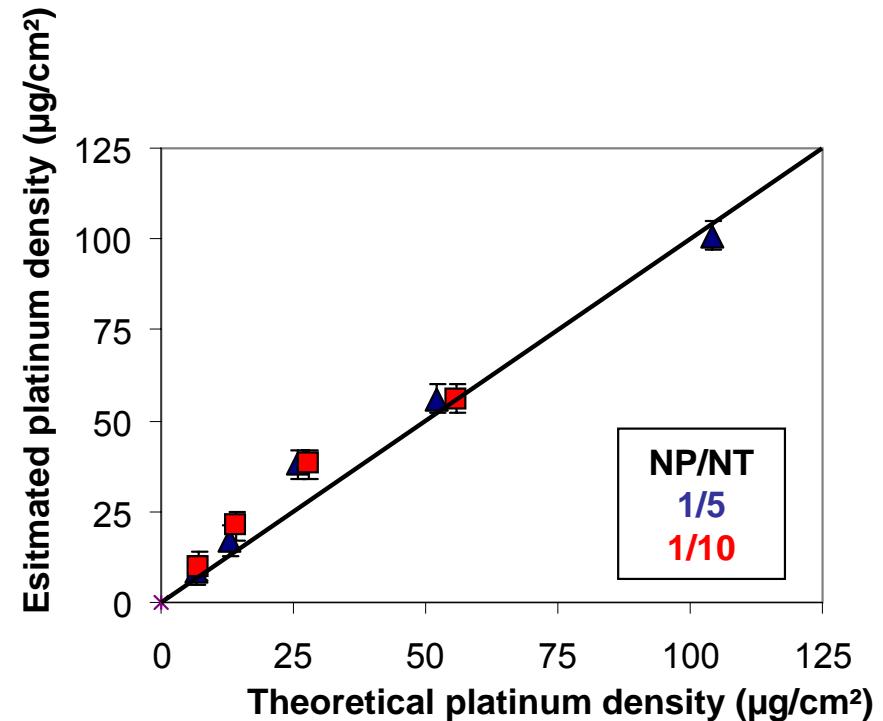
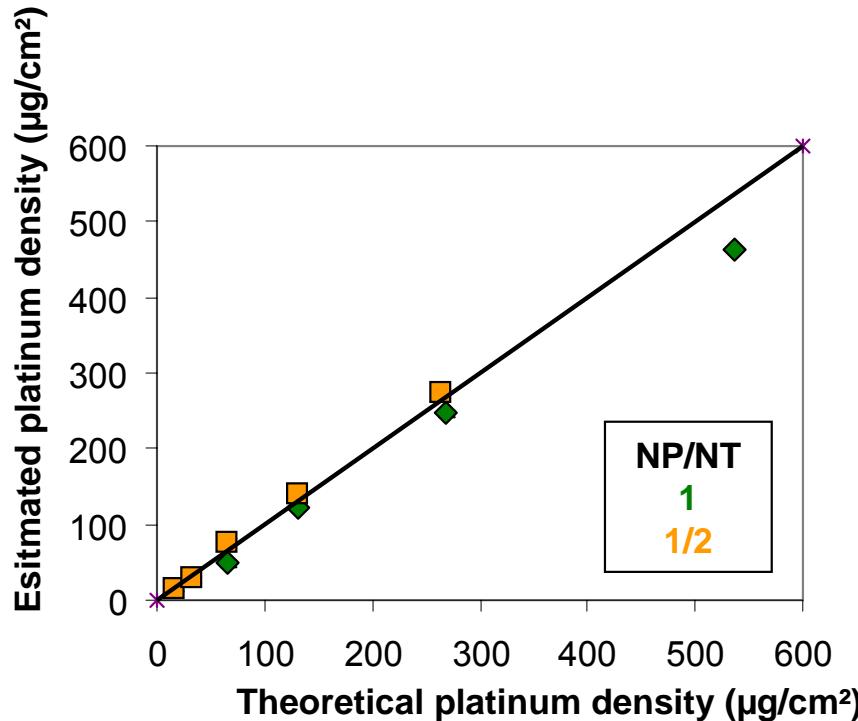
Electrode formation by filtration of the liquid nanocomposite dispersion



As a function volume and NP/NT ratio platinum loading can be controlled over a wide range

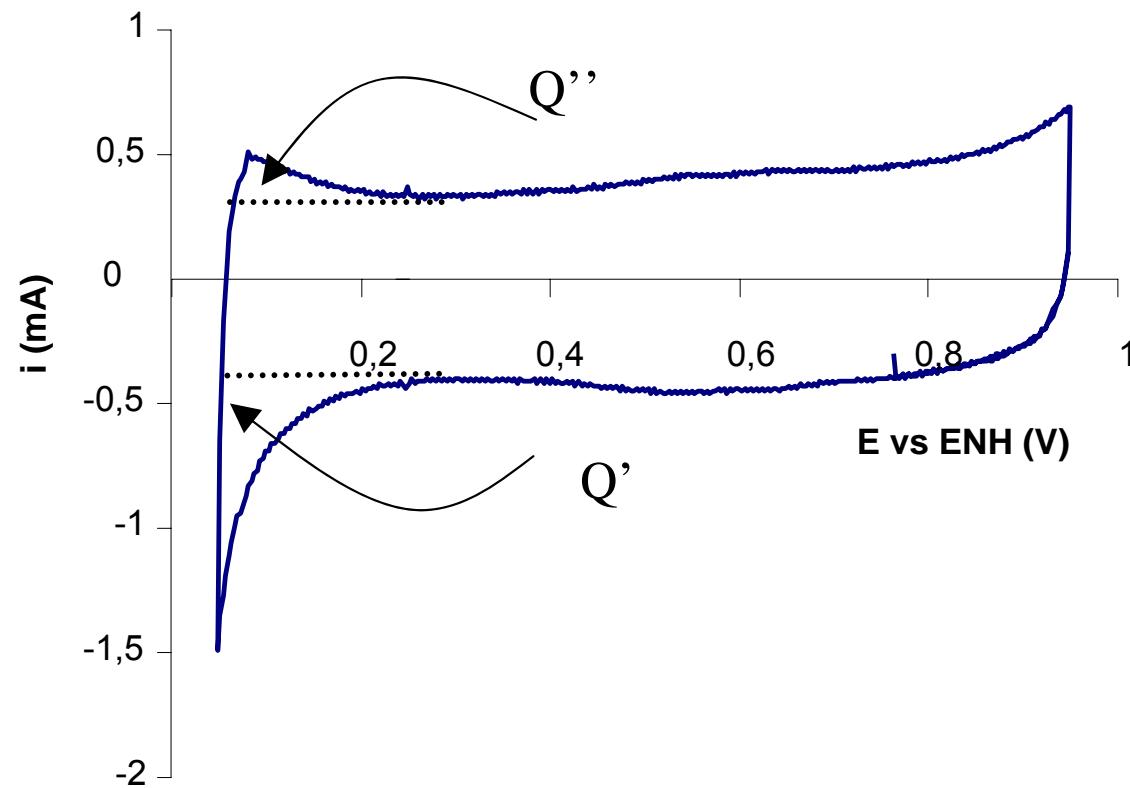
Part 3: Elaboration and properties of nanocomposite based on organically capped platinum nanoparticles and carbon nanotubes

→ Platinum loading can be controlled over a wide range



Part 3: Elaboration and properties of nanocomposite based on organically capped platinum nanoparticles and carbon nanotubes

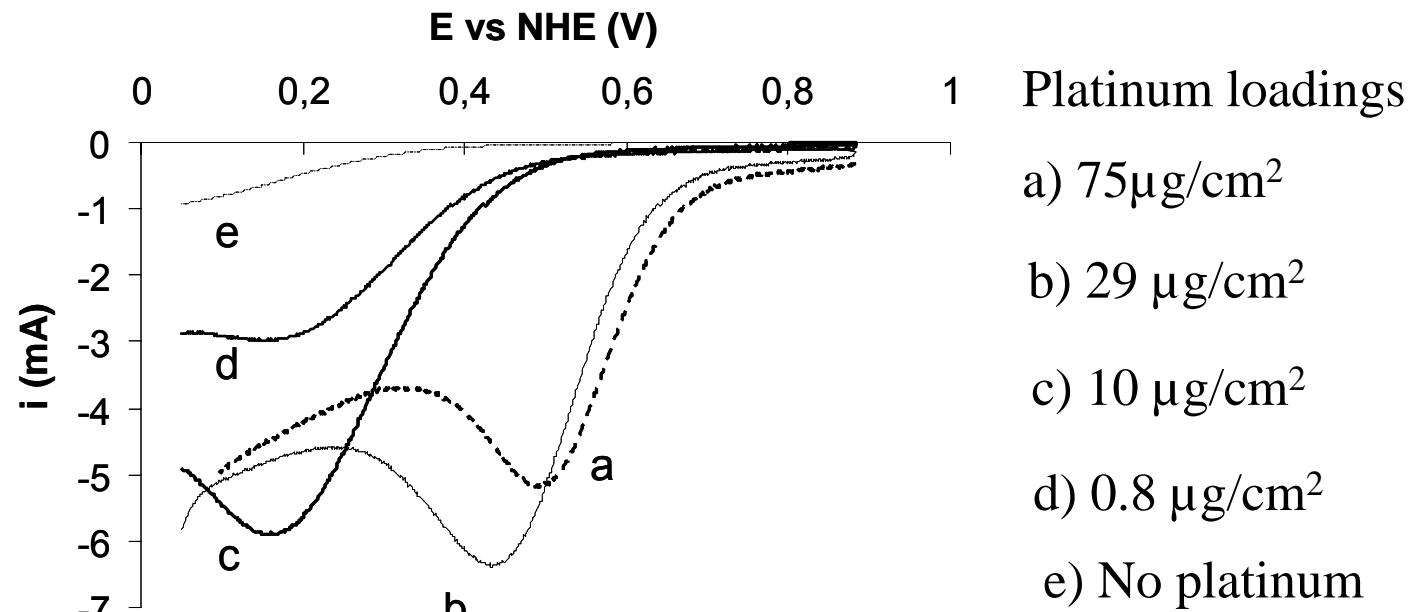
→ Electrochemical behaviour



Same feature for H upd....

Part 3: Elaboration and properties of nanocomposite based on organically capped platinum nanoparticles and carbon nanotubes

→ Electrochemical behaviour towards oxygen reduction



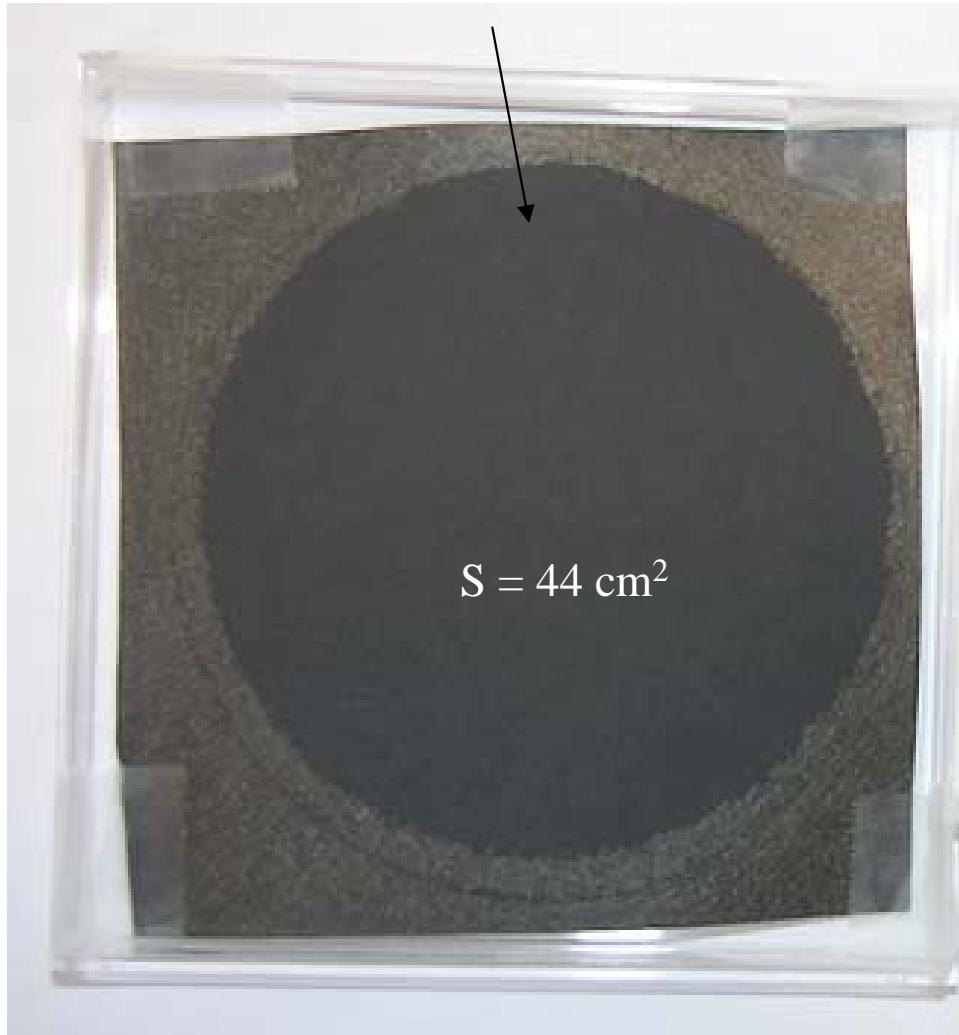
Oxygen reduction can be evidenced over a wide of platinum loading and up ultra low loading

B. Baret Ph-D Thesis 2008

Part 3: Elaboration and properties of nanocomposite based on organically capped platinum nanoparticles and carbon nanotubes

→ Fuel cell test preliminary results

Fuel cell test electrode



ex-situ characterization (three-electrode cell)



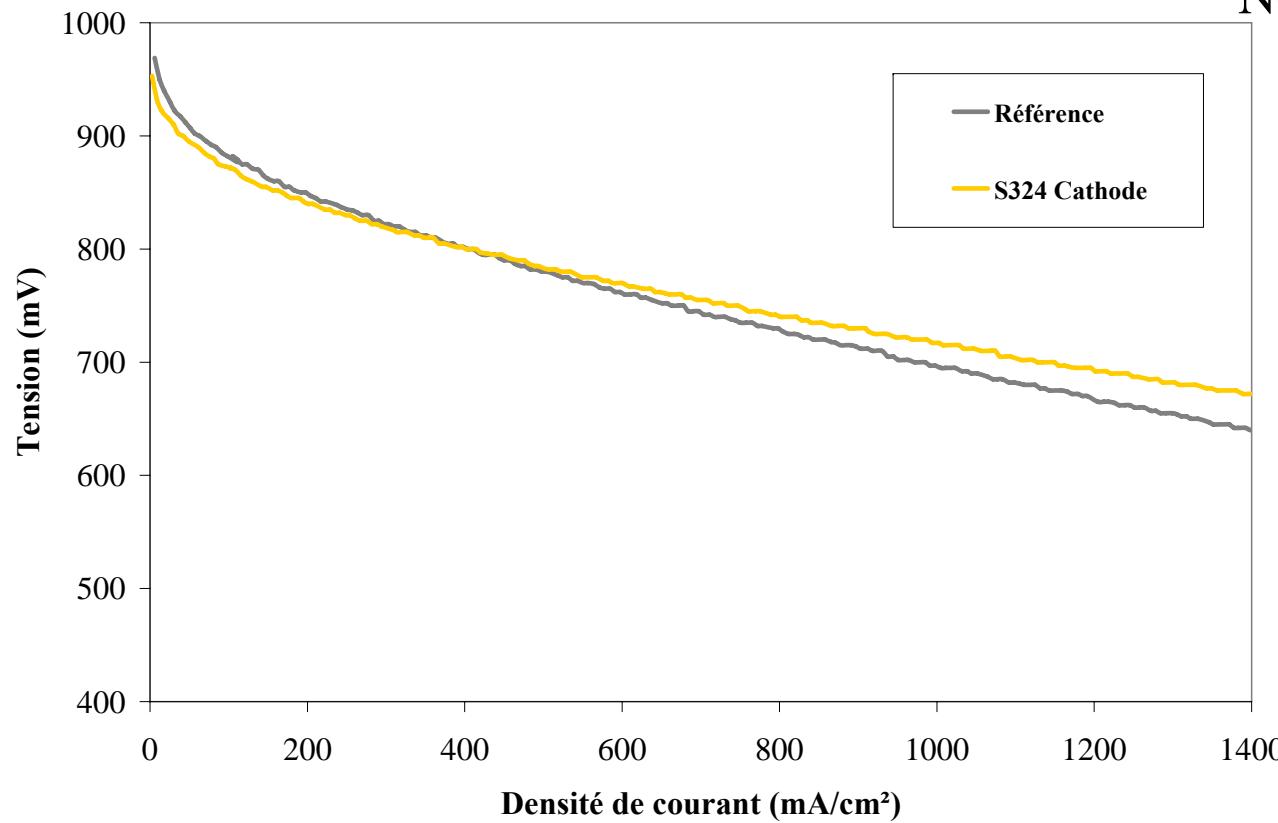
Part 3: Elaboration and properties of nanocomposite based on organically capped platinum nanoparticles and carbon nanotubes

- Fuel cell test (A. Morin CEA Technological Research Division Grenoble) :

Reference Membrane Electrode Assembly: Commercial Anode et cathode $500 \mu\text{g/cm}^2$

Test Membrane Electrode Assembly : Anode $500 \mu\text{g/cm}^2$ cathode nanocomposite ($115 \mu\text{g/cm}^2$)

No activation treatment



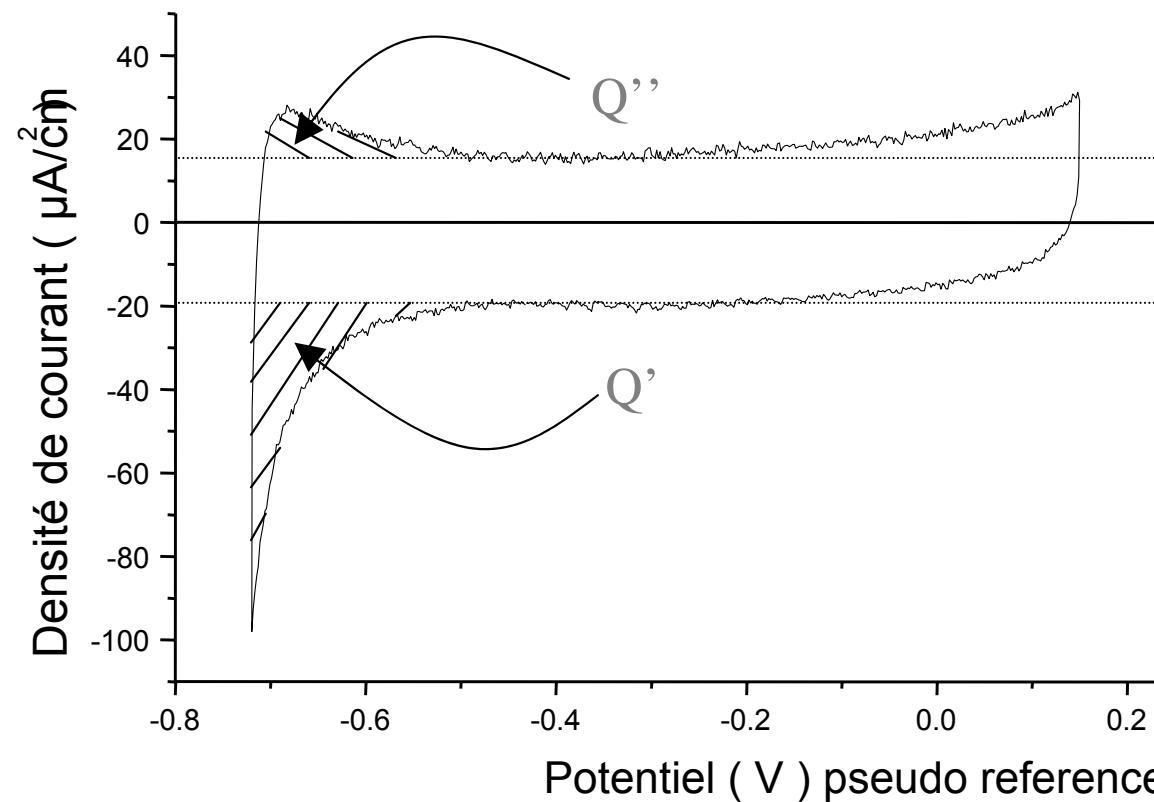
- Demonstrate the possibility to decrease significantly the cathode platinum loading (close to factor 5) while keeping high performances

Conclusion

- Capped platinum nanoparticles can provide efficient oxygen reduction catalyst
 - - the sites concerned by oxygen reduction ?
 - reliability of H upd measurement versus oxygen reduction potentialities ?
- Determine electrochemical parameters directly related to oxygen reduction in nanocomposite porous electrodes ...

Part 2: Elaboration and properties of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

Specifical behaviour towards Hydrogen underpotential deposition

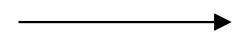
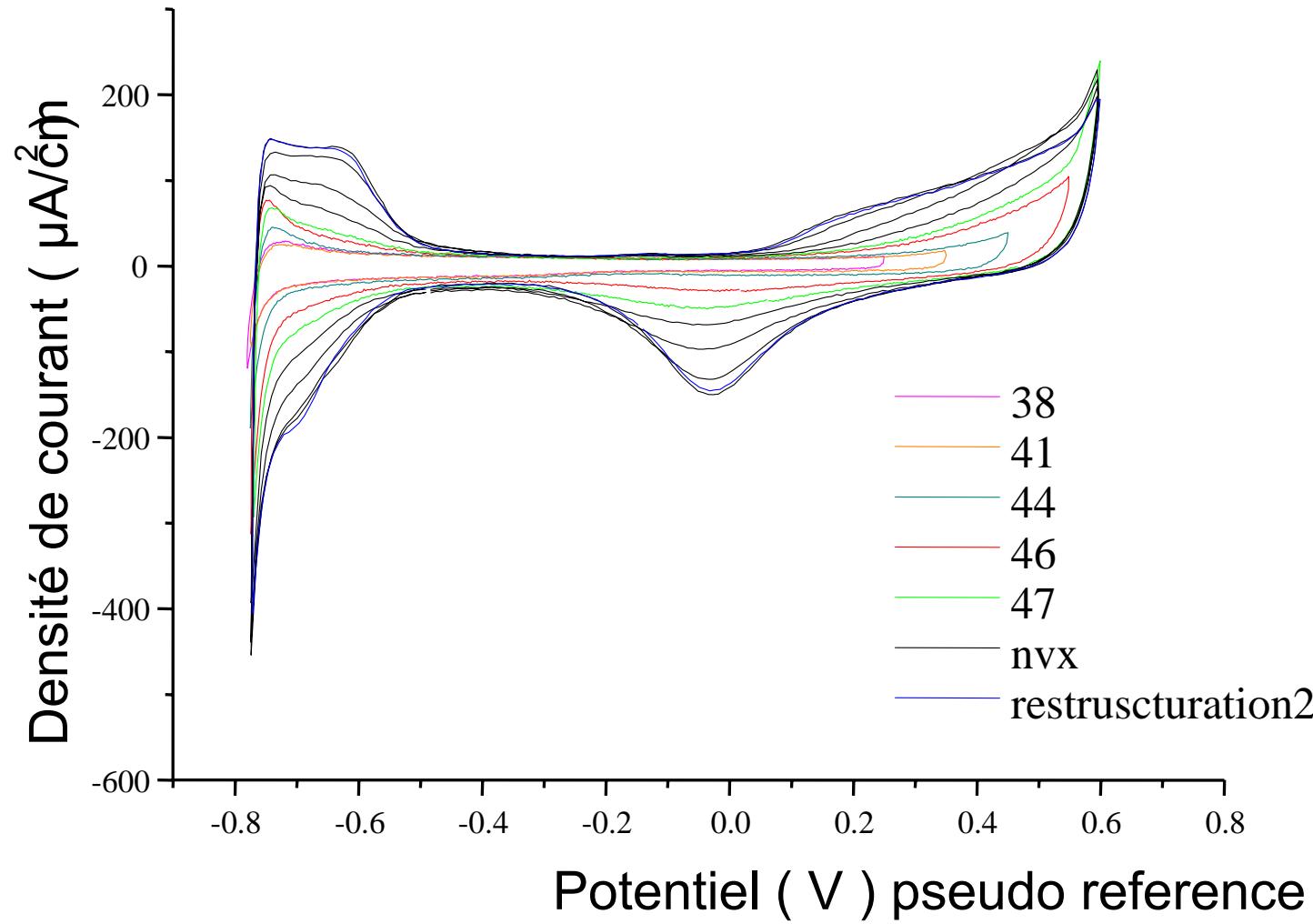


- $Q' \neq Q''$
- Low electroactive surfaces



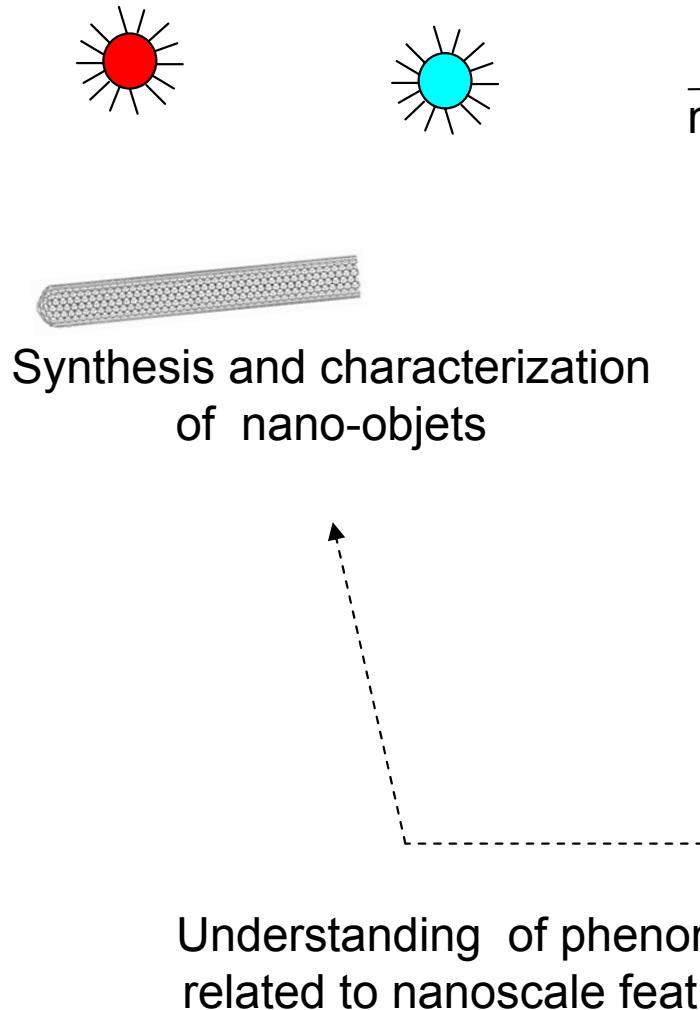
- Reliable measurement ?

Part 2: Elaboration and properties of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

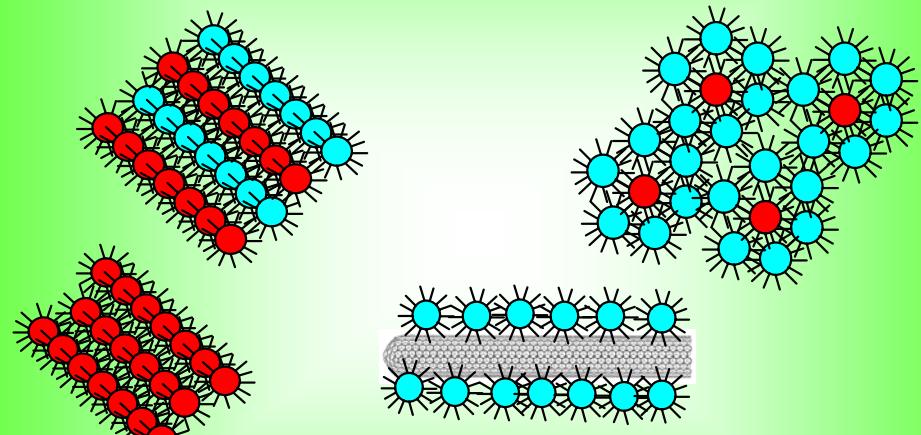


Modify the platinum core....

DEVELOPMENT AND ELECTROCHEMICAL BEHAVIOUR OF PLATINUM BASED NANOCOMPOSITE MODEL STRUCTURES BUILT USING THE BOTTOM UP APPROACH



Part 2: Mixed LB films based on organically capped platinum nanoparticles

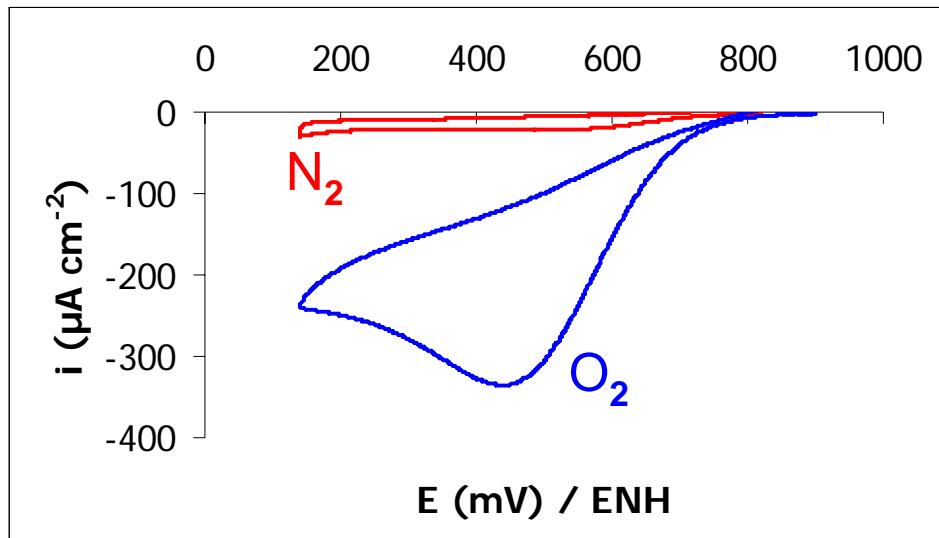


Elaboration and characterization of solid state nanostructures from preformed nano-objects

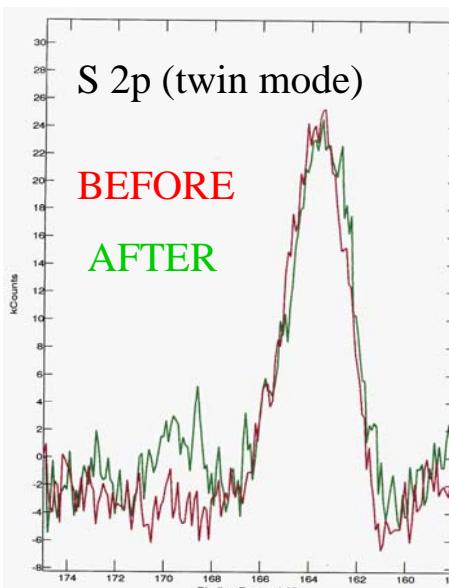
PART 3: ELECTROCHEMICAL PROPERTIES

Oxygen reduction :
a direct electrochemical activity

→ 5 LB layers LB Pt-1/Fatty acid (50/50)

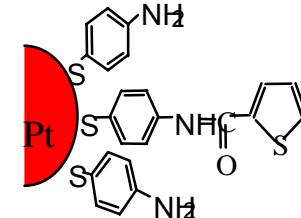


HClO_4 1 mol L⁻¹, 20 mV s⁻¹



before cycling	after cycling
$\text{Pt } 4f/\text{S } 2p$ $\text{S } 2p \text{ 161-166 eV}$	3.77 4.04
$\text{Pt } 4f/\text{Au } 4f$	0.15 0.16

Prolonged cycling keep the organic crown
essentially unchanged

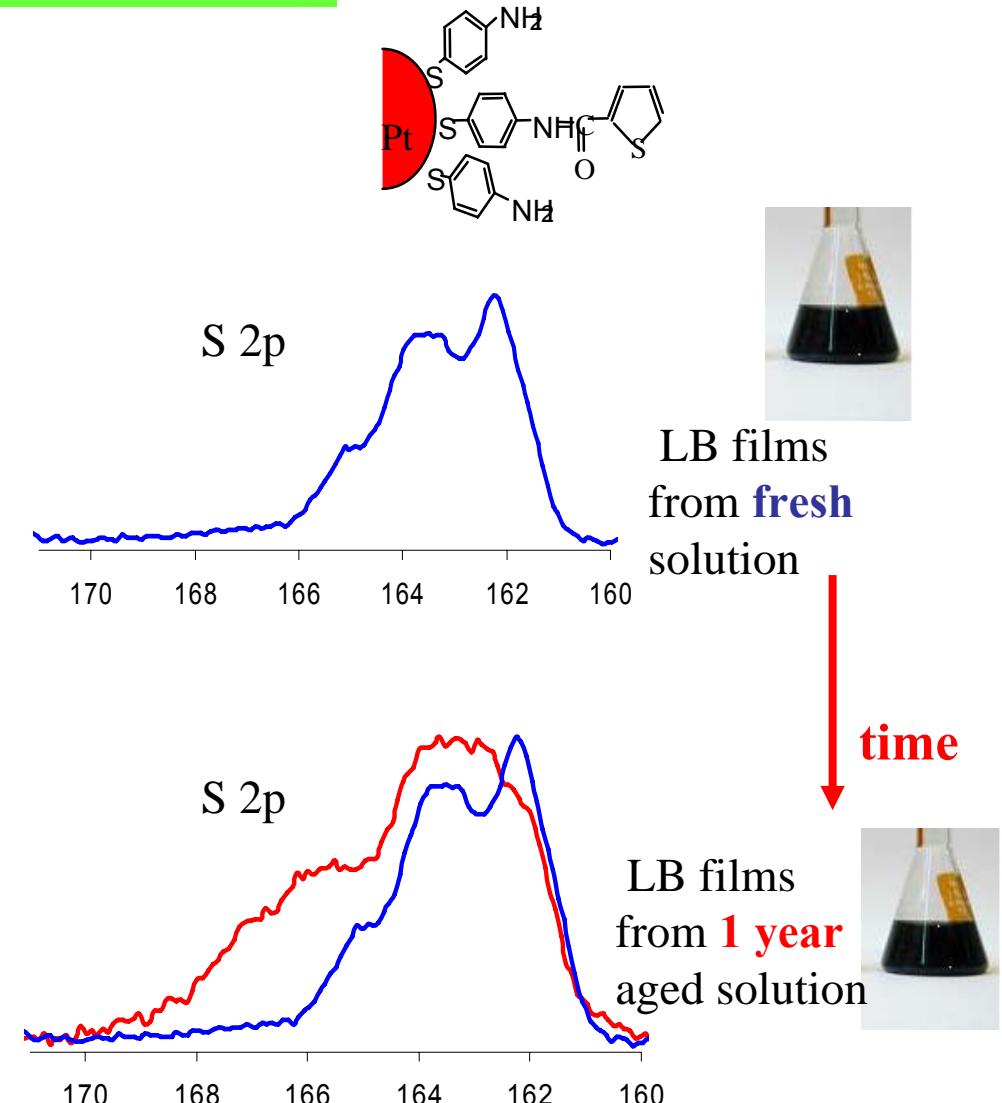
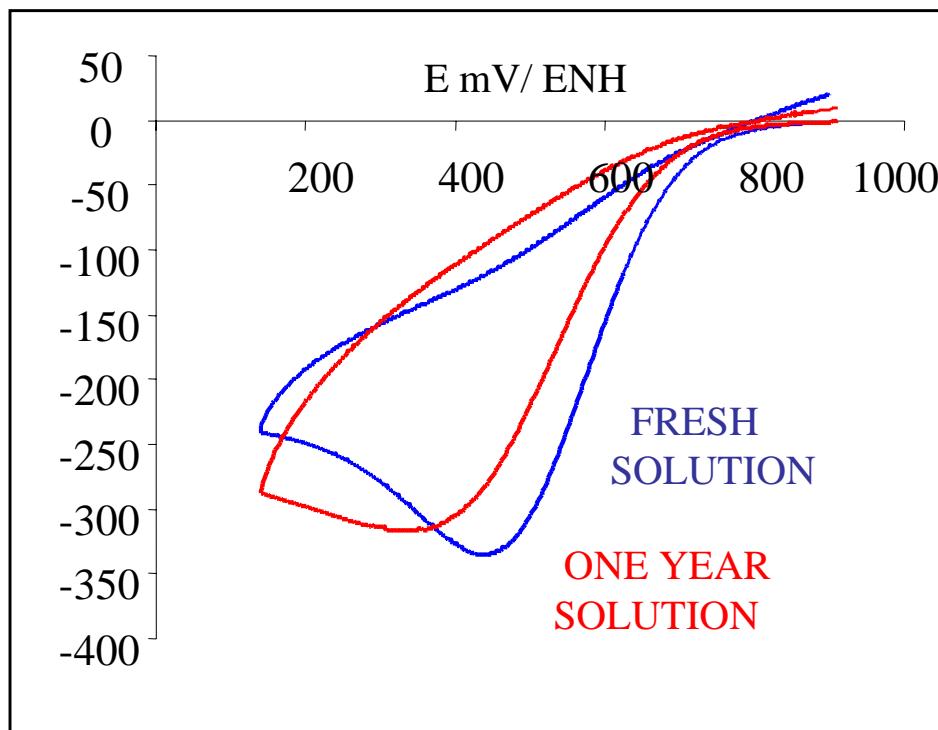


Cavaliere S. Raynal, F. Etcheberry A., Herlem M., Perez H.
Electrochim. Solid State Let. 7 (10): A358-A360 2004

PART 3: ELECTROCHEMICAL PROPERTIES

Stability of stock solution towards O₂ reduction

→ O₂ reduction HClO₄ 1 mol L⁻¹, 20 mV s⁻¹



PART 3: ELECTROCHEMICAL PROPERTIES

Influence of different parameters on the electrochemical behaviour

- Effect of organic crown modification
- Effect of fatty acid elimination (versus organic crown effect)
- Effect of platinum density
- Effect of fatty removal (versus platinum density effect)

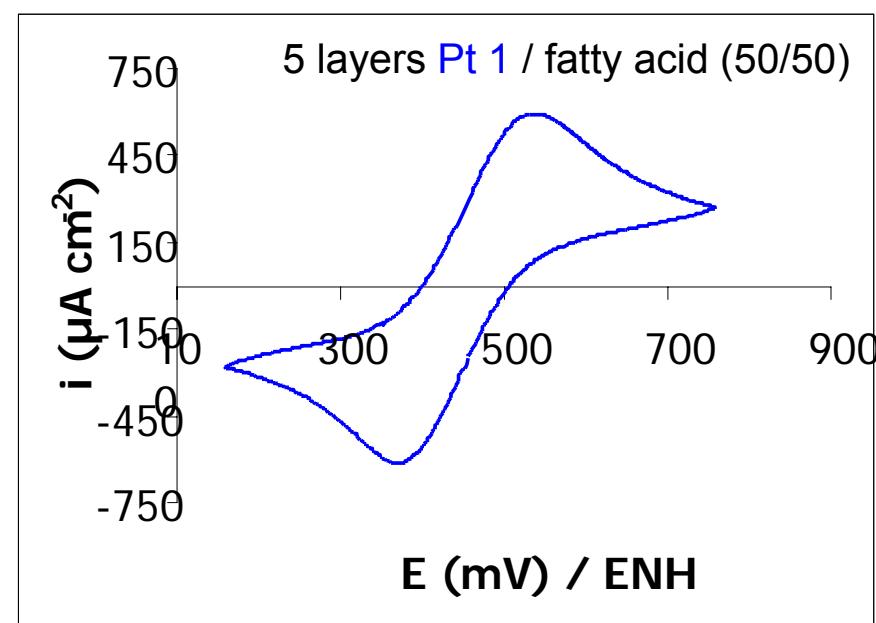
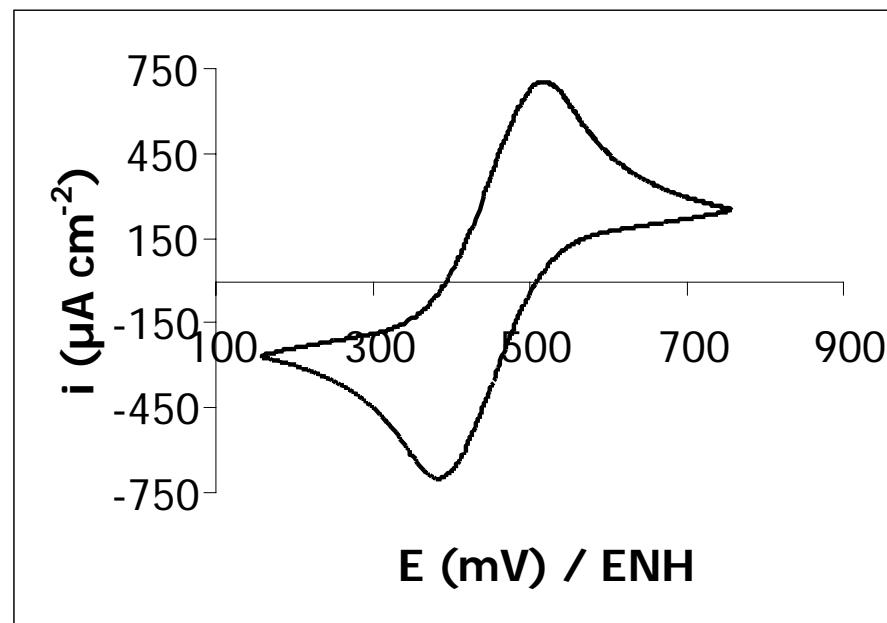
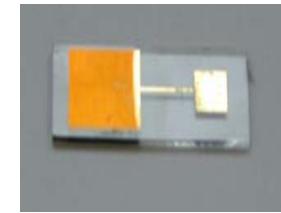
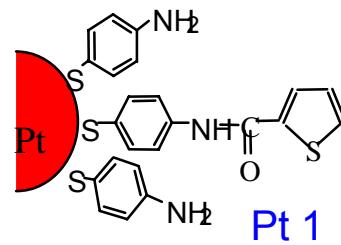
PART 3: ELECTROCHEMICAL PROPERTIES

Effect of the organic crown (mixed films)

→ $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox probe

5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in 0.1 M Na_2SO_4 @ 20 mV s⁻¹

Bare gold electrode



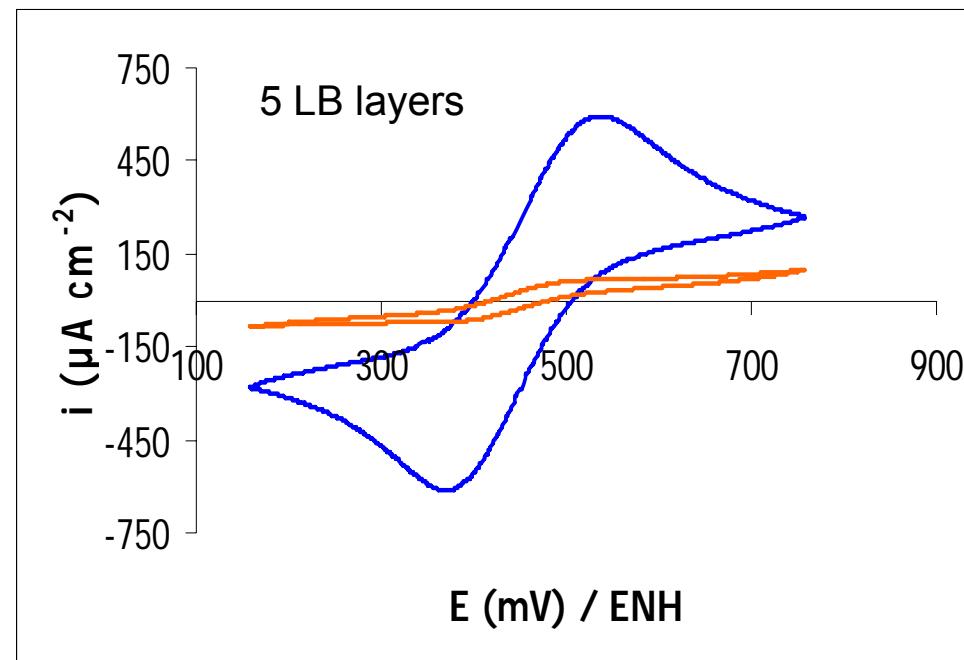
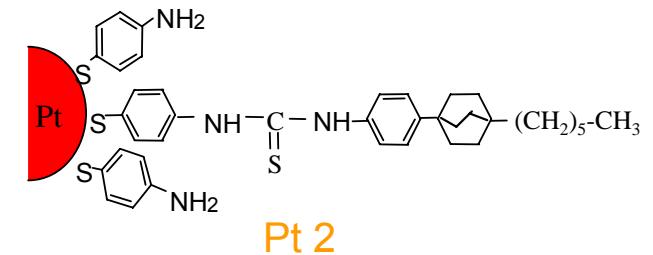
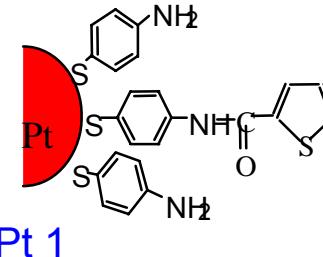
$[\text{Fe}(\text{CN})_6]^{3-/4-}$ behaves as quasi reversible system with Pt 1

PART 3: ELECTROCHEMICAL PROPERTIES

Effect of the organic crown (mixed films)

→ $[\text{FeCN}_6]^{3-/\text{4}-}$ redox probe

5 mM $[\text{FeCN}_6]^{3-/\text{4}-}$ in 0.1 M Na_2SO_4 @ 20 mV s⁻¹

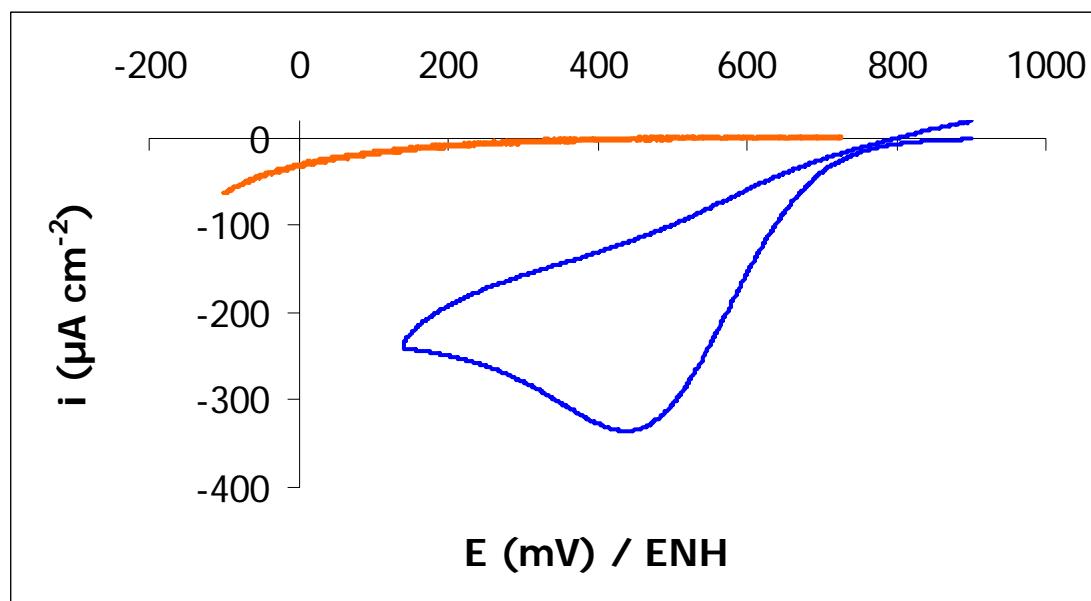
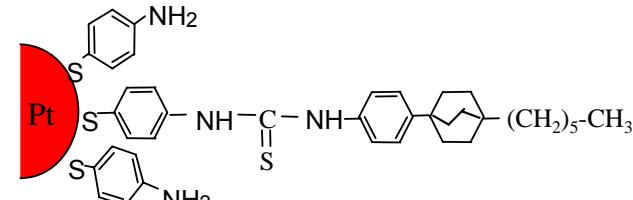
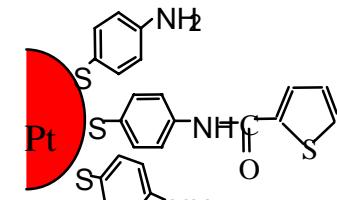


$[\text{FeCN}_6]^{3-/\text{4}-}$ electrochemical response is blocked with Pt 2
(Residual response could be due to pinholes)

PART 3: ELECTROCHEMICAL PROPERTIES

Effect of the organic crown (mixed films)

→ Oxygen reduction



HClO_4 1 mol L⁻¹, 20 mV s⁻¹

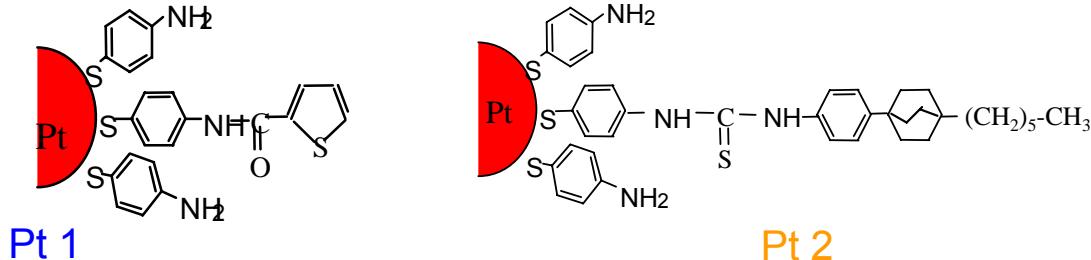


Strong effect of local environment on
The electrochemical activity

PART 3: ELECTROCHEMICAL PROPERTIES

Effect of the organic crown (mixed films)

→ Reasons for Pt 2 inactivity ?



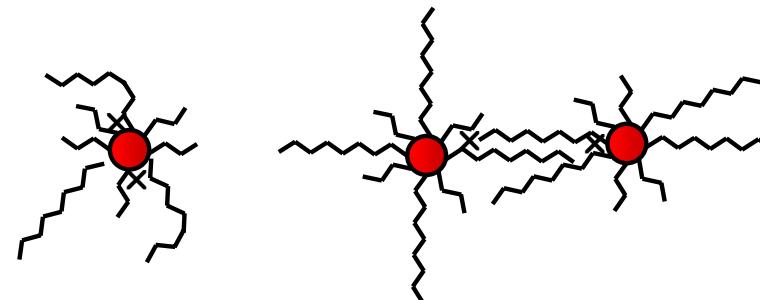
Different features of **Pt 1** and **Pt 2**

- D.C. conductivity



Particule	$\sigma_{//} (S \text{ cm}^{-1})$
Pt-1	$8,5 \times 10^{-4}$
Pt-2	$3,0 \times 10^{-7}$

- Steric hindrance in **Pt 2** ?



- **Pt 2** is soluble in non polar solvents: Hydrophobicity and wettability ?

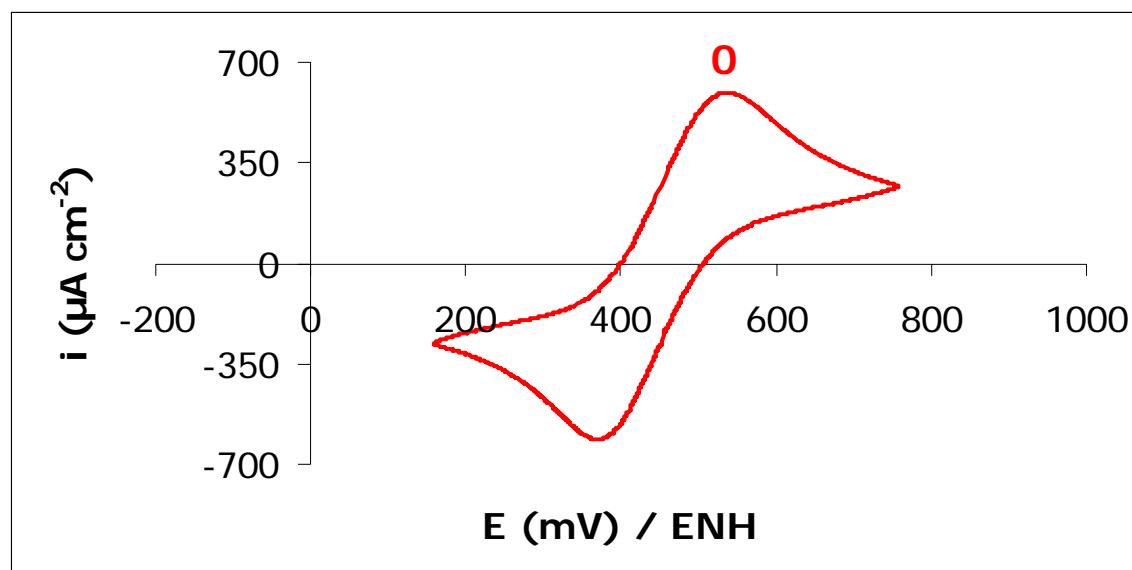
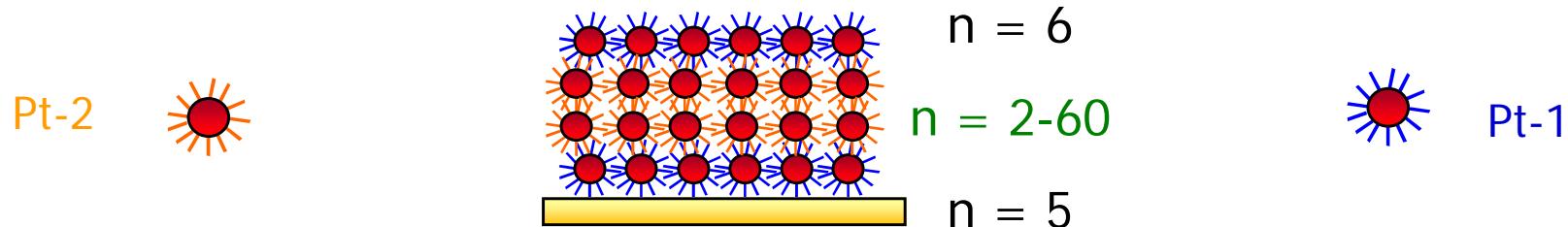
PART 3: ELECTROCHEMICAL PROPERTIES

Effect of the organic crown (mixed films)

→ Reasons for Pt 2 inactivity D.C.conductivity ?



Behaviour of sandwich like structures



$[\text{Fe}(\text{CN})_6]^{3-/-4-}$ 5 mmol L⁻¹ dans Na_2SO_4 0,1 mol L⁻¹, 20 mV s⁻¹

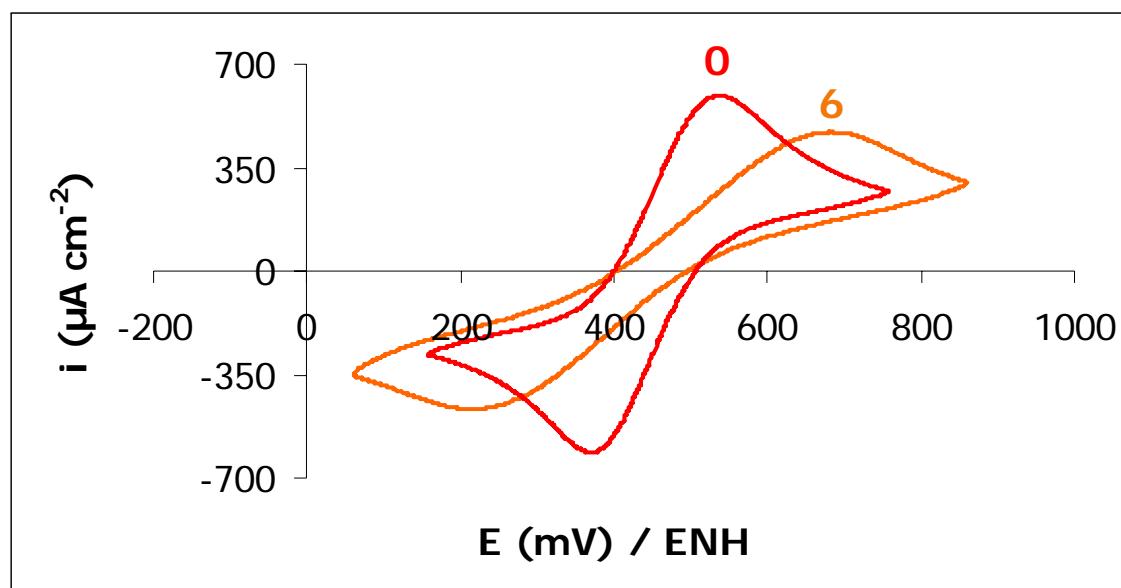
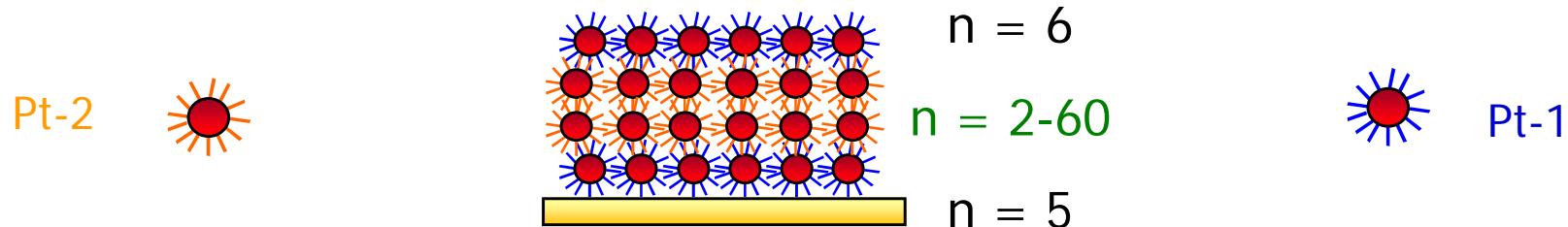
PART 3: ELECTROCHEMICAL PROPERTIES

Effect of the organic crown (mixed films)

→ Reasons for Pt 2 inactivity D.C.conductivity ?



Behaviour of sandwich like structures



$[\text{Fe}(\text{CN})_6]^{3-/-4-}$ 5 mmol L⁻¹ dans Na_2SO_4 0,1 mol L⁻¹, 20 mV s⁻¹

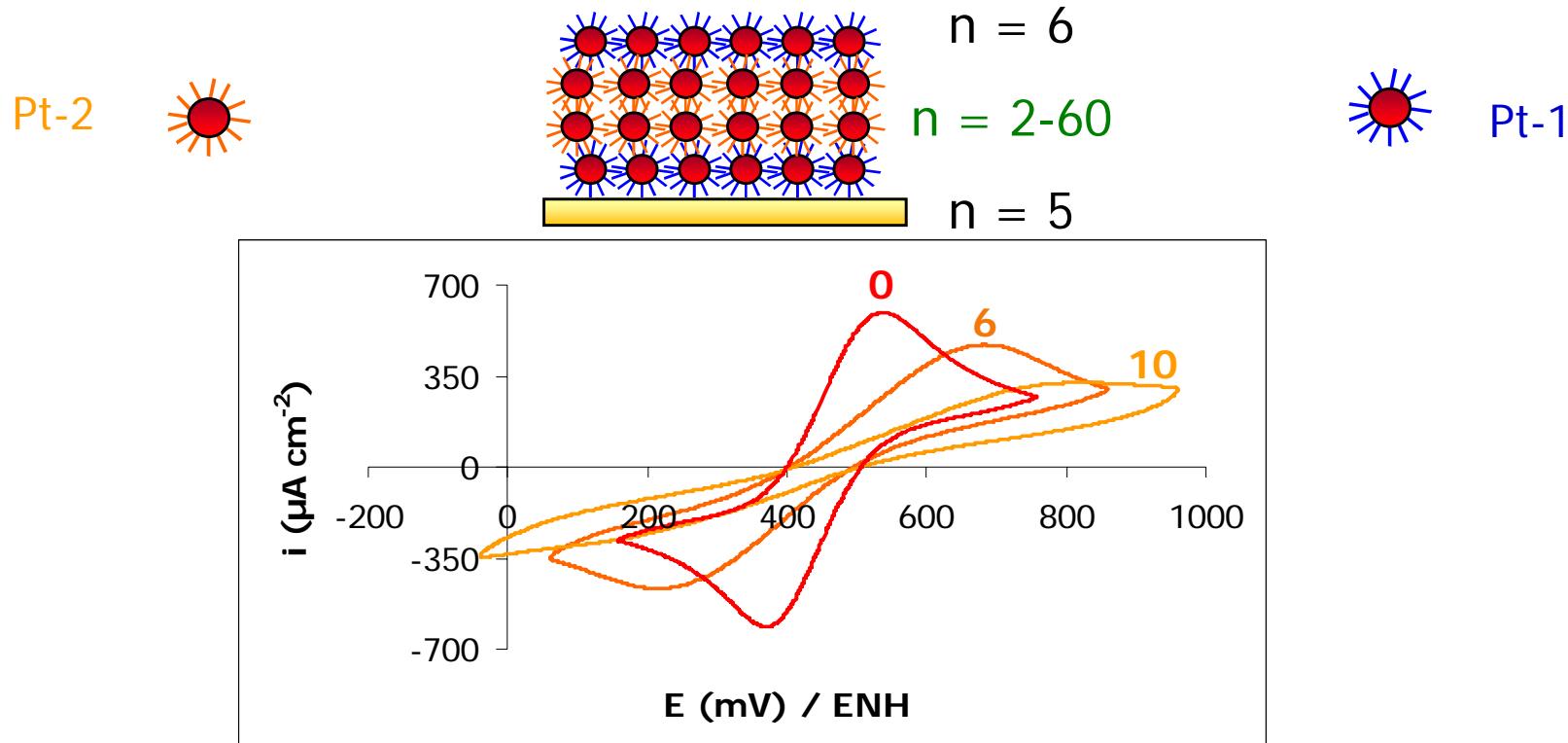
PART 3: ELECTROCHEMICAL PROPERTIES

Effect of the organic crown (mixed films)

→ Reasons for Pt 2 inactivity D.C.conductivity ?



Behaviour of sandwich like structures

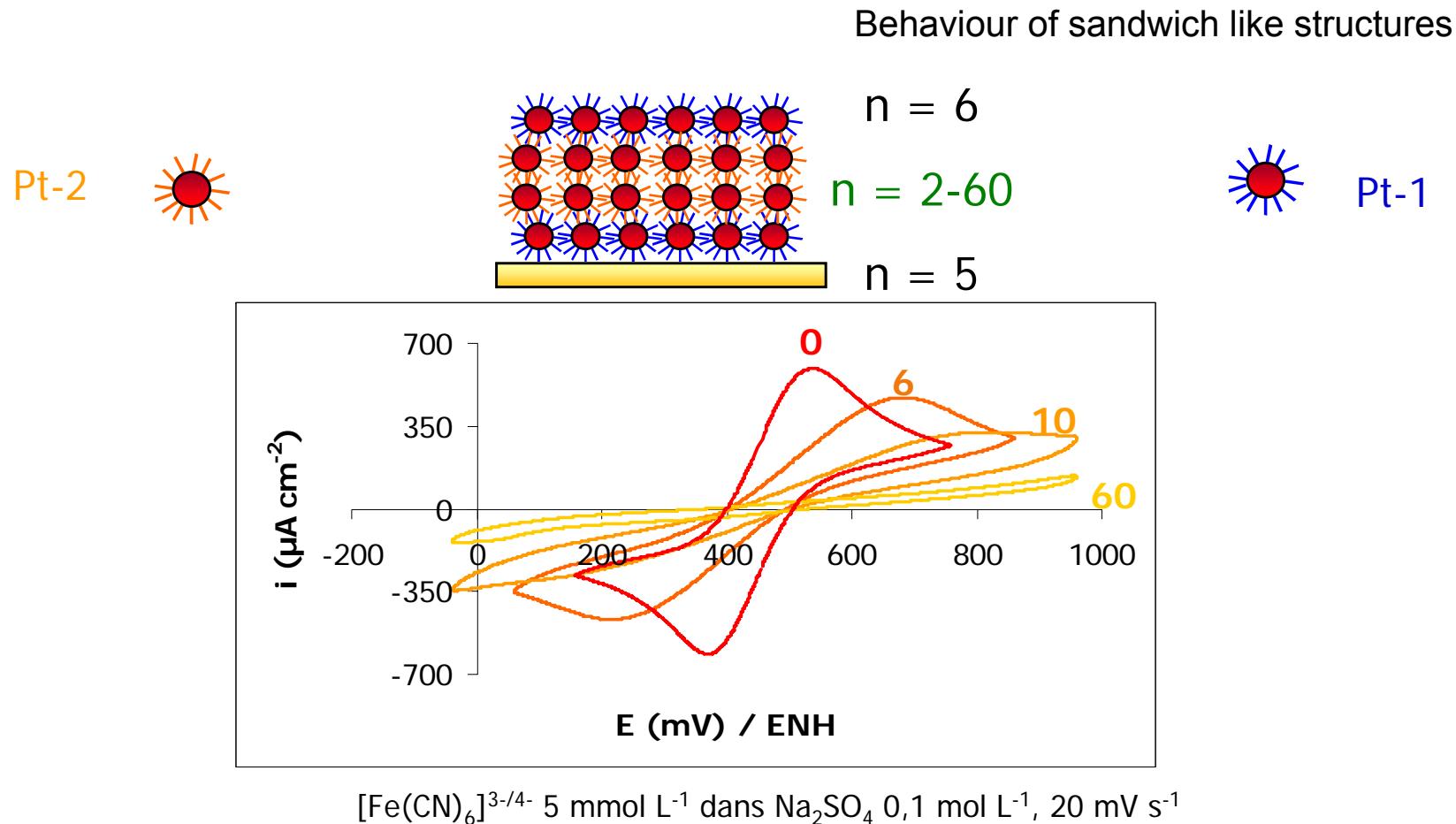


$[\text{Fe}(\text{CN})_6]^{3-/-4-}$ 5 mmol L⁻¹ dans Na_2SO_4 0,1 mol L⁻¹, 20 mV s⁻¹

PART 3: ELECTROCHEMICAL PROPERTIES

Effect of the organic crown (mixed films)

→ Reasons for Pt 2 inactivity D.C.conductivity ?

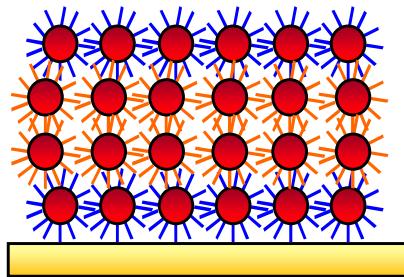


S. Cavaliere-Jaricot Ph.D Thesis 2006 University of Versailles Saint Quentin

S. Cavaliere-Jaricot, A. Etcheberry, V. Noël, M. Herlem, H. Perez
Electrochimica Acta 51 (2006) 6076–6080

PART 3: ELECTROCHEMICAL PROPERTIES

Effect of the organic crown (mixed films)



$n = 6$

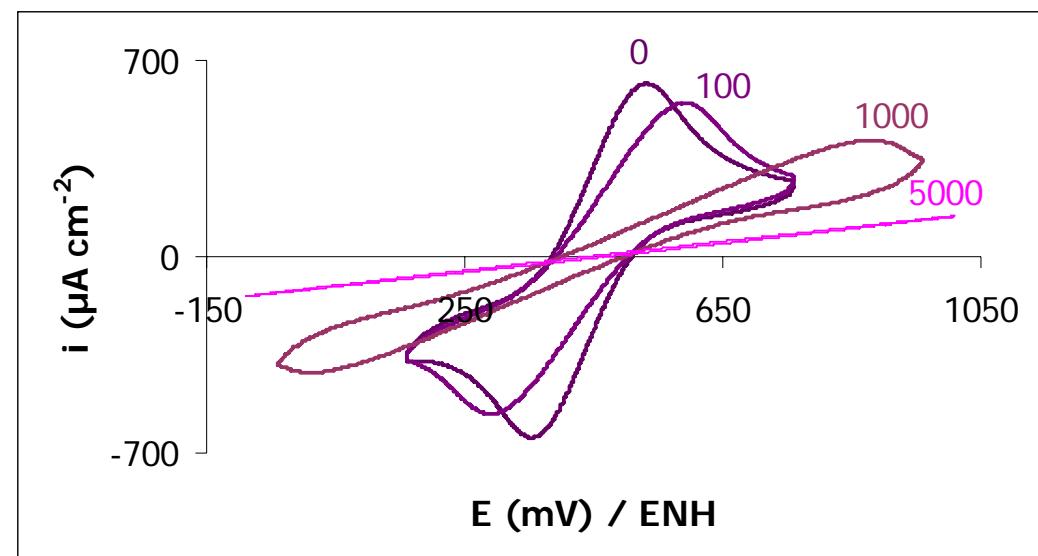
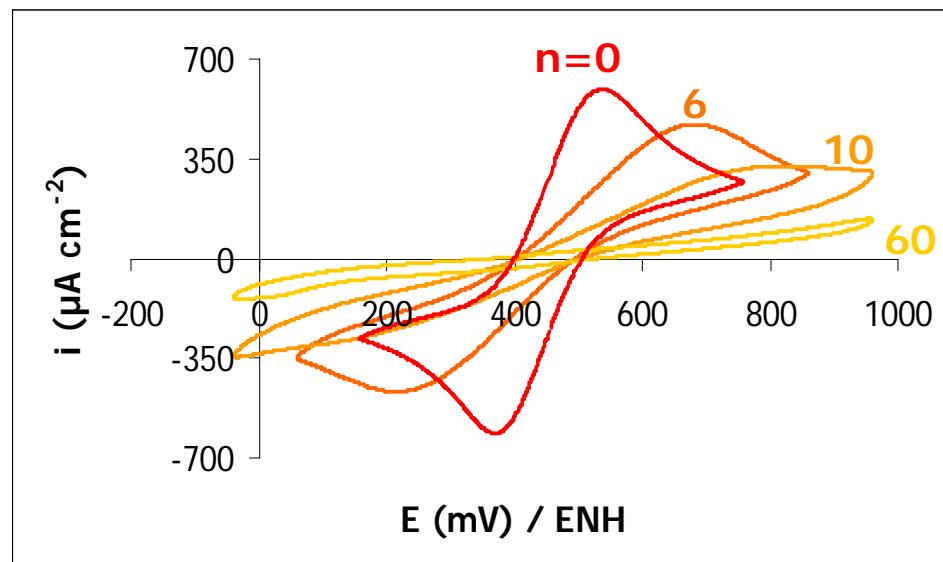
$n = 2-60$

$n = 5$

Same behaviour when a simple variable resistance is intercalated for electrochemical measurements



5 layers Pt-1 +
Variable resistance inserted

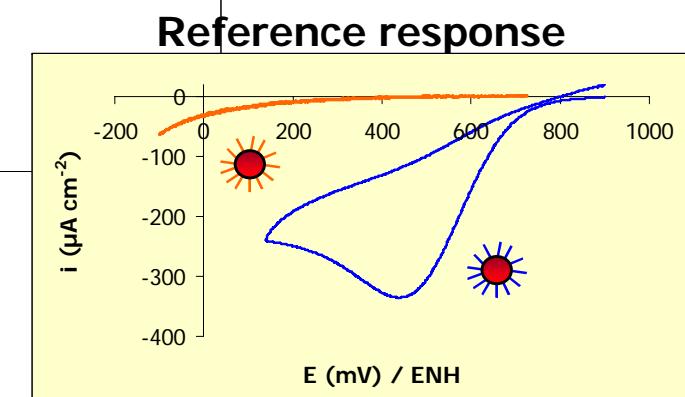
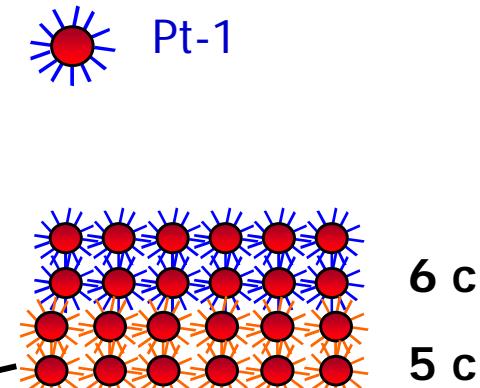
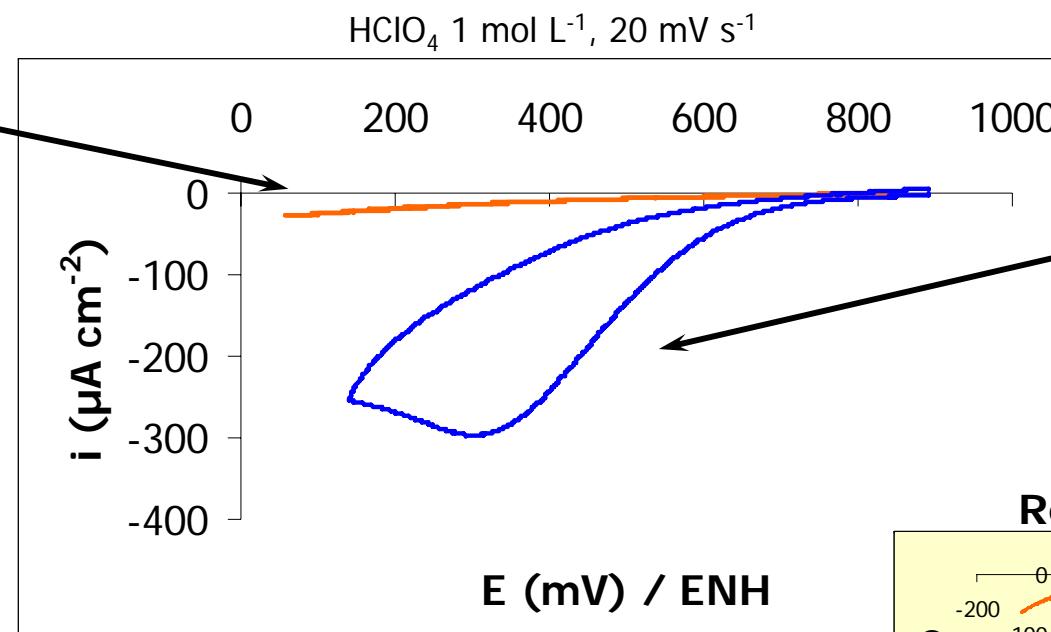
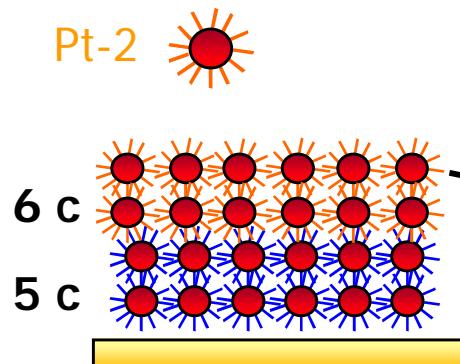


↓ Conductivity estimated to 10^{-8} S.cm

PART 3: ELECTROCHEMICAL PROPERTIES

Effect of the organic crown (mixed films)

→ Reasons for Pt 2 inactivity D.C.conductivity ?



D.C.conductivity does not look responsible for Pt-2 inactivity

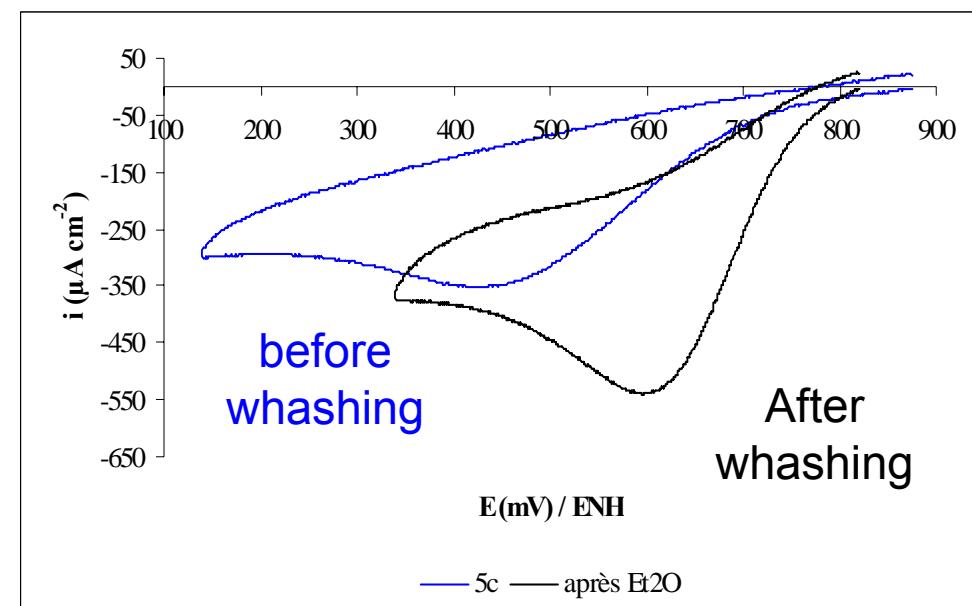
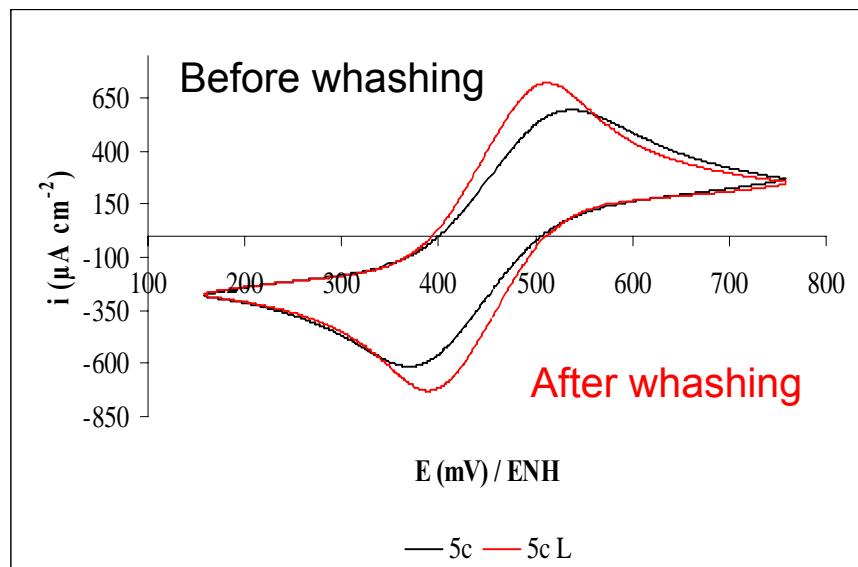
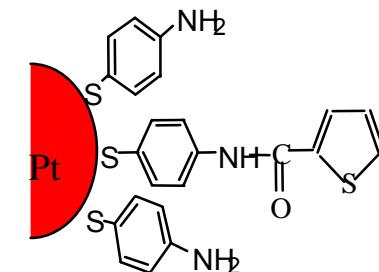
Steric hindrance for redox species?

Hydrophobicity and wettability disturb Helmholtz layer?

PART 3: ELECTROCHEMICAL PROPERTIES

Effect of fatty acid elimination

→ $\text{Fe}(\text{CN})_6^{3-/4-}$ and O_2



$\text{Fe}(\text{CN})_6^{3-/4-}$ 5 mmol L⁻¹, Na_2SO_4 0, 1 mol L⁻¹, 20 mV s⁻¹

HClO_4 1 mol L⁻¹, O_2 , 20 mV s⁻¹

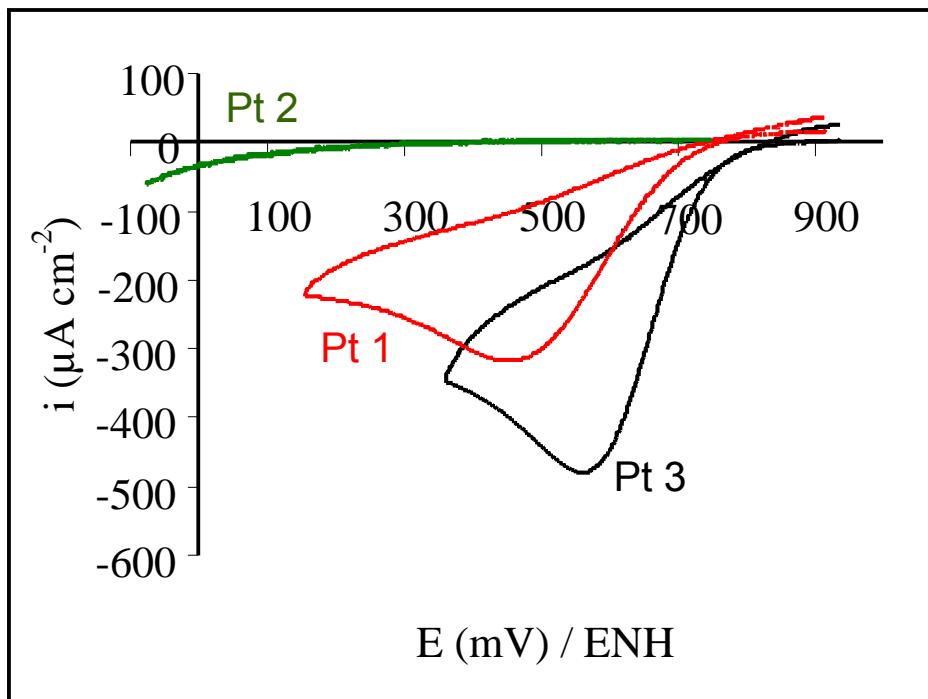


Strong modification appears in oxygen reduction (improvement)

PART 3: ELECTROCHEMICAL PROPERTIES

Effect of organic crown versus fatty acid elimination

→ O₂ saturated 1 M HClO₄ @ 20 mV s⁻¹



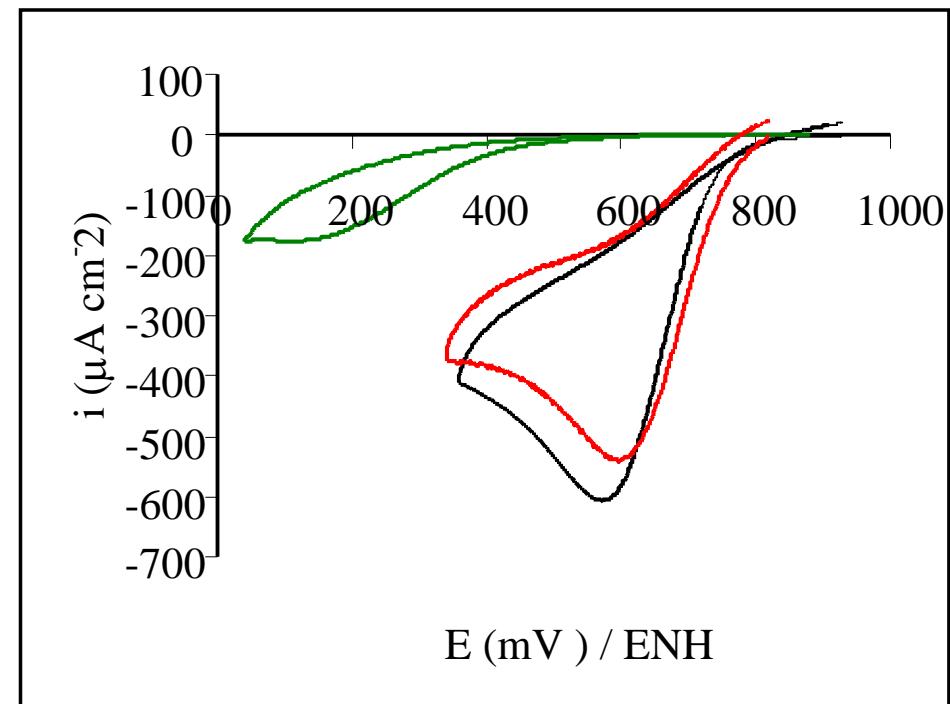
Before whashing



The effect of organic crown is still present



Differences between actives particles tend to vanish



After whashing

PART 3: ELECTROCHEMICAL PROPERTIES

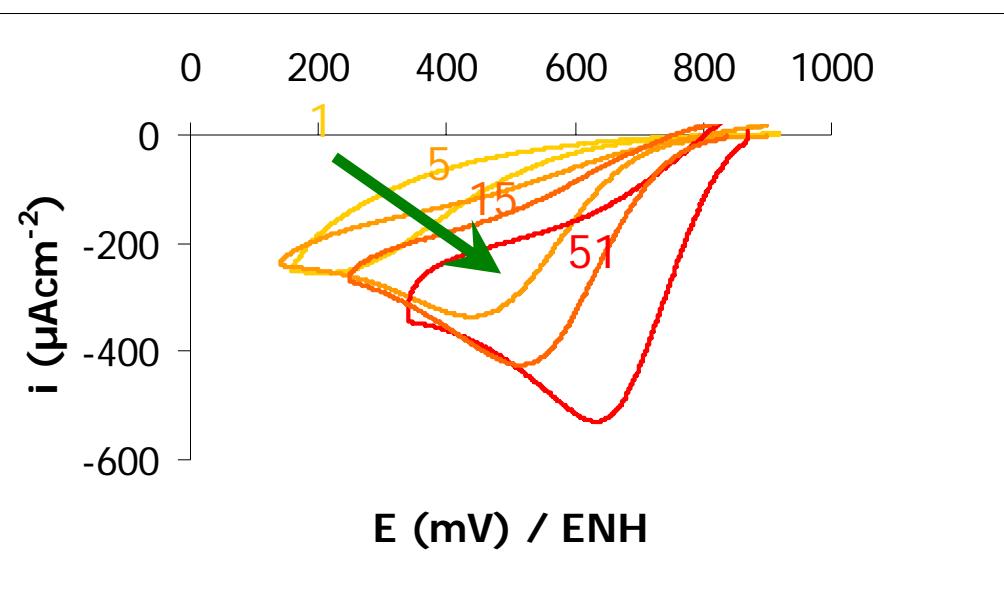
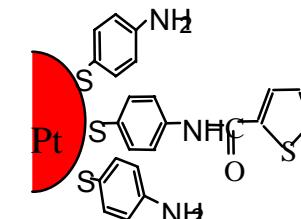
Effect of platinum loading on O₂ reduction

→ Effect of platinum density towards O₂ reduction (mixed films)

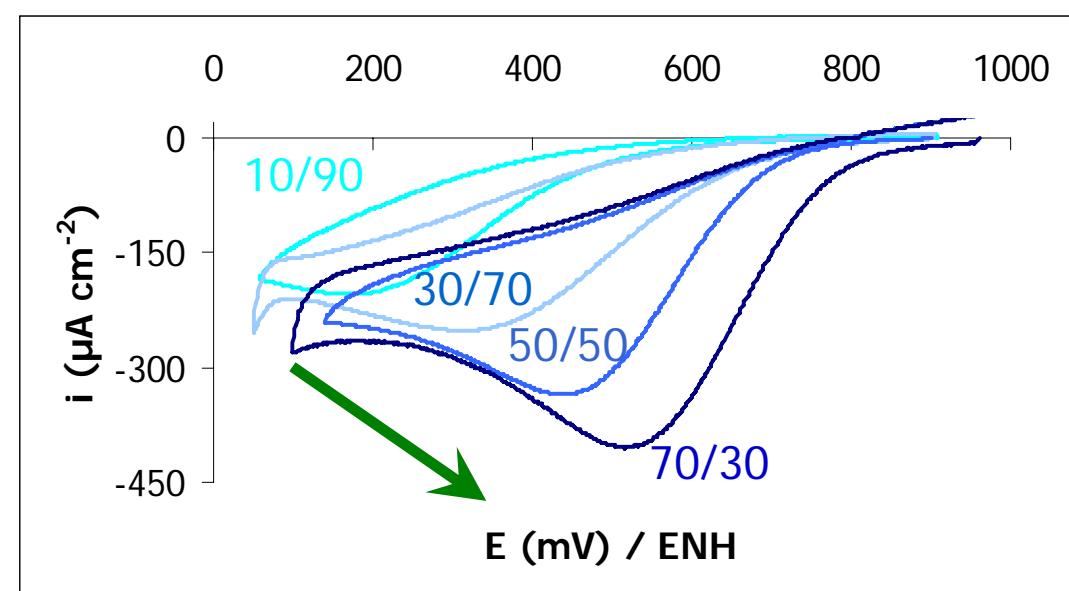
Two ways to modify platinum density

A
Fixed density in the layer
Increasing number of layers

B
Fixed number of layer
density in one monolayer $\sim 0.1 \mu\text{g}/\text{cm}^2$ to $\sim 0.8 \mu\text{g}/\text{cm}^2$



O₂ saturated 1 M HClO₄ @ 20 mV s⁻¹



O₂ saturated 1 M HClO₄ @ 20 mV s⁻¹



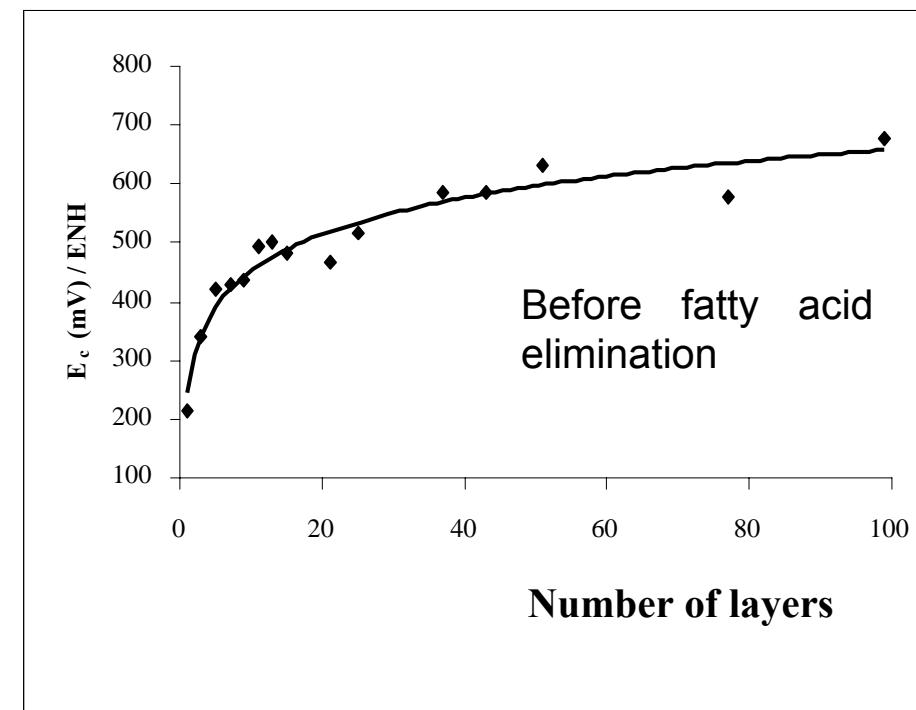
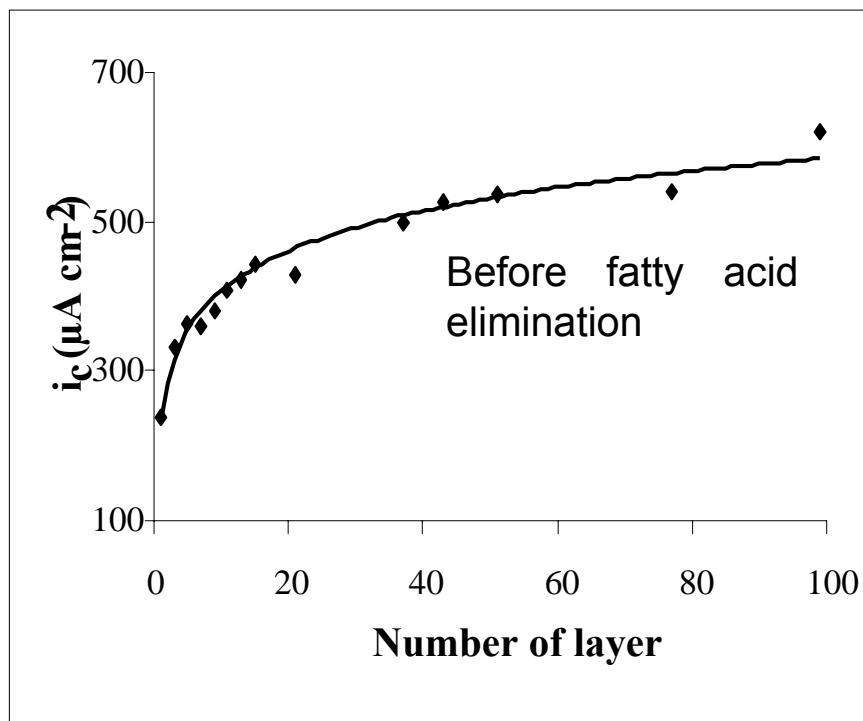
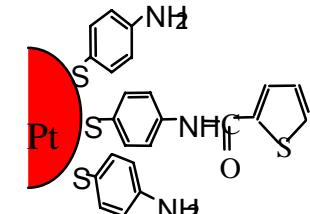
Both kinds of dilution lead to the same strong effect on current and potential

PART 3: ELECTROCHEMICAL PROPERTIES

Effect platinum loading before fatty acid elimination

→ Platinum density effect after fatty acid elimination (50/50 Pt-1/fatty acid ratio)

(O₂ saturated 1 M HClO₄ @ 20 mV s⁻¹)



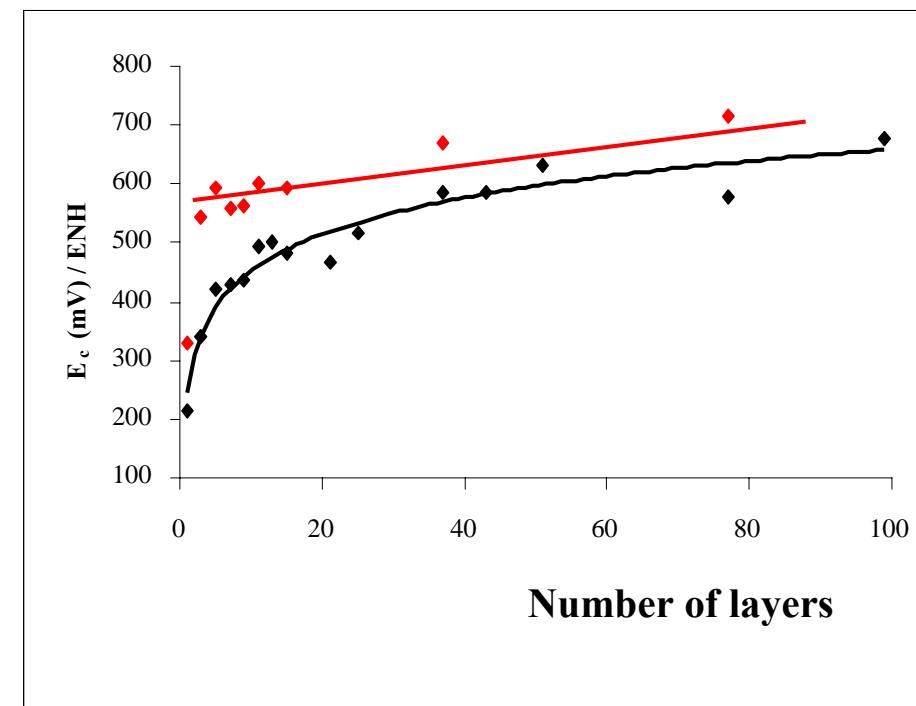
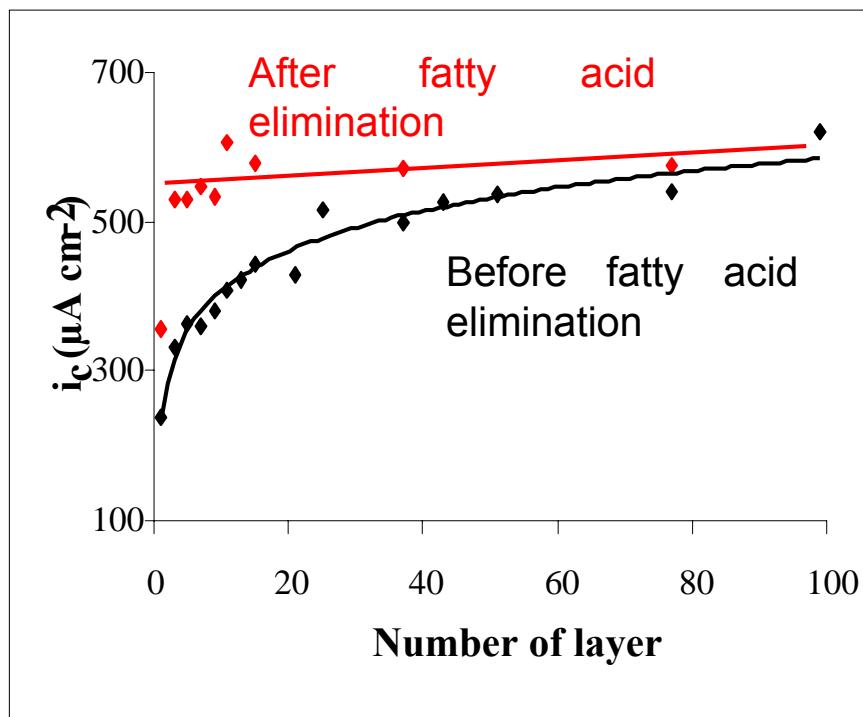
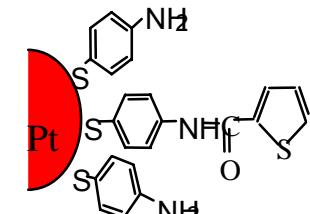
Slow improvement of electrochemical response

PART 3: ELECTROCHEMICAL PROPERTIES

Effect platinum loading after fatty acid elimination

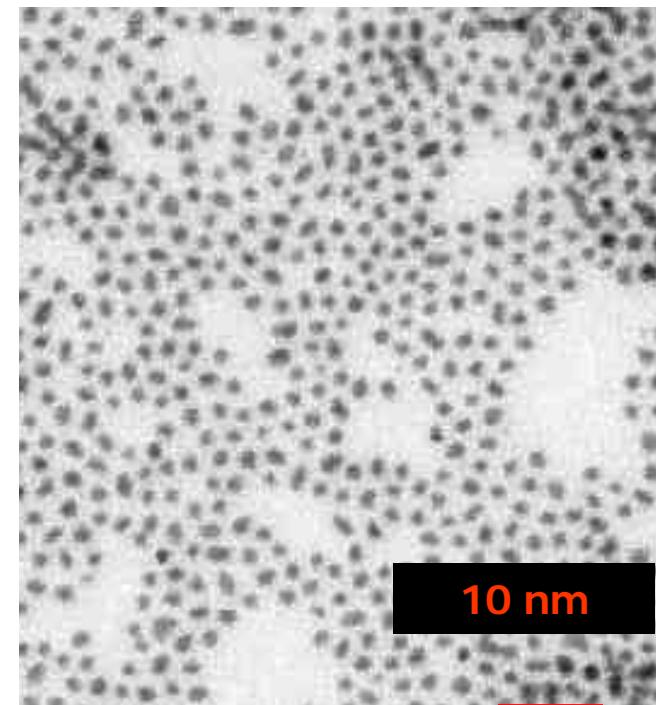
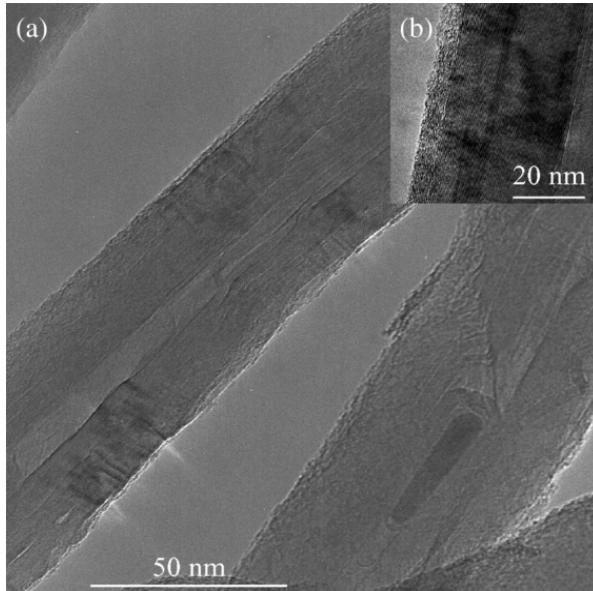
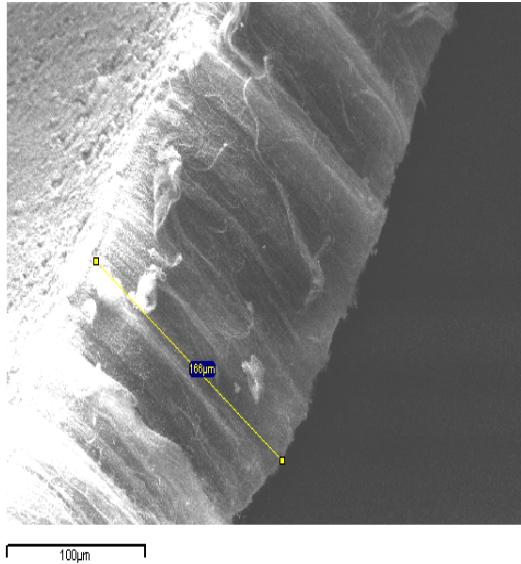
→ Platinum density effect after fatty acid elimination (50/50 Pt-1/fatty acid ratio)

(O₂ saturated 1 M HClO₄ @ 20 mV s⁻¹)



After fatty acid elimination one layer loading gives the same electrochemical response as several layers

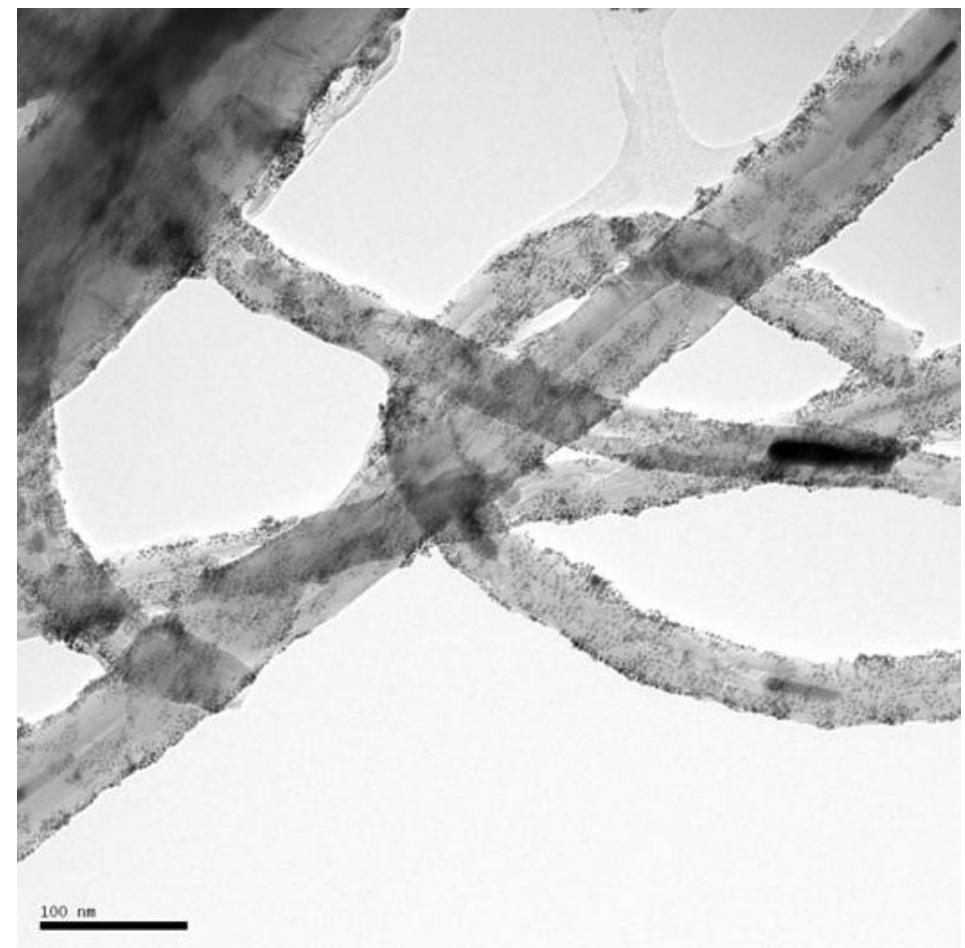
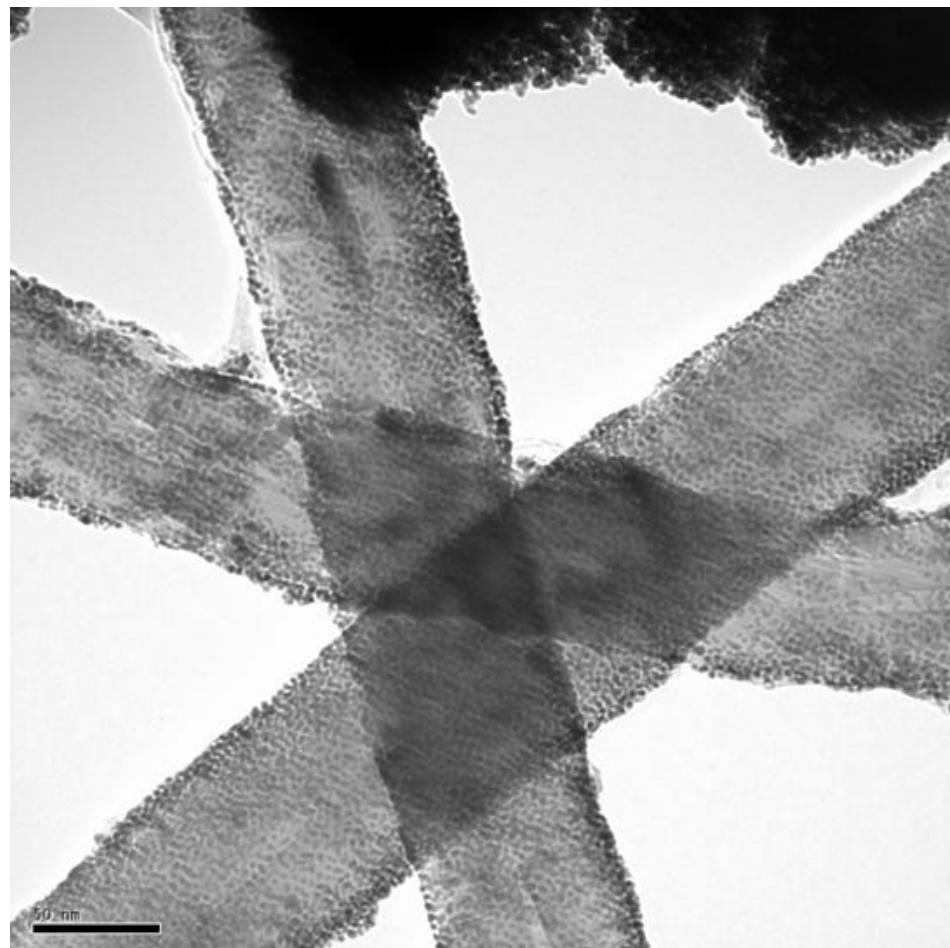
Nanostructures based on carbon nanotubes and platinum nanoparticles through the bottom-up



*M. Pinault, M. Mayne-L'Hermite, C. Reynaud,
O. Beyssac, J. N. Rouzaud and C. Clinard
Diamond and Related Materials 13 (2004) 1266–1269*

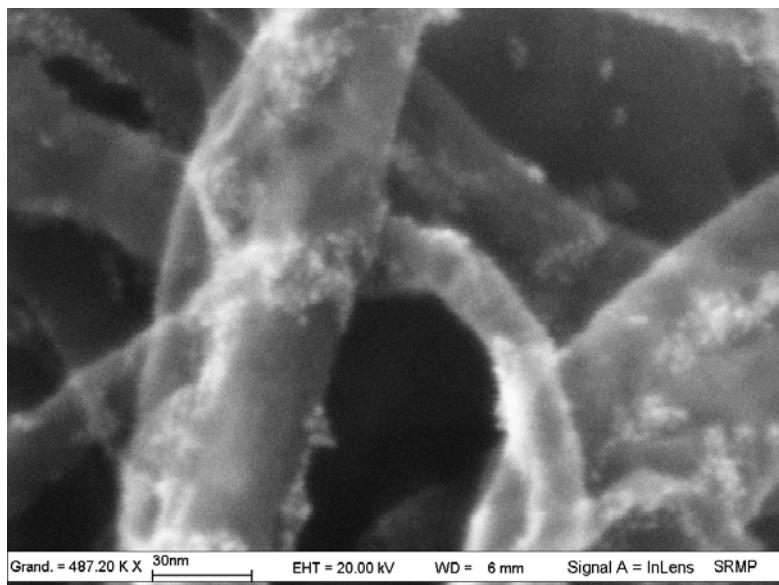
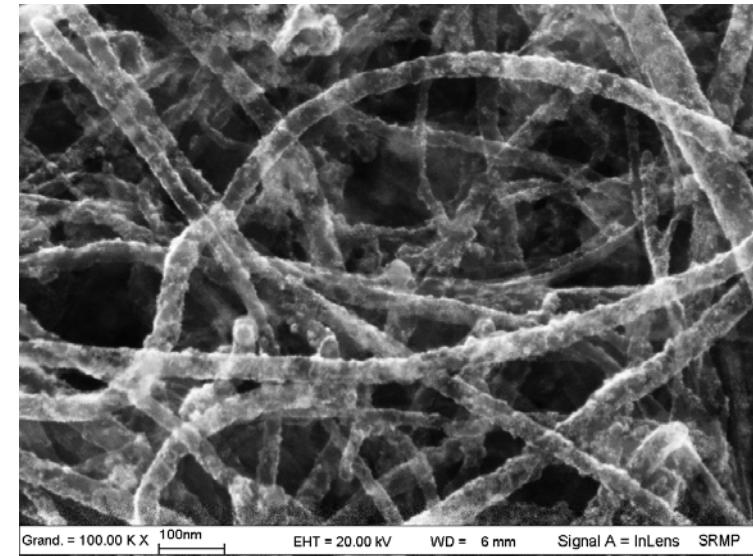
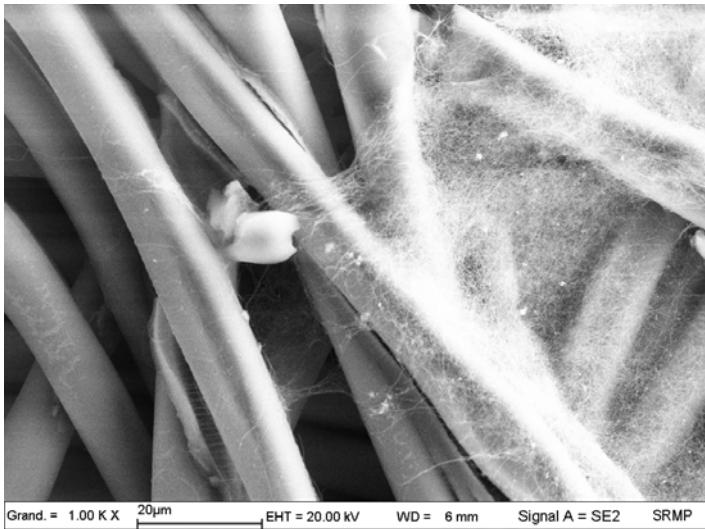
RECENT DEVELOPMENTS

Nanostructures based on carbon nanotubes and platinum nanoparticles through the bottom-up



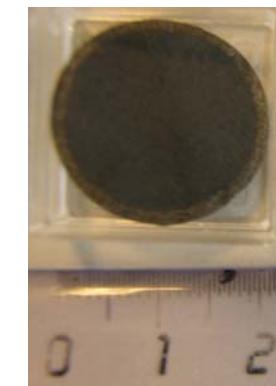
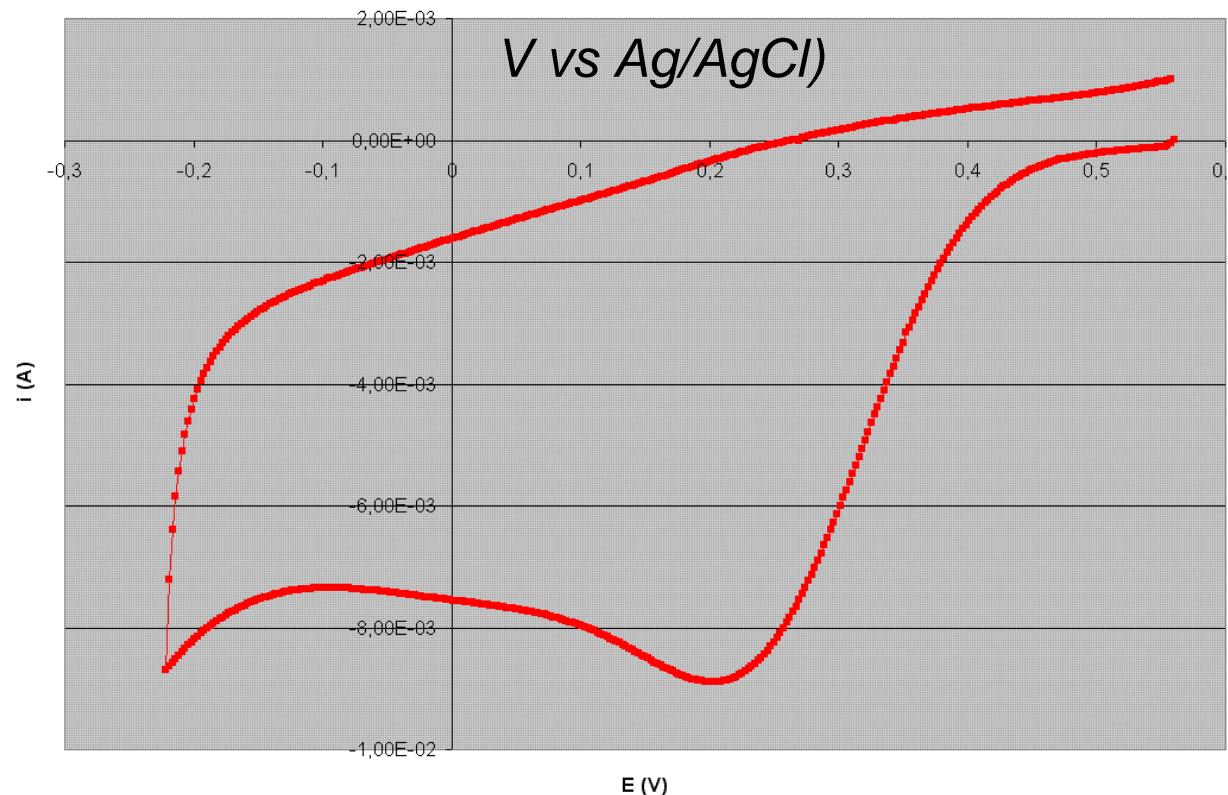
RECENT DEVELOPMENTS

Nanostructures based on carbon nanotubes and platinum nanoparticles through the bottom-up



MEB images:
P. Bonnaillie
CEA-DEN-SRMP-Saclay France

Nanostructures based on carbon nanotubes and platinum nanoparticles through the bottom-up



Platinum density $50 \mu\text{g}/\text{cm}^2$

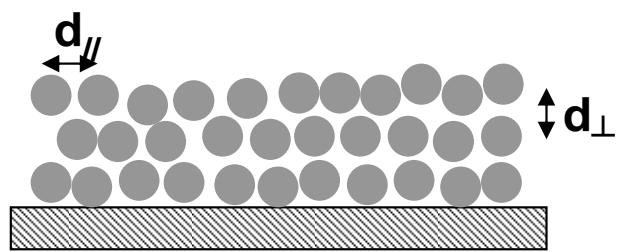
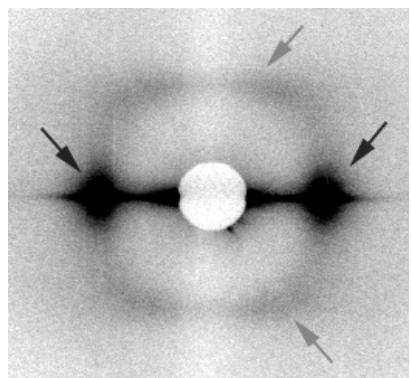
- Electrochemical study in progress (B. Baret Ph.D Thesis)...
- Fuel cell related studies, confidential....
- Evaluating LB approach

CONCLUSION

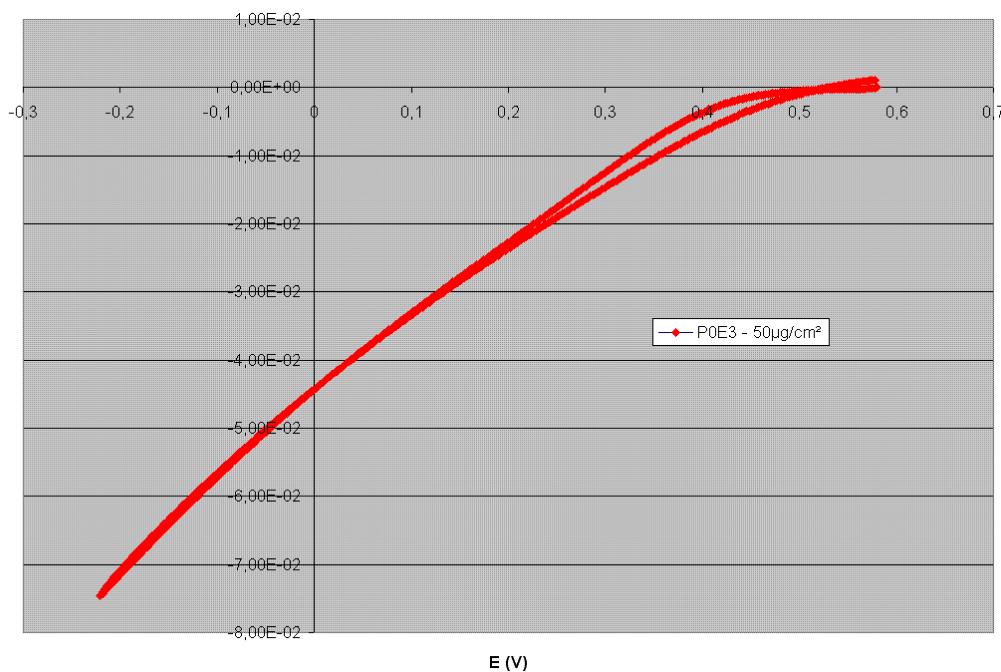
- The bottom up approach presents real advantages to realize model systems in electrochemistry as shown in the case of platinum electrocatalysts
 - Very good control of electroactive material amount (μg scale)
 - Evidence of the influence the local environnement of electrocatalyst (organic crown effect)
 - Evidence of the effect at mesoscopic scale (effect of the fatty acid matrix)
- Coupling of modelling and experimental results recorded on such well controlled nanostructures is an interesting tool to understand electrochemical reponses...

ACKNOWLEDGEMENTS

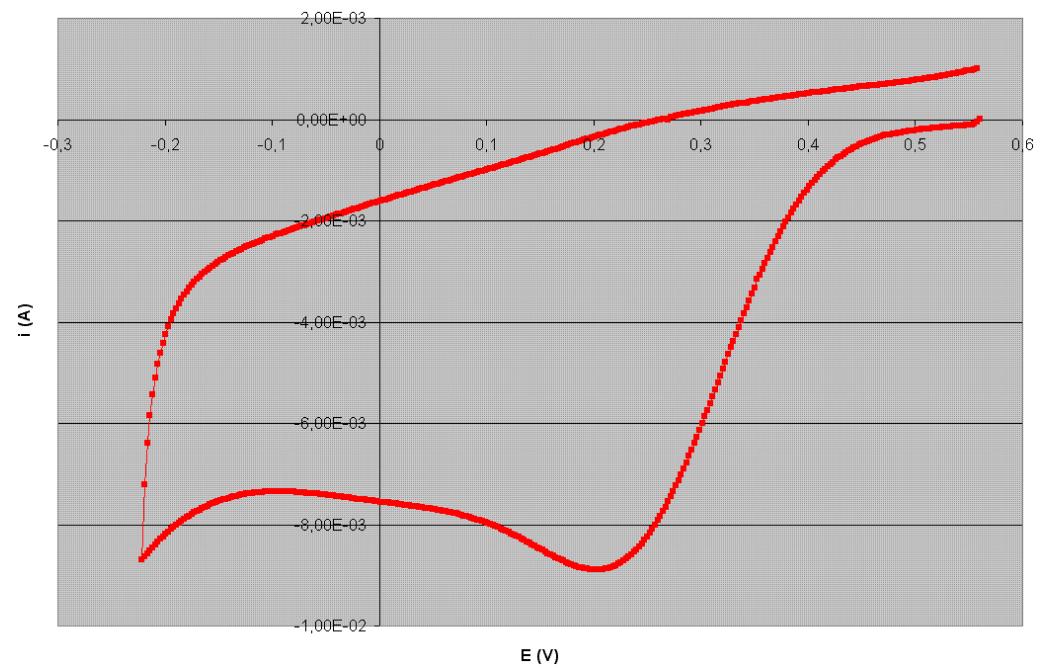
- A. Etcheberry, IREM-CNRS Versailles University UMR 8637
- P-A Albouy, Paris-Sud University IREM-CNRS UMR 8502
- S. Cavaliere Ph.D Thesis University of Versailles Saint Quentin 2006
- B. Baret (Ph.D Student), M. Mayne-L'hermitte, C. Reynaud, CEA-Saclay



Réponse de « type 1 »

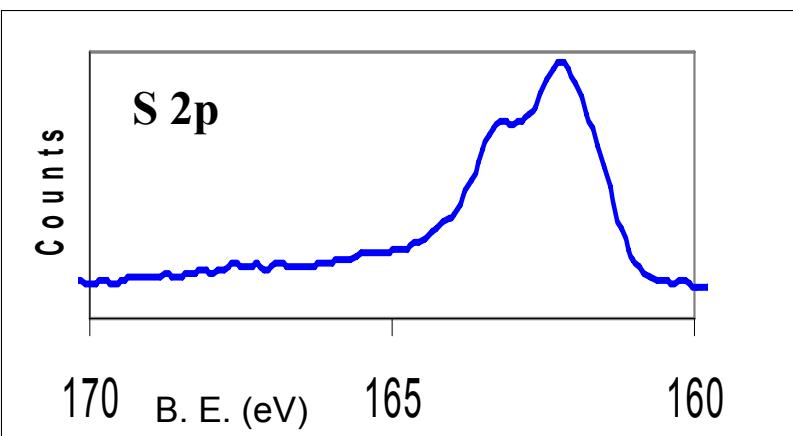


Réponse de « type 2 »

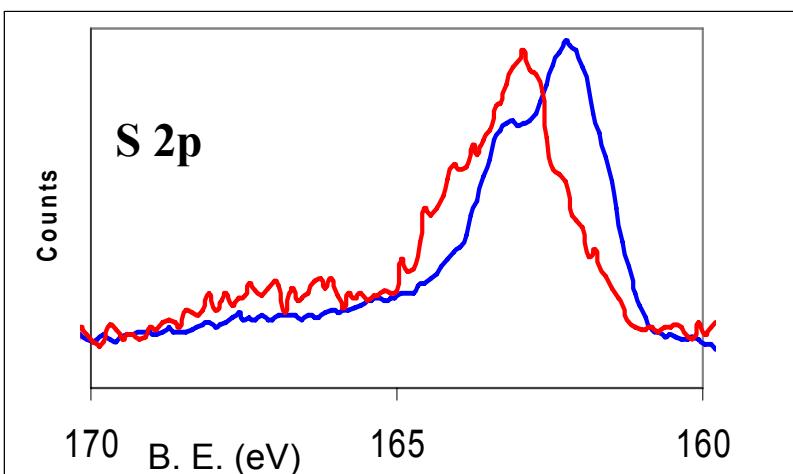
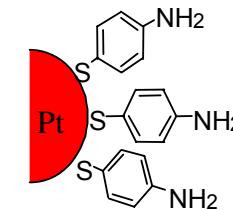


CHARACTERIZATION ON LB FILM STRUCTURES

→ X-ray photo-electron spectroscopy (XPS)



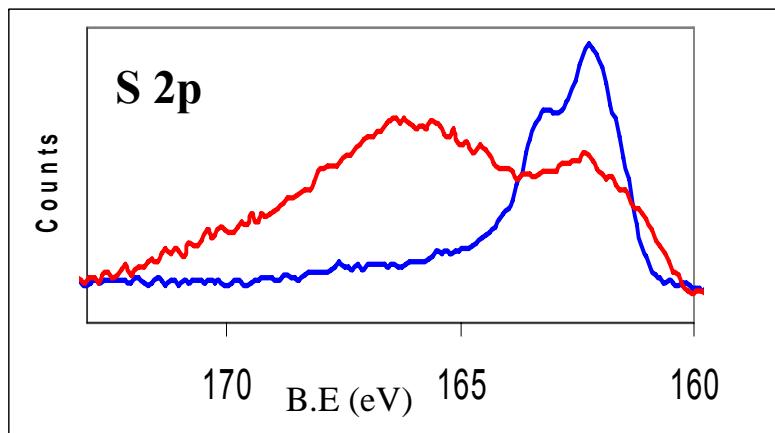
LB films
from **fresh**
solution



LB films
from **3 months**
aged solution

time

F. Raynal, A. Etcheberry, S. Cavaliere,
V. Noël, H. Perez
Appl Surf Sci 252 (6) 2422-2431 2006

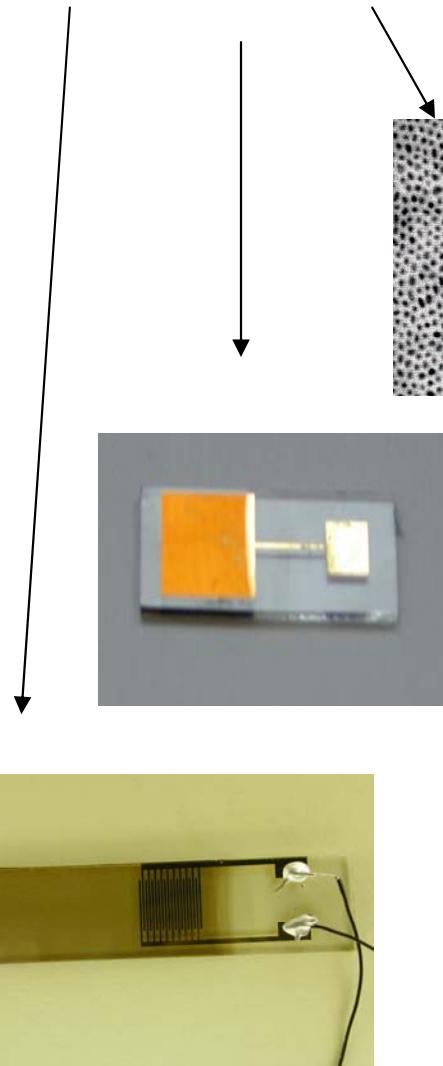


precipitate

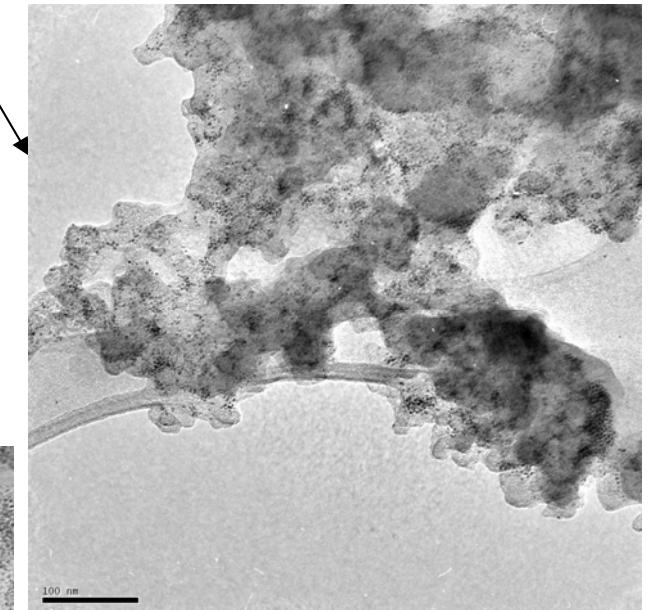
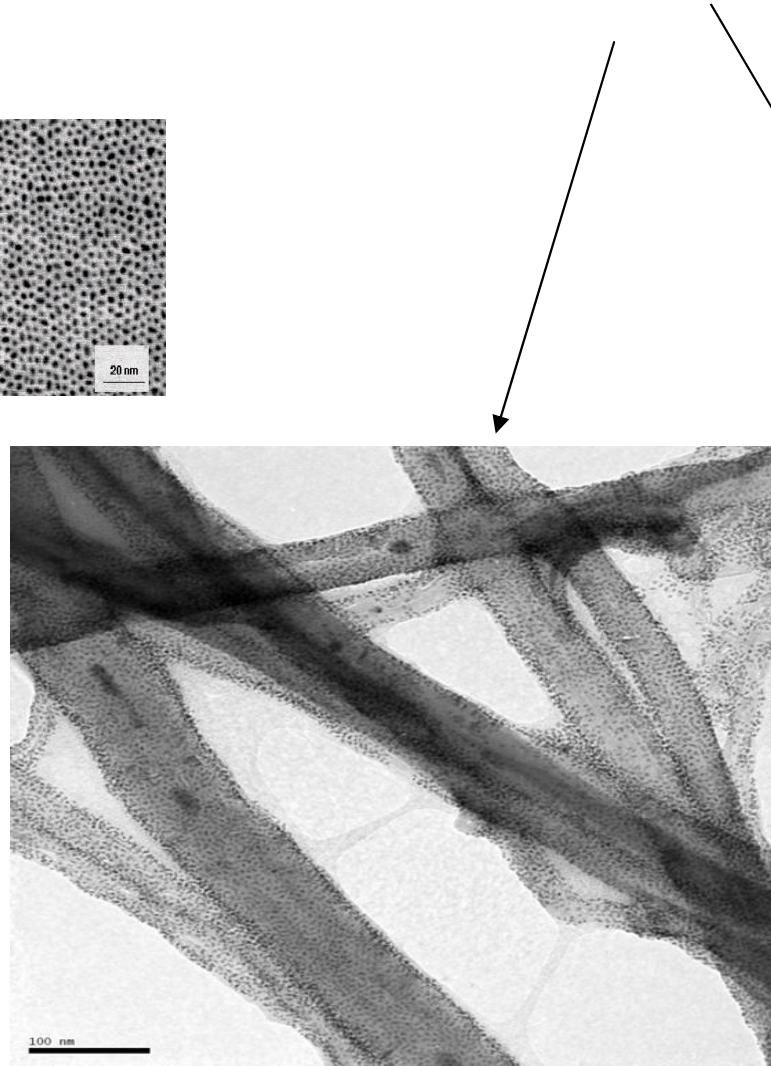


Making of nanocomposites structures

Bulk substrates



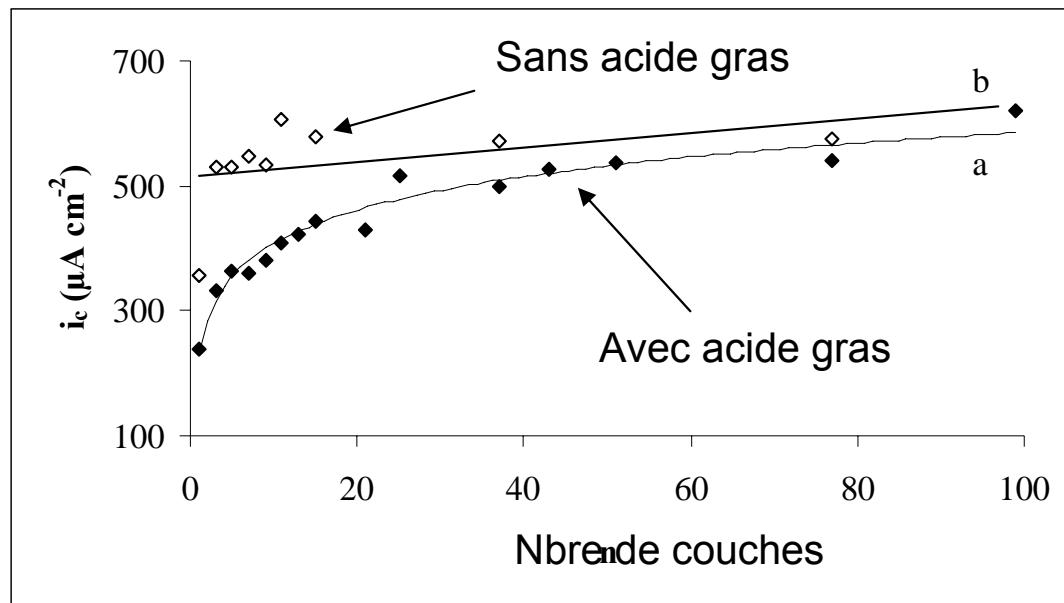
Finely divided substrates



NANOParticules de platine à enrobage organique modifiable

Comportement électrochimique

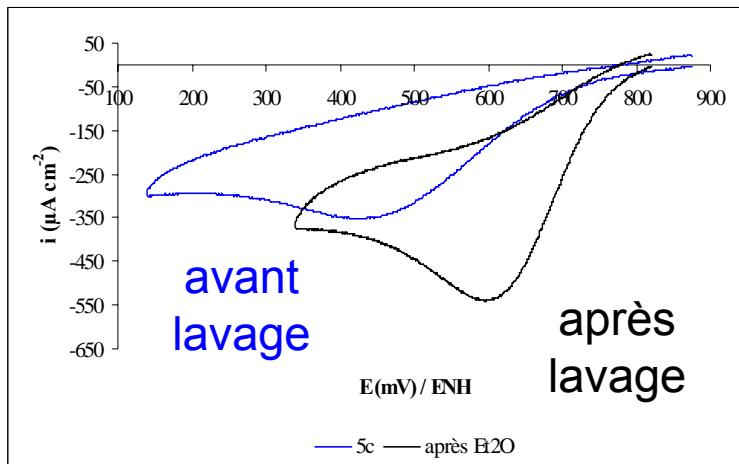
- Effet de l'élimination de l'acide gras
(réduction de O₂ HClO₄ 1M 20 mV.s⁻¹)



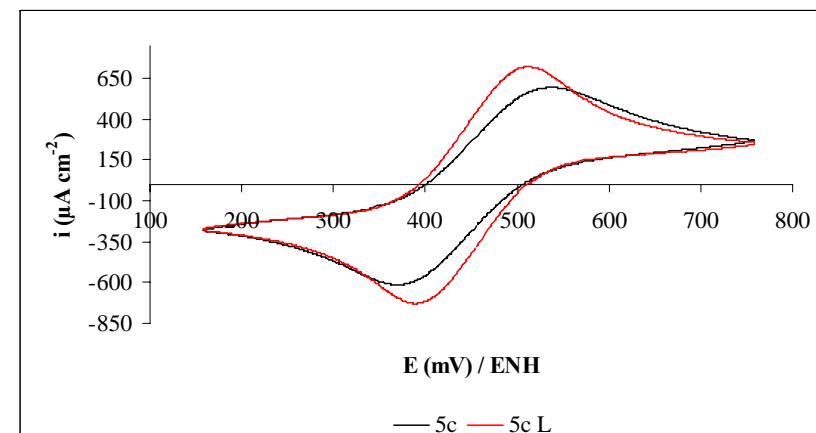
NANOParticules de Platine A Enrobage organique modifiable

Comportement électrochimique

→ Effet de l'élimination de l'acide gras selon la sonde redox

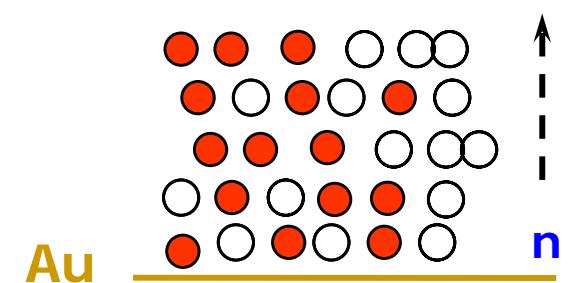
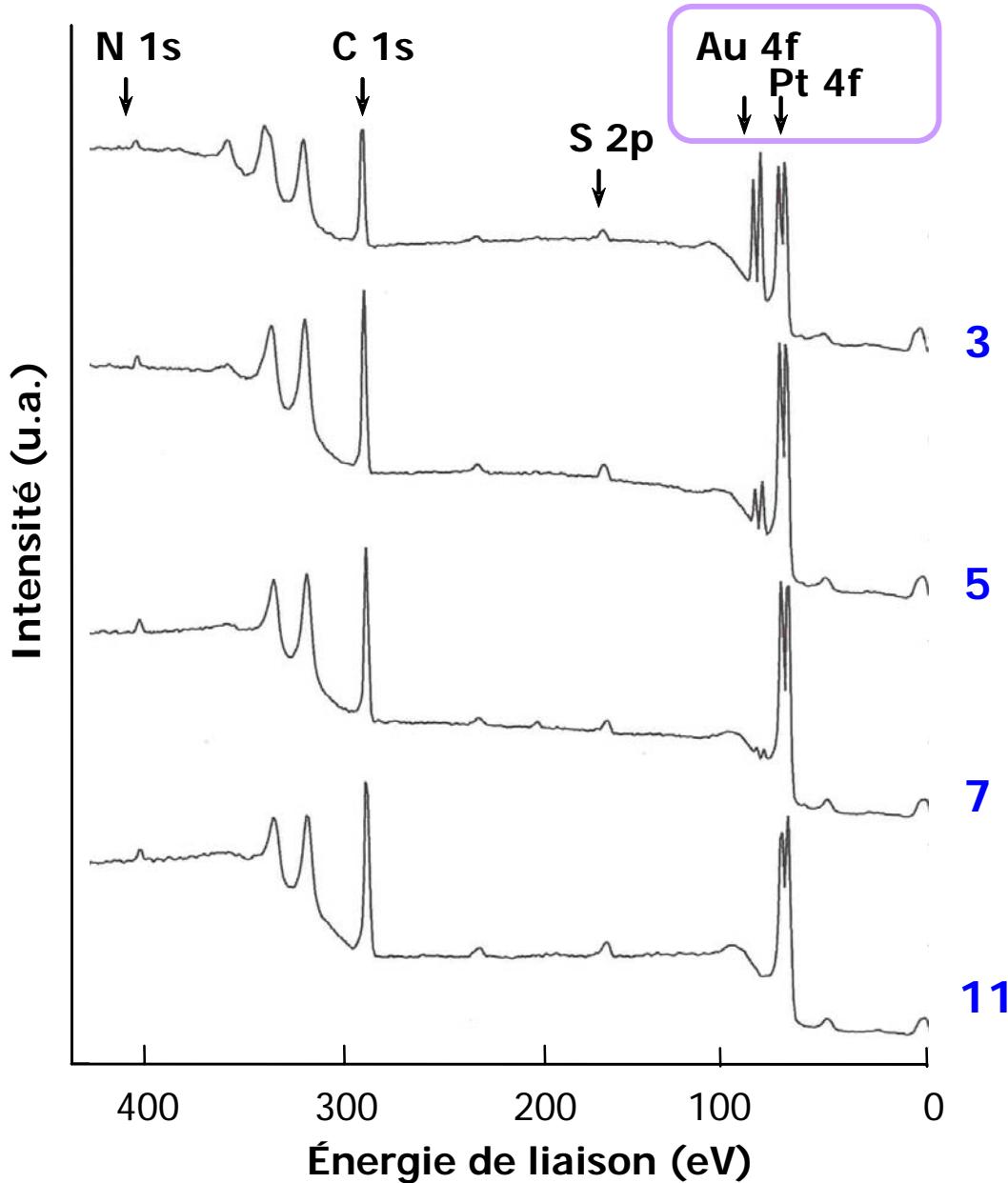


HClO_4 1 mol L⁻¹, O_2 , 20 mV s⁻¹



$\text{Fe}(\text{CN})_6^{3-/4-}$ 5 mmol L⁻¹, Na_2SO_4 0, 1 mol L⁻¹, 20 mV s⁻¹

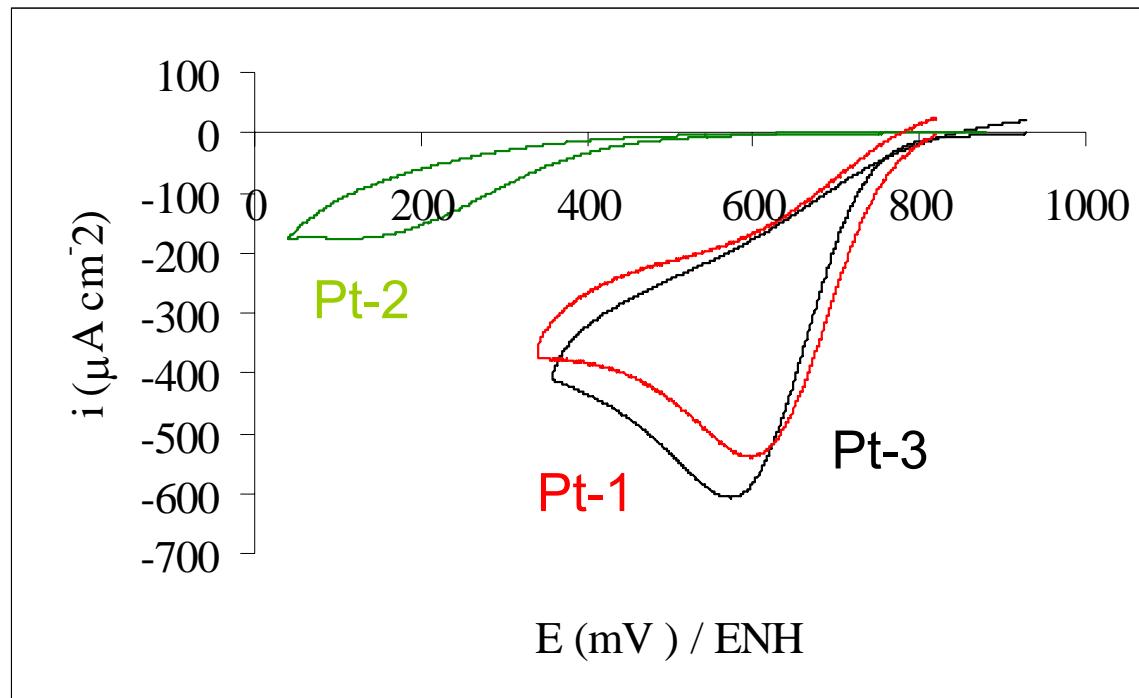
XPS



NANOParticules de Platine A Enrobage organique modifiable

Comportement électrochimique

- Effet de l'enrobage organique des nanoparticules (après élimination de l'acide gras)



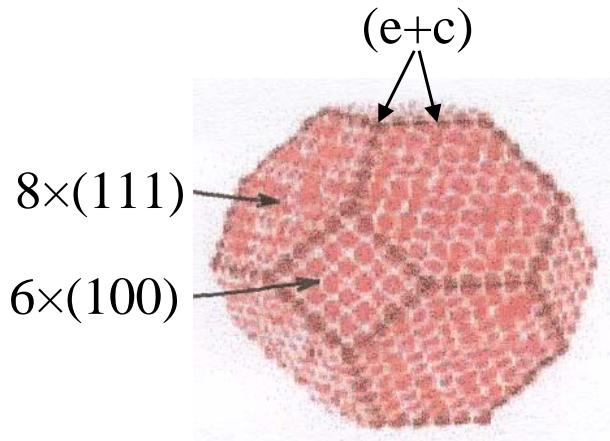
Réd. O_2 dans HClO_4 1 M, 20 mV s^{-1}

NANOParticules de Platine A Enrobage Organique Modifiable

•

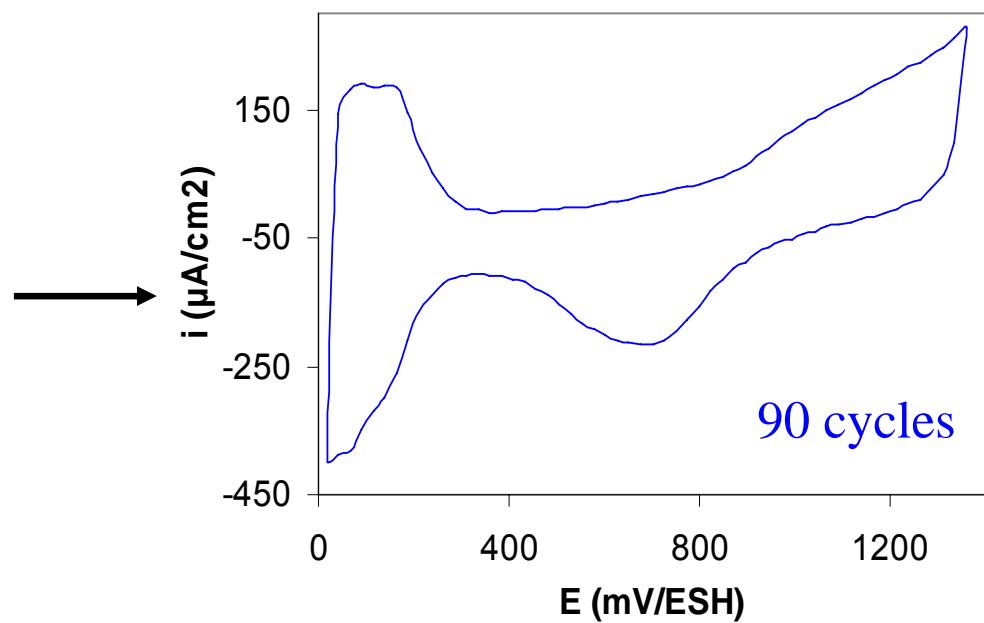
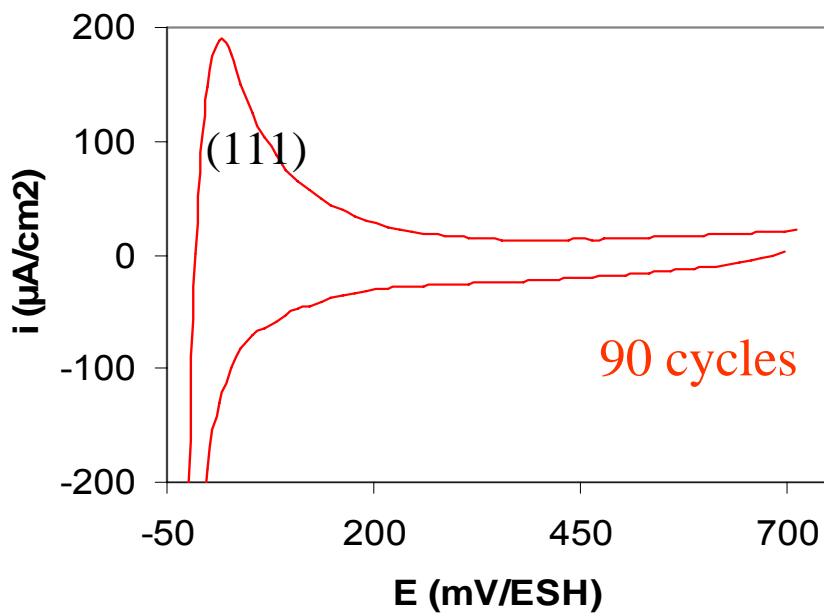
Comportement électrochimique

→ Etude des faces cristallines actives (réduction H+, désorption H+)



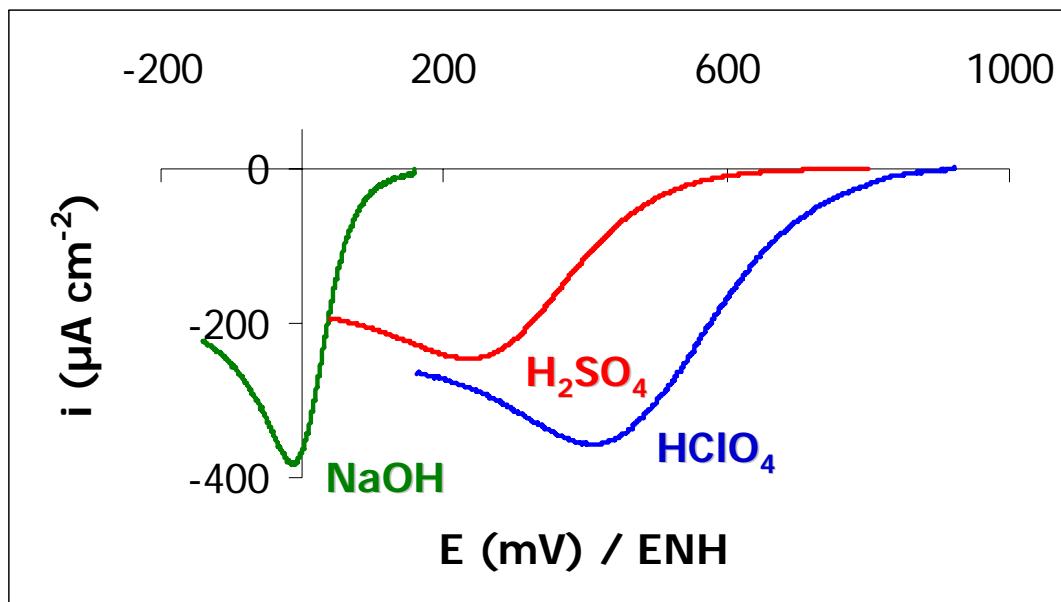
cycles $E_a > 0,8 \text{ V/ESH}$

reconstructions/
élimination enrobage ?



Comportement électrochimique

→ Etude des faces cristallines actives en O_2 activité selon le milieu



Pt (111)
essentiellement
responsable de
l'activité ?

5 couches Pt-thiophène/BHA 50/50, O_2 , 20 mV s^{-1}

Sur monocristaux de Pt (littérature) :



Pt(110) > Pt(100) > Pt(111)

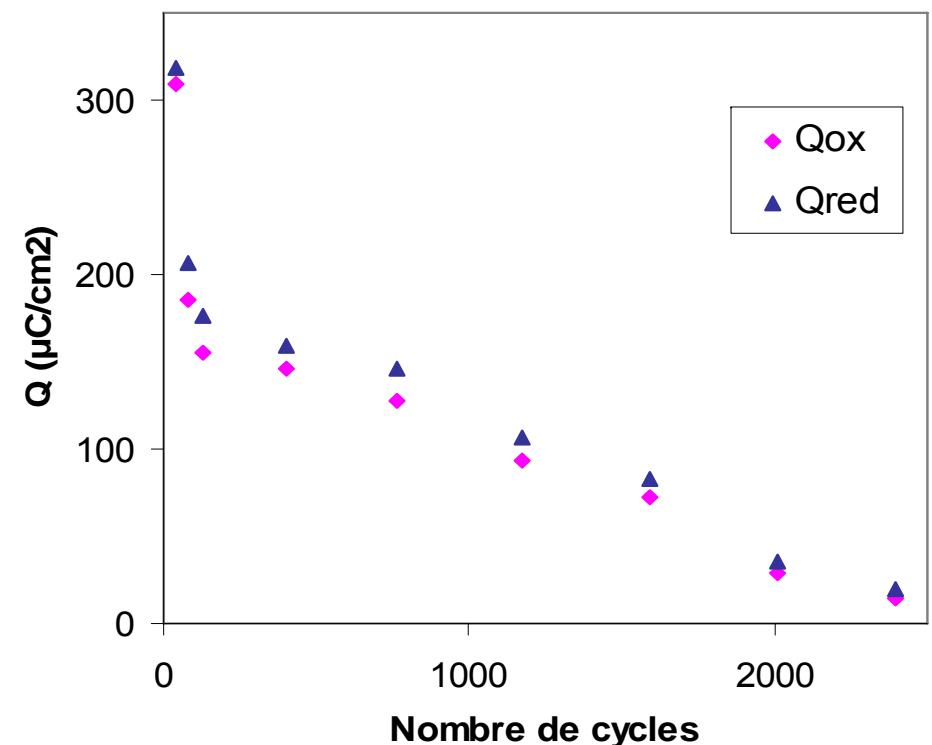
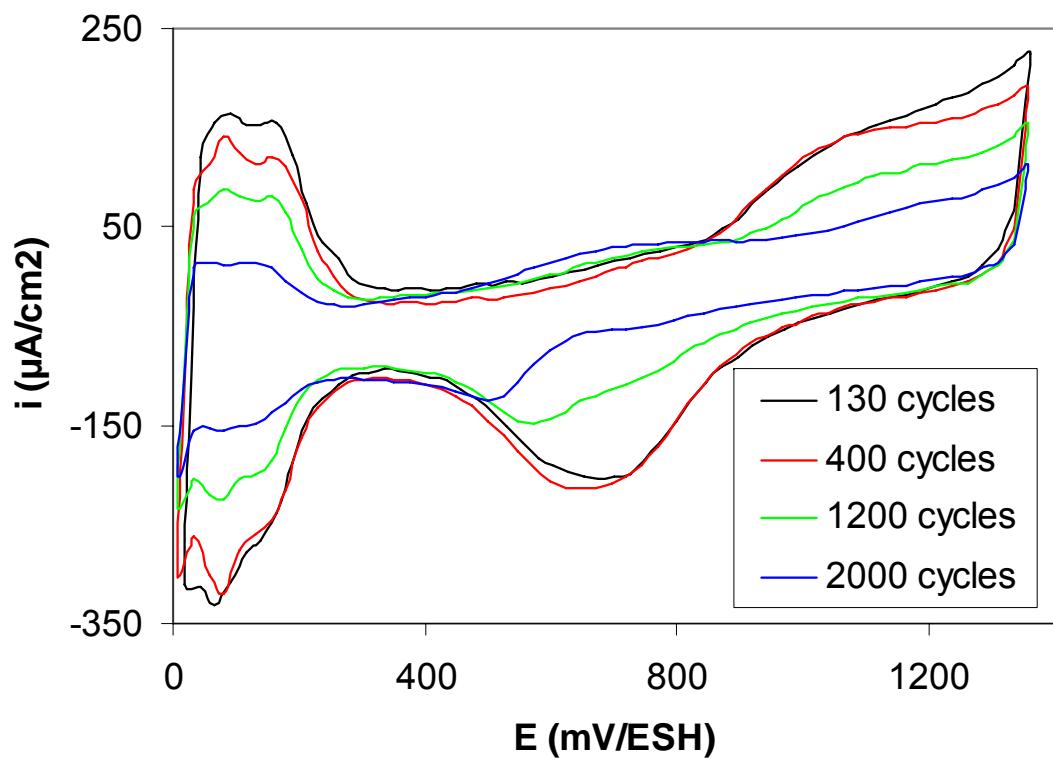
Pt(110) > Pt(111) > Pt(100)

Pt(111) > Pt(110) > Pt(100)

NANOParticules de Platine A Enrobage Organique Modifiable

Comportement électrochimique

→ Etude de la dégradation du platine



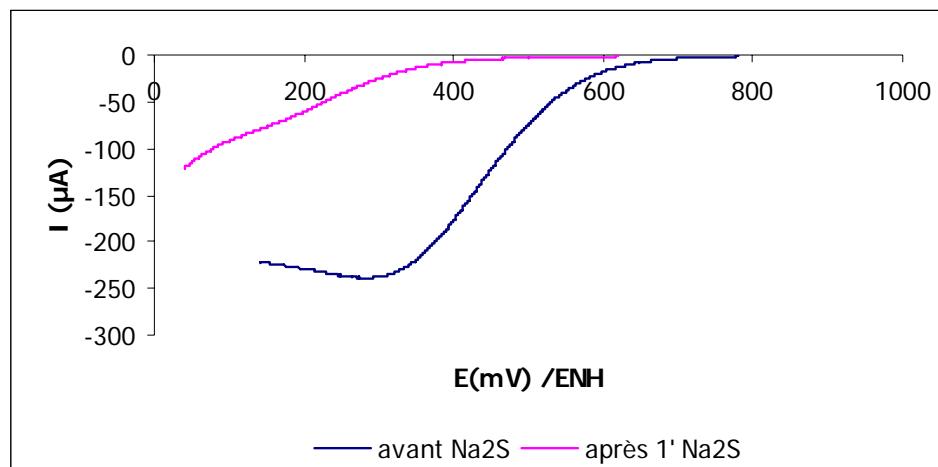
Diminution de l'aire électro-active

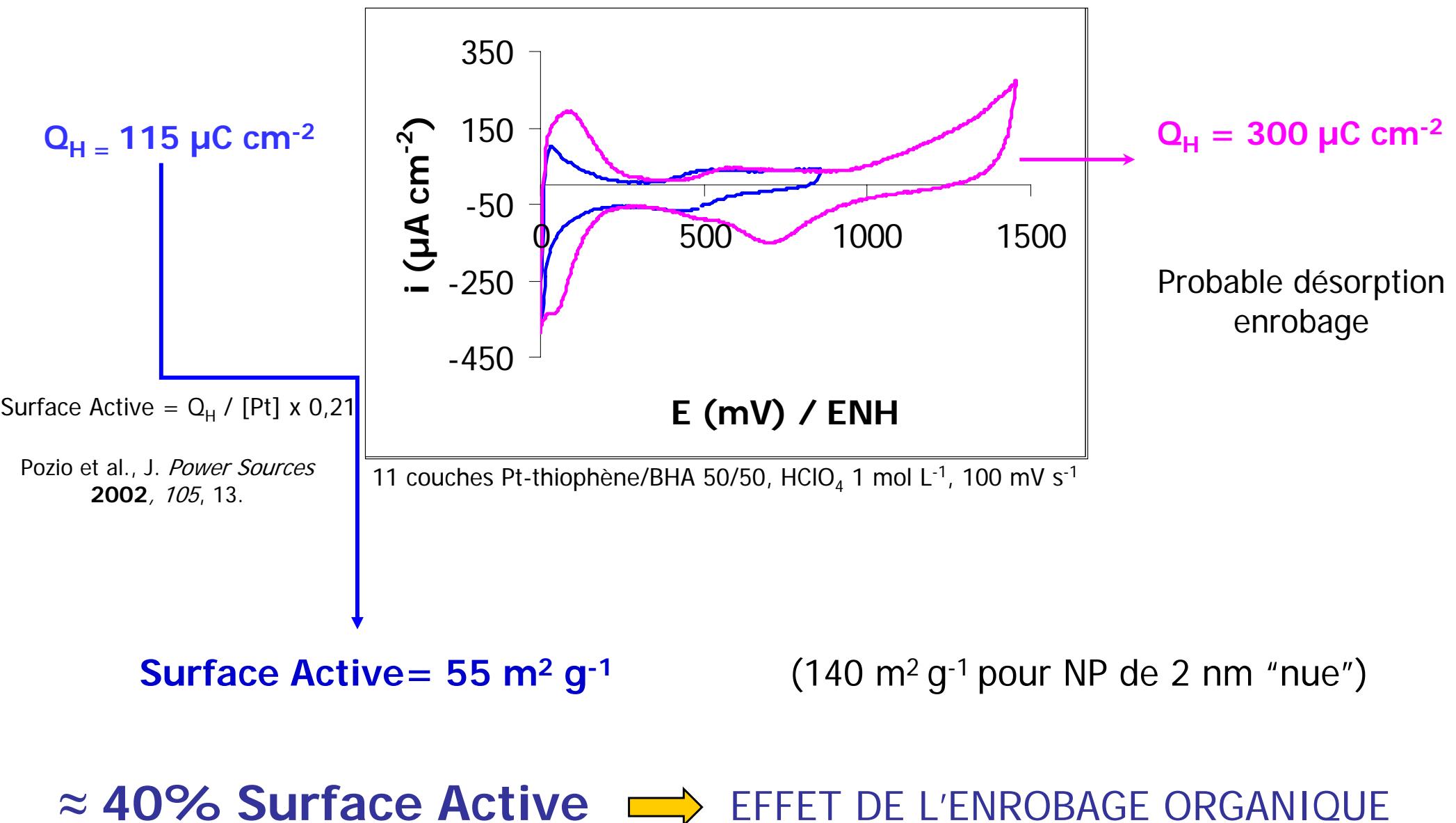
→ Dissolution Pt ?

NANOParticules de Platine A Enrobage organique modifiable

Comportement électrochimique

- Etude des espèces chimiques qui « empoisonne » le catalyseur (effet S²⁻)





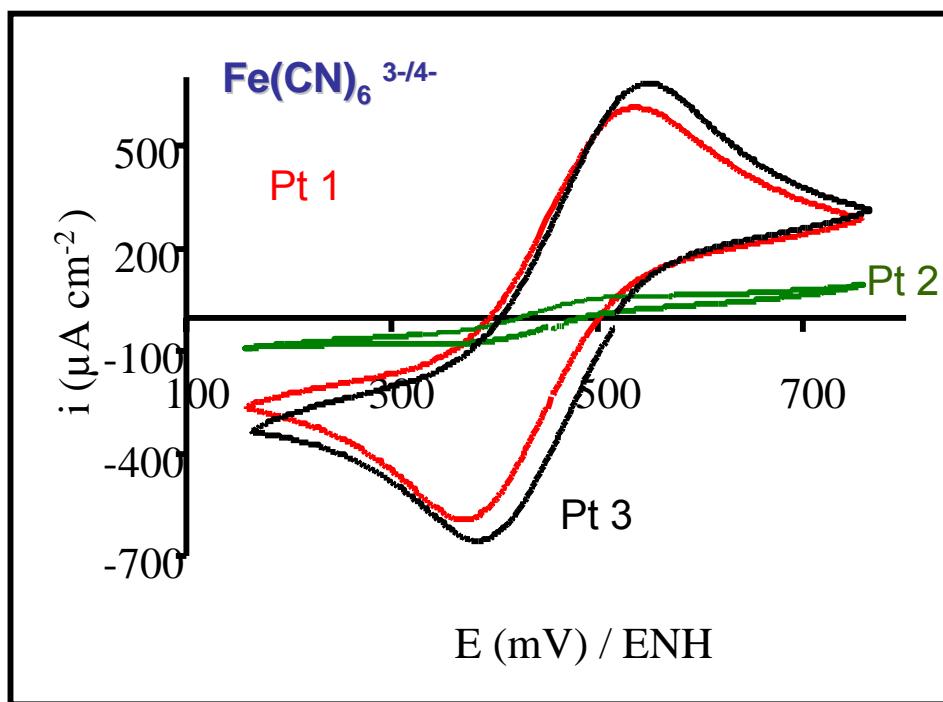
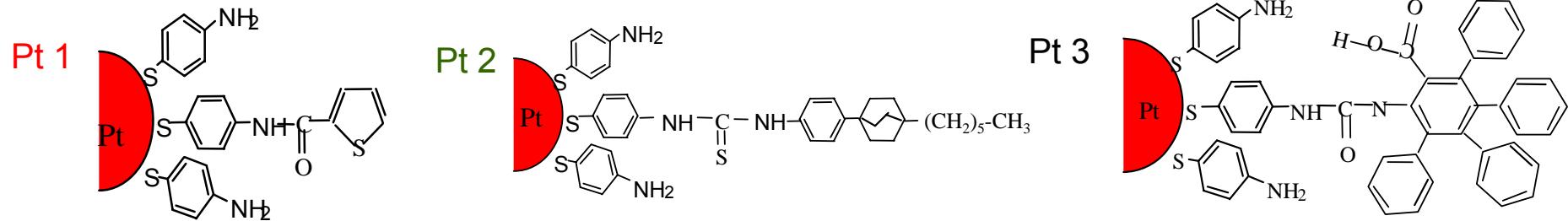
DEVELOPPEMENT D' ELECTROCATALYSEURS MODELES DE PAC PAR L'APPROCHE BOTTOM-UP

CONCLUSION

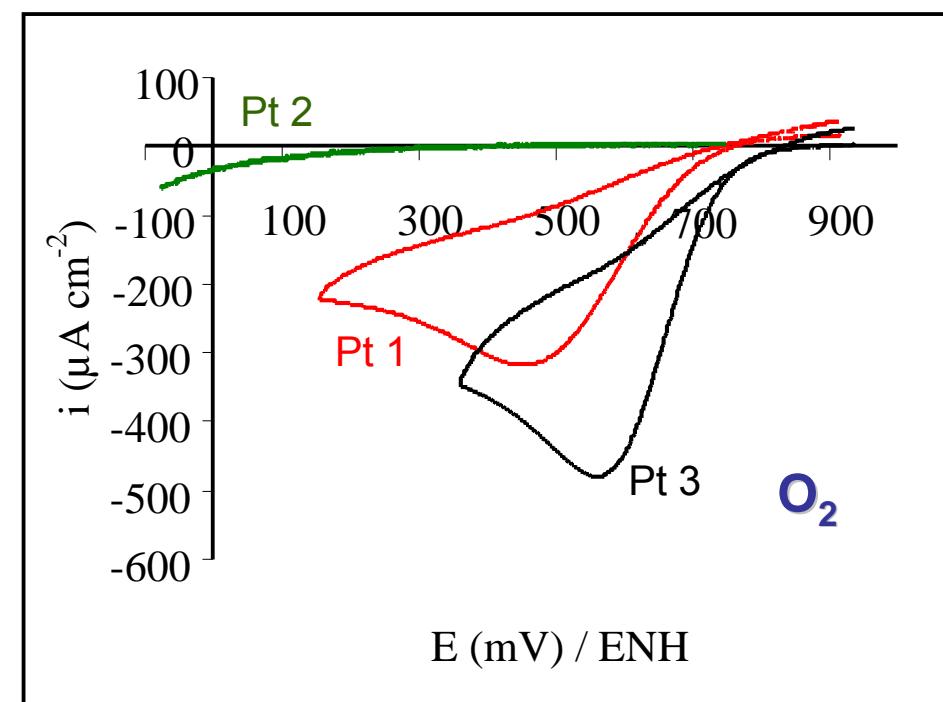
- L'approche adoptée permet d'accéder à des systèmes dont les caractéristiques sont assez bien déterminées
 - Quantité de catalyseur mise en jeu
 - Structure et environnement de la couche catalytique...
- Les systèmes à base de platine **couplés à des études de modélisations** peuvent probablement apporter des éléments de compréhension des phénomènes fondamentaux mis en jeu dans les catalyseurs de PEMFC...

PART 3: ELECTROCHEMICAL PROPERTIES

Effect of the organic crown (mixed films)



$5 \text{ mM } [\text{FeCN}_6]^{3-/4-} \text{ in } 0.1 \text{ M Na}_2\text{SO}_4 @ 20 \text{ mV s}^{-1}$

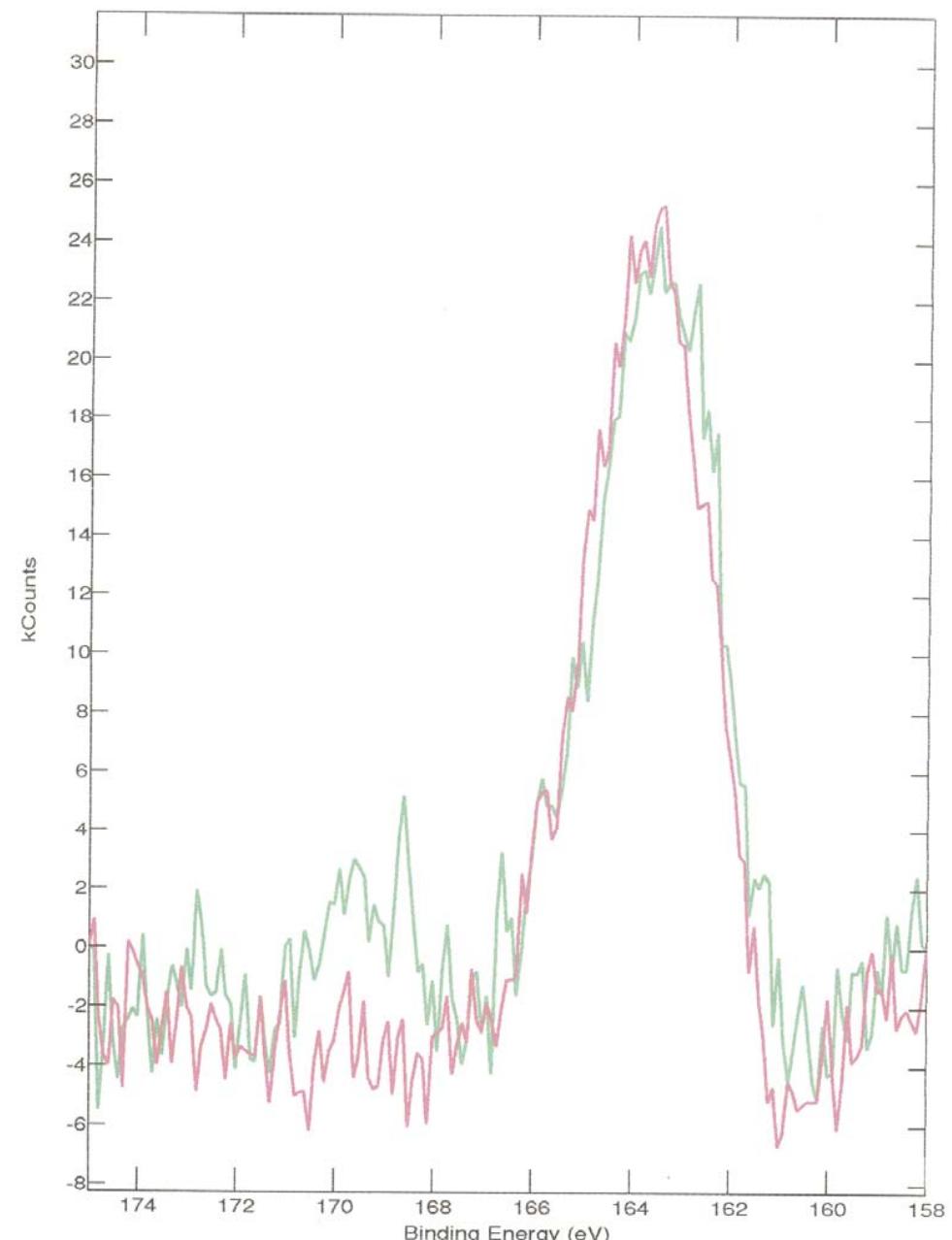
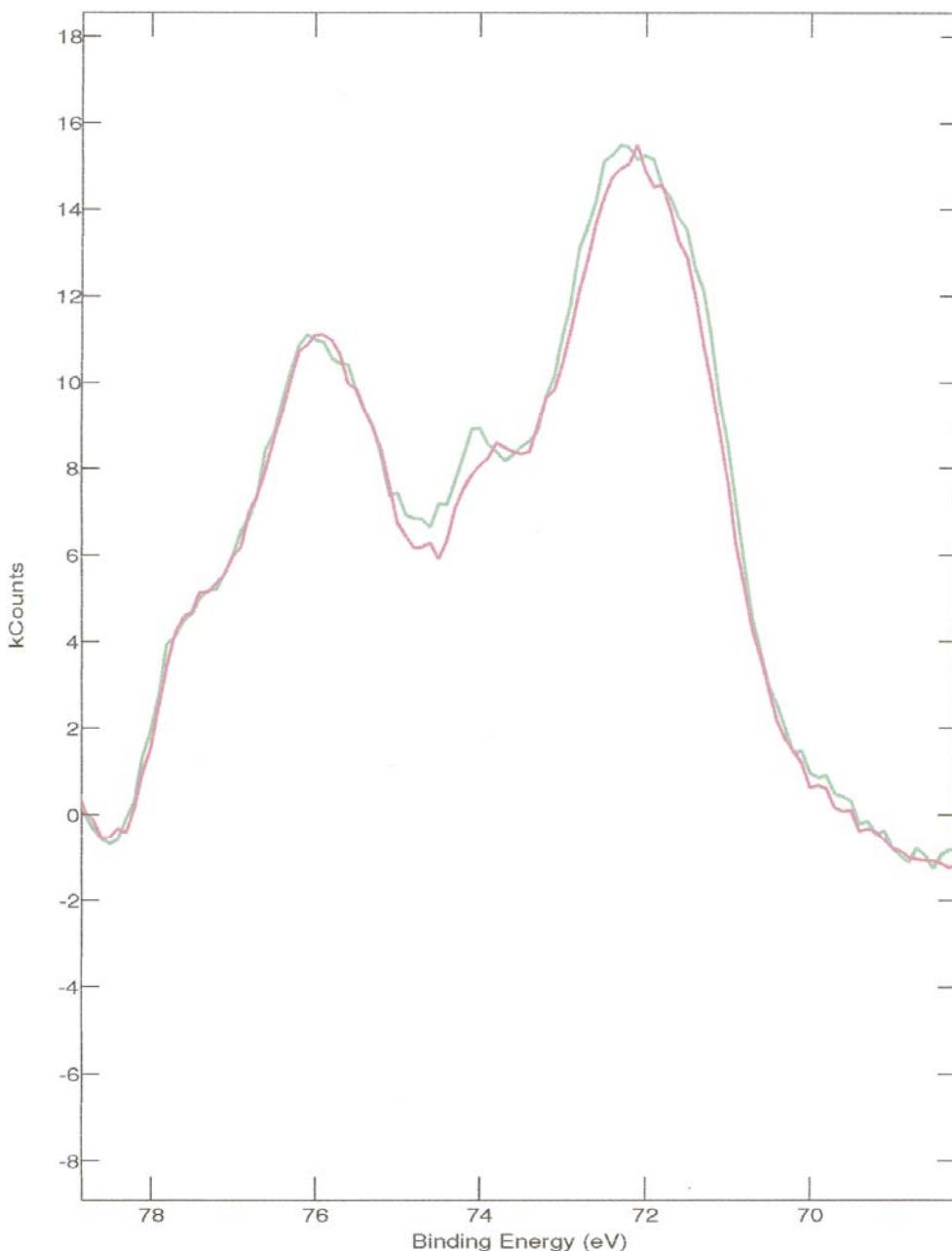


O_2 saturated $1 \text{ M HClO}_4 @ 20 \text{ mV s}^{-1}$



More pronounced in oxygen reduction

STABILITE DANS HClO_4



STABILITE DANS HClO_4

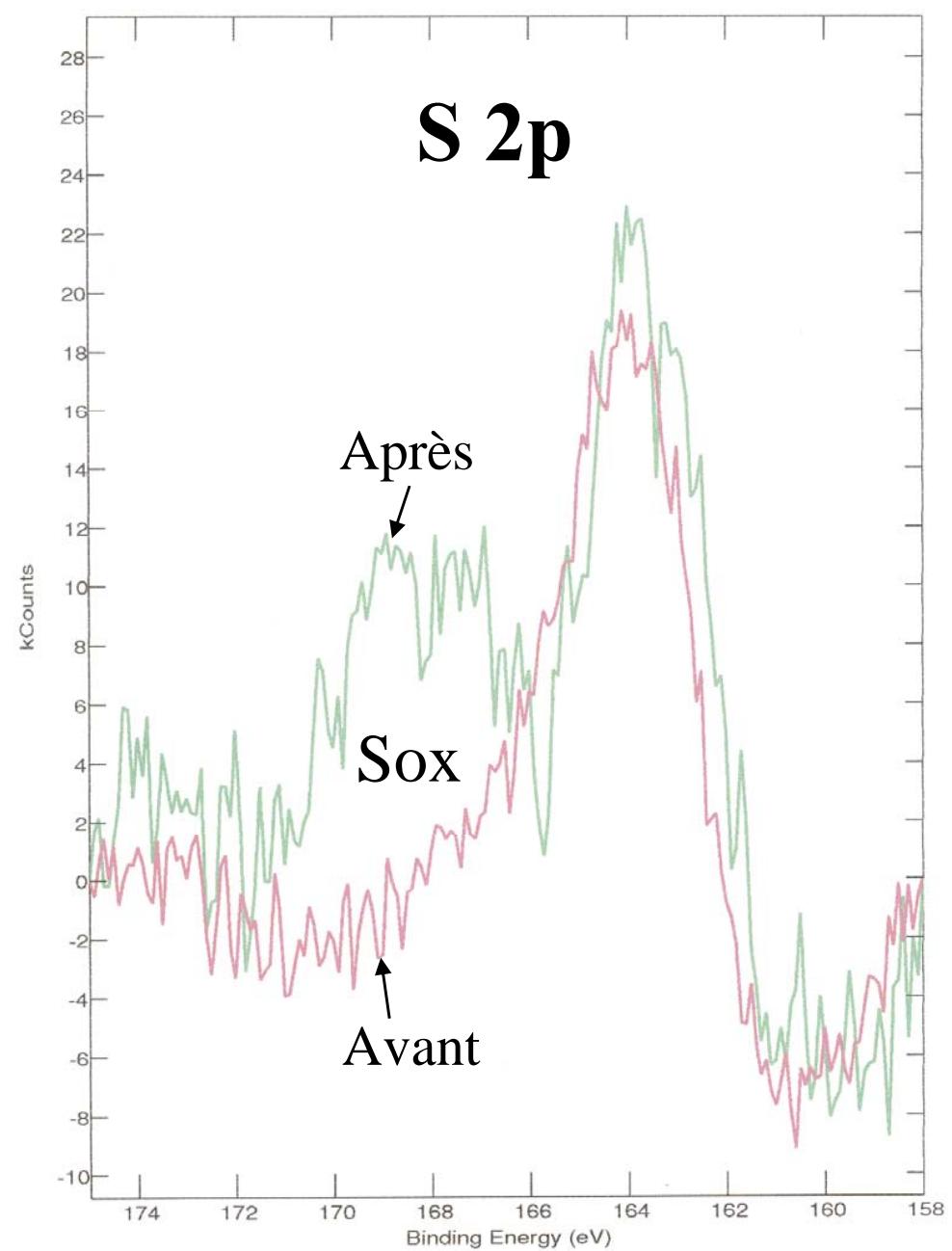
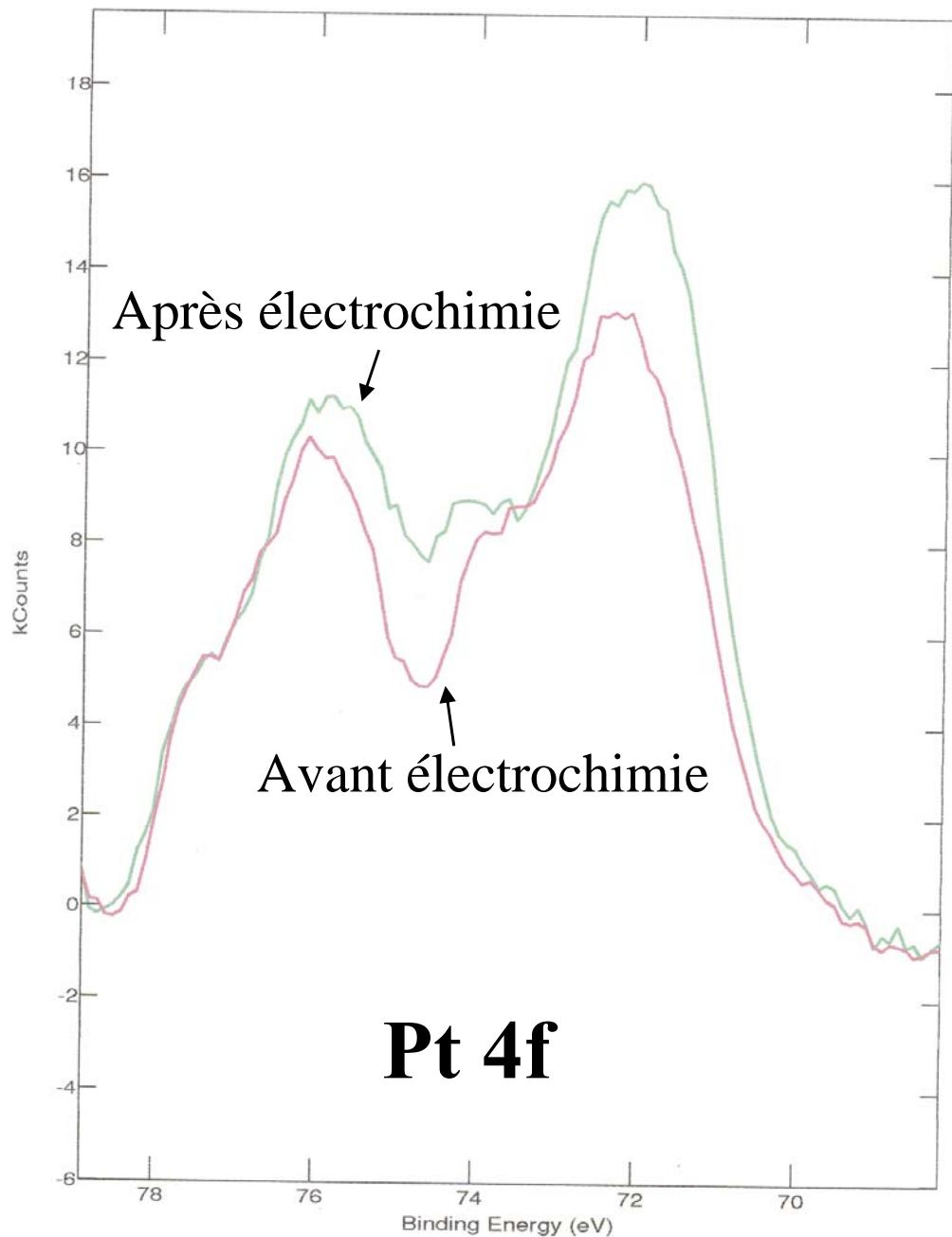
	Avant électrochimie	Après électrochimie
Pt 4f/S 2p <i>S 2p 161-166eV</i>	3,77	4,04
Pt 4f/S 2p <i>S 2p 161-171eV</i>	3,77	3,49
Pt 4f/Au 4f	0,15	0,16

Sox représente 13% du soufre restant après électrochimie

STABILITE DANS NaOH

	Avant électrochimie	Après électrochimie
Pt 4f/S 2p <i>S 2p 161-166eV</i>	3,85	7,04
Pt 4f/S 2p <i>S 2p 161-171eV</i>	3,85	4,68
Pt 4f/Au 4f	0,14	0,19

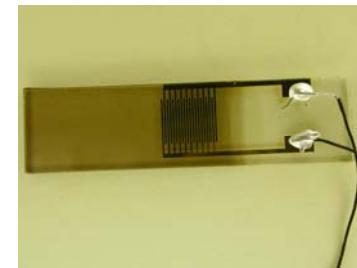
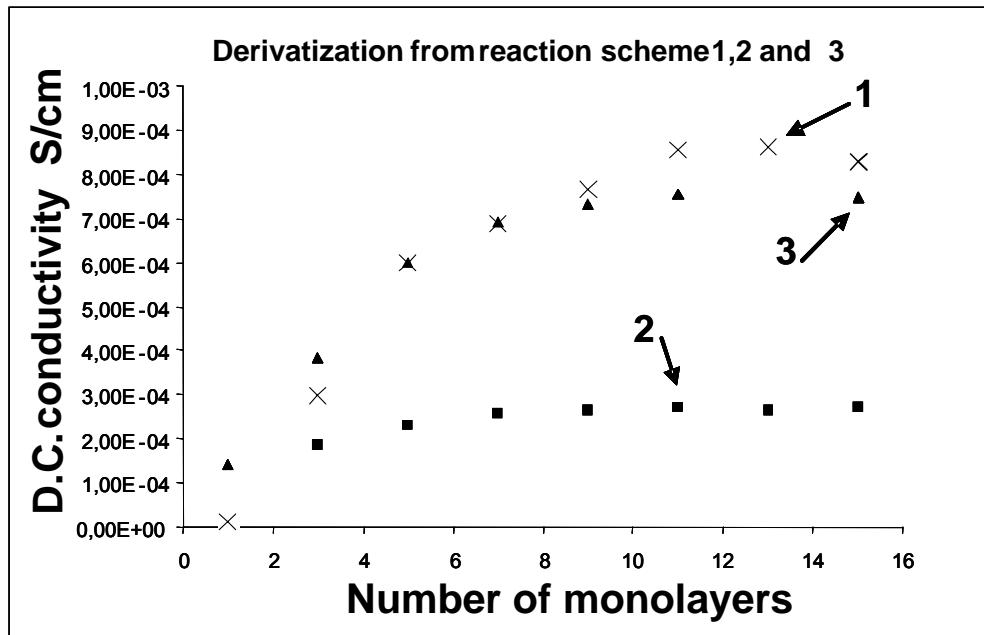
Sox représente 33% du soufre restant après électrochimie



ELECTRICAL AND ELECTROCHEMICAL PROPERTIES OF PLATINUM NANOPARTICLES ASSEMBLIES

Electrical behaviour

→ D.C. conductivity as function of the number of monolayers (mixed film 50/50 ratio area)



→ Possible influence of percolation, defects, nanoparticles domain size

- Activation energy: $\sigma = \sigma_0 \cdot e^{-Ea / RT}$ Ea lies between 70 meV and 90 meV

→ Ea is mainly related to the core diameter

ELECTRICAL AND ELECTROCHEMICAL PROPERTIES OF PLATINUM NANOPARTICLES ASSEMBLIES

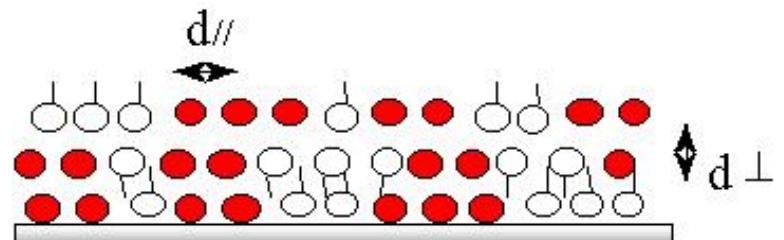
Electrical behaviour

→ D.C. conductivity level and evolution

	Functionalized Particle	Reaction Scheme 1	Reaction Scheme 2	Reaction Scheme 3	Reaction Scheme 4
Conductivity with fatty acid S.cm^{-1}	$1.0 \cdot 10^{-2}$	$8.5 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$	$7.5 \cdot 10^{-4}$	$3.0 \cdot 10^{-7}$

→ D.C. conductivity evolution is probably related to interparticle distance

	Functionalized Particle	Reaction Scheme 1	Reaction Scheme 2	Reaction Scheme 3	Reaction Scheme 4
Interparticle distance nm	$d_{//}$ 3.7 d_{\perp} 3.6	4.1	4.3	4.0	4.8



Steps involved in the bottom-up approach

→ Synthesis and characterization of nano-objects

- Chemical composition
- Size polydispersity
- Structure cristalline
- Forme géométrique, faces cristallines

→ Making solution of individualized object with known concentration

- Control of the amount of material

ELECTRICAL AND ELECTROCHEMICAL PROPERTIES OF PLATINUM NANOPARTICLES ASSEMBLIES

Electrical properties

- D.C. conductivity

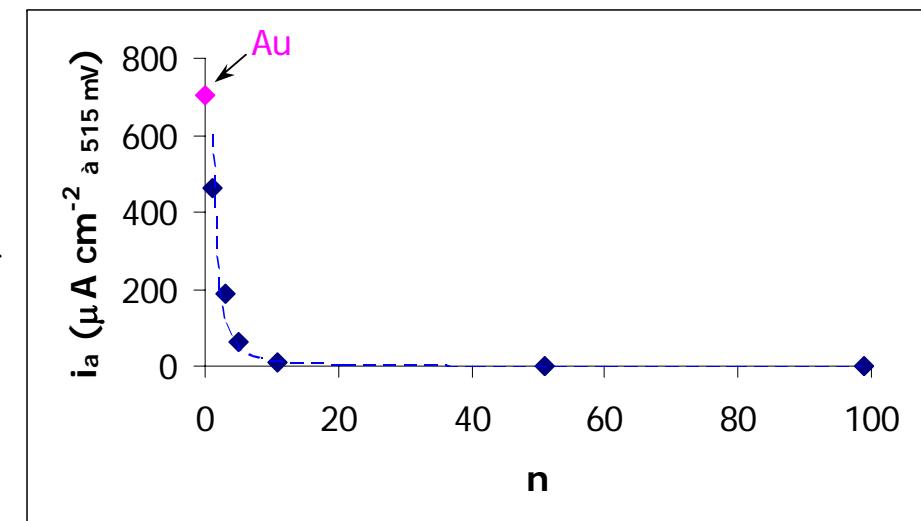
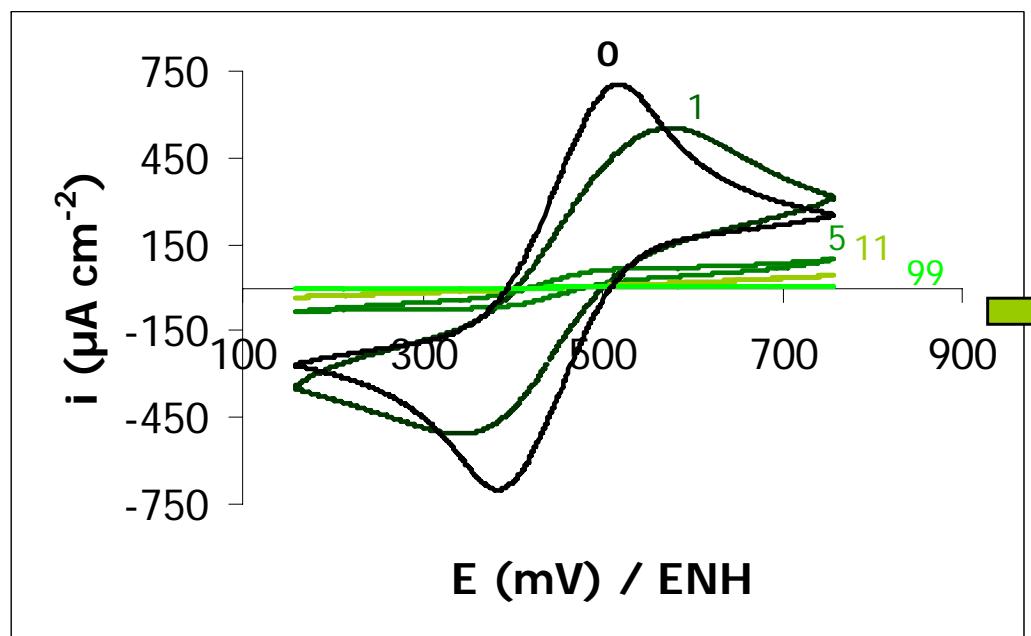
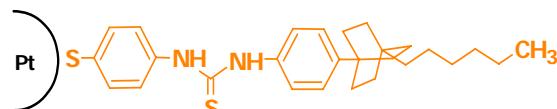
	Functionalized Particle	Reaction Scheme 1	Reaction Scheme 2	Reaction Scheme 3	Reaction Scheme 4
Conductivity with fatty acid S.cm ⁻¹	1.0. 10 ⁻²	8.5. 10 ⁻⁴	2.5.10 ⁻⁴	7.5.10 ⁻⁴	3.0.10 ⁻⁷



→ Conductivity is probably related to interparticle distances

	Functionalized Particle	Reaction Scheme 1	Reaction Scheme 2	Reaction Scheme 3	Reaction Scheme 4
Interparticle distance nm	3.7	4.1. 10 ⁻⁴	2.5.10 ⁻⁴	7.5.10 ⁻⁴	3.0.10 ⁻⁷

Pt-2



INTRODUCTION

PEMFC and Platinum as electrocatalyst

- Platinum widely used in PEMFC and widely studied as electrocatalyst for oxygen reduction
 - Some of the important points are:
 - in PEMFC, having low loading/ high degree of utilization of Pt,
 - In fundamental studies, having well defined system (structure, composition...)
-  to have a good control in the manipulation and the amount and environment of catalyst involved
-  Way of synthesis of catalysts is a key point in order to reach such a control

Ref: J-H Wee et al, *Journal of power sources* 165 (2007) 667-677

INTRODUCTION

Platinum, oxygen reduction and PEMFC

Different ways of synthesis of finely divided platinum :

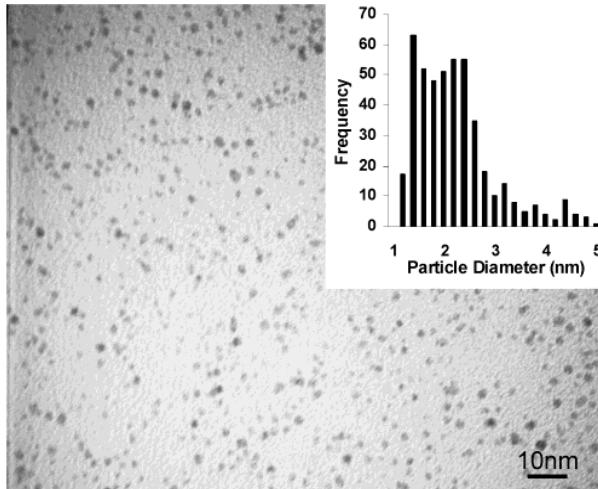
- Impregnation/reduction (carbon support)
- Electrodeposition
- Sputtering, CVD
- Solution synthesis (wet chemistry) with capping agent



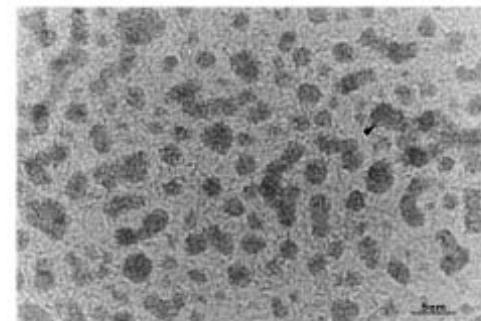
Isolable and redispersible particles are of special interest

INTRODUCTION

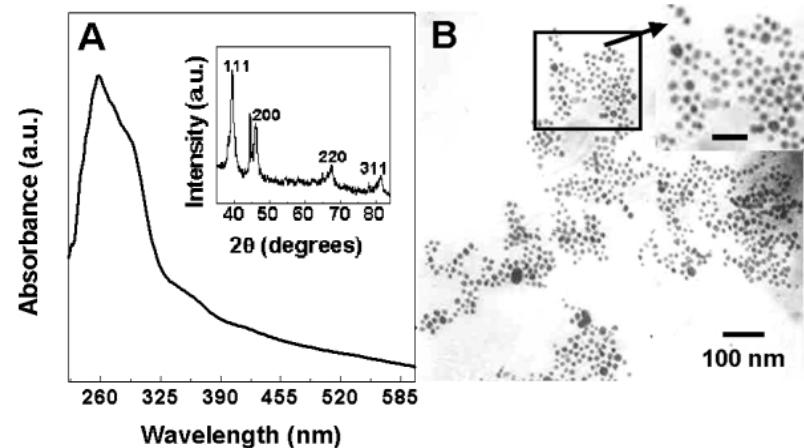
Platinum, oxygen reduction and PEMFC



Eklund S.E. and D. E. Cliffel
Langmuir 20 (14): 6012-6018 JUL 6 2004



Sarah L. Horswell, Christopher J. Kiely,
Ian A. O'Neil, and David J. Schiffrin
J. Am. Chem. Soc., Vol. 121, No. 23, 1999



S. Mandal, PR. Selvakannan, D. Roy, Raghunath
V. Chaudhari and M. Sastry*
Chem. commun. 2002, 3002

Isolable, redispersible particles in solvents (like molecules or polymers)



New possibilities by combining with the bottom-up approach developed in nanosciences and nanotechnologies

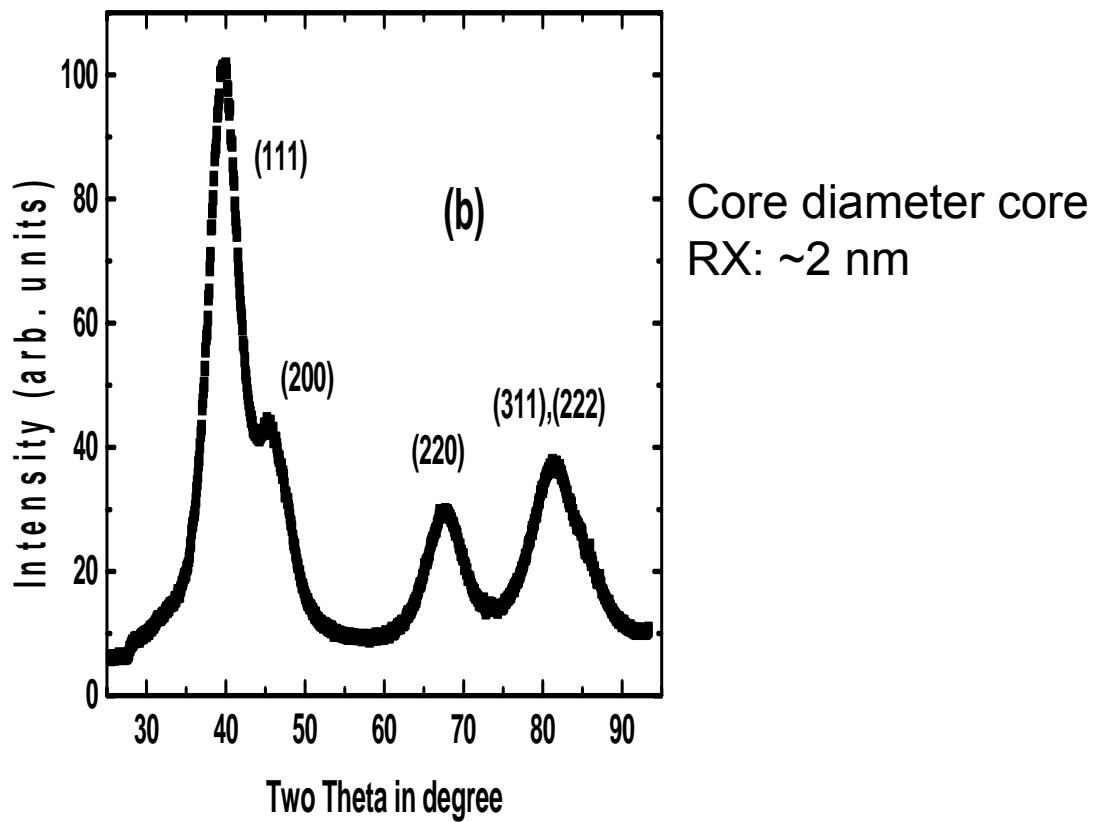
PART 1: SYNTHESIS AND CHARACTERIZATION OF NANO-OBJECTS

Structural features of platinum nanoparticles

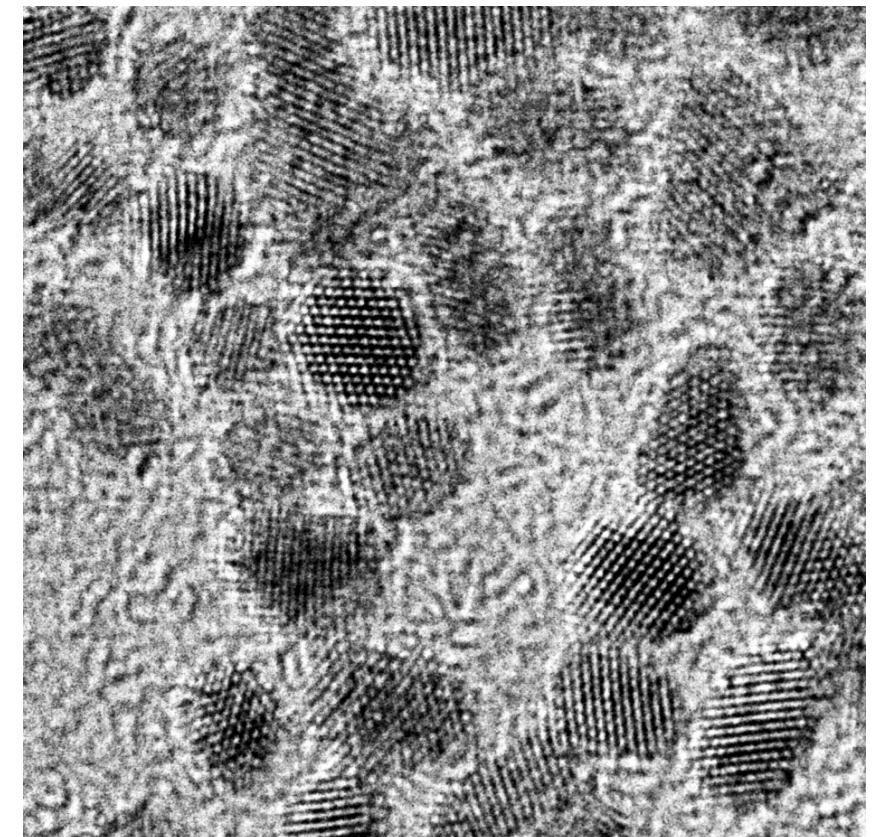
→ Nanoparticles are crystallised et faceted

X-ray diffraction (wide angles)

FCC Structure



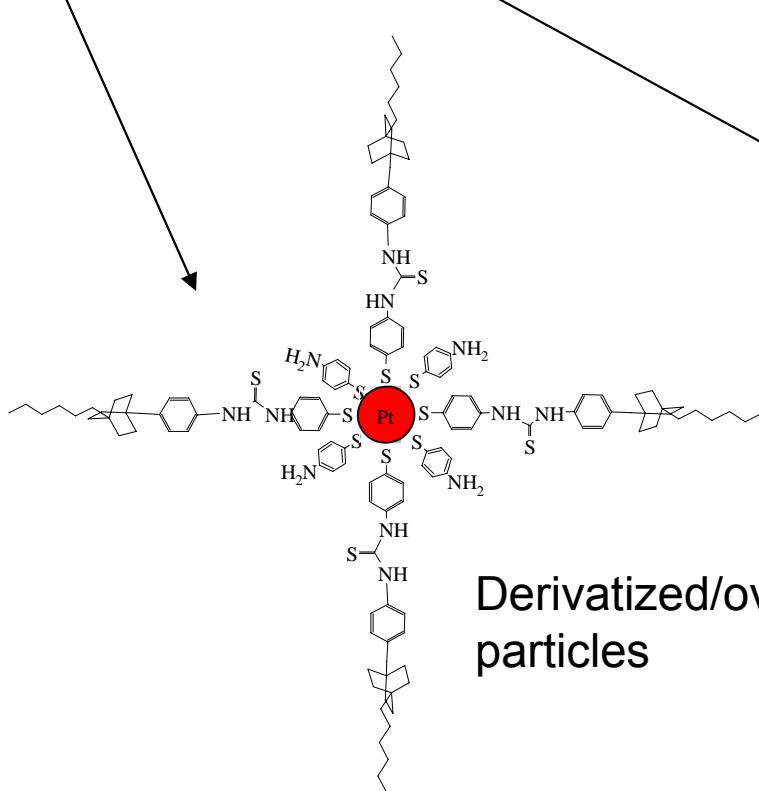
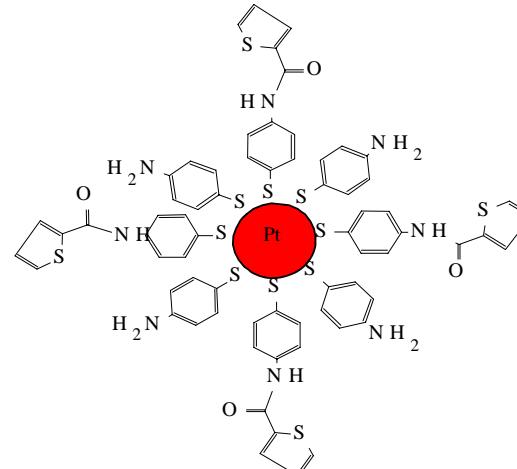
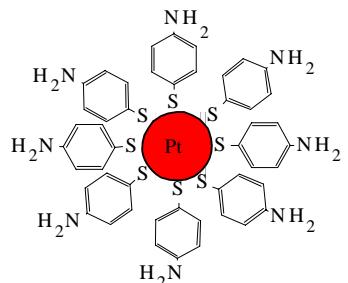
High resolution
T.E.M



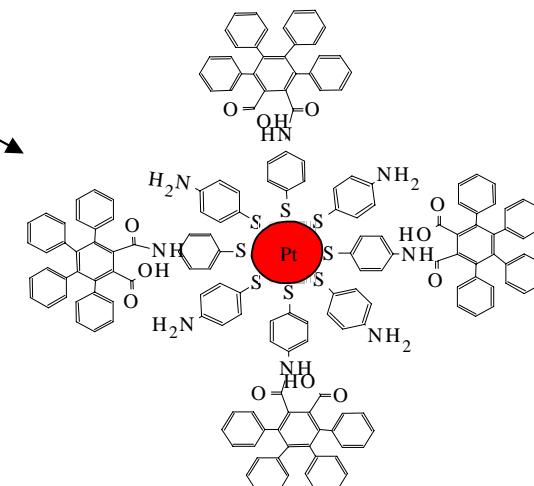
PART 1: SYNTHESIS AND CHARACTERIZATION OF NANO-OBJECTS

Making different bricks from by modification through over-grafting reactions

Mother brick



Derivatized/overgrafted particles

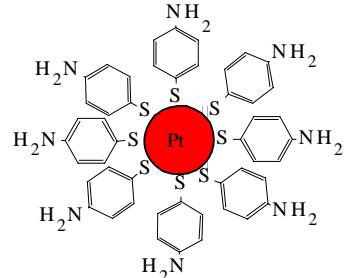


Partial over grafting:
Double crown structure

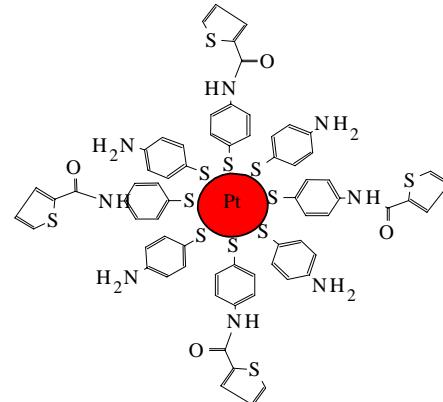
PART 1: SYNTHESIS AND CHARACTERIZATION OF NANO-OBJECTS

Characterizing partial over grafting

→ Organic content (Thermal Gravimetric Analysis)



13.7 à 14.9 %



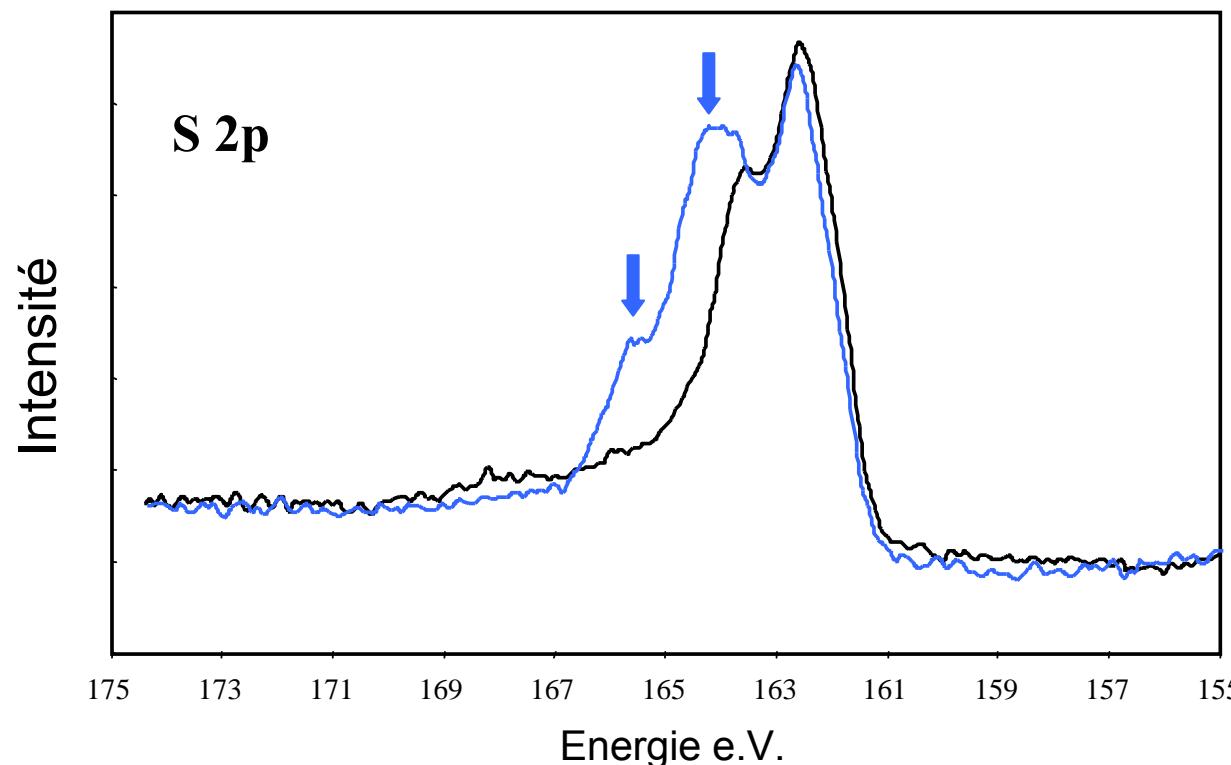
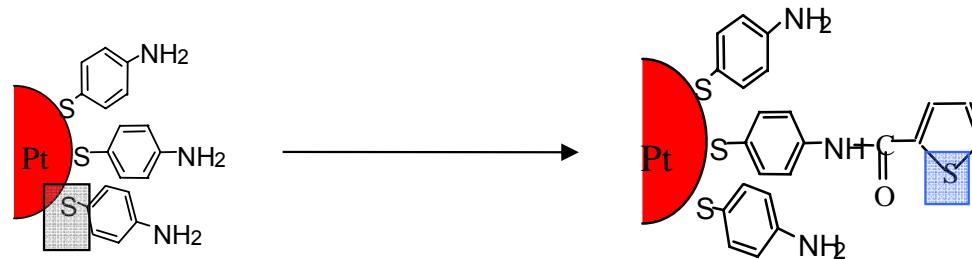
18.6 à 19.07. %

→ Over grafting ratio: % of reacted NH_2 functions

PART 2: ELABORATION AND CHARACTERIZATION OF SOLID STATE NANOSTRUCTURES FROM PREFORMED NANO-OBJETS

Characterization of Langmuir-Blodgett films

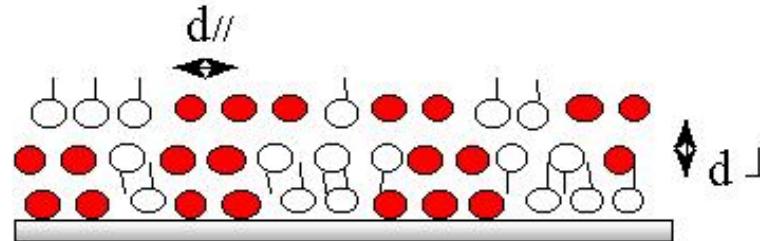
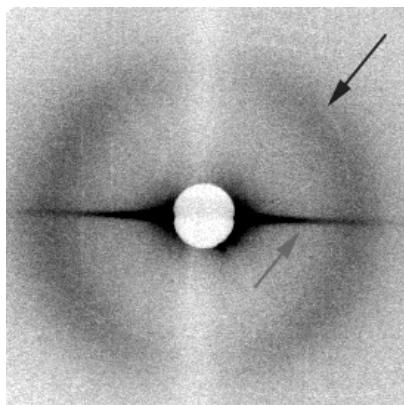
→ X-ray photo-electron spectroscopy (XPS)



PART 2: ELABORATION AND CHARACTERIZATION OF SOLID STATE NANOSTRUCTURES FROM PREFORMED NANO-OBJETS

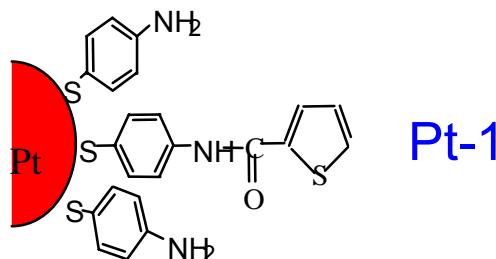
Characterization of Langmuir-Blodgett films

→ X-Rays diffraction at small angles

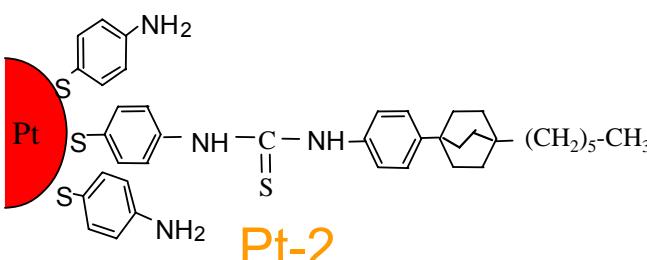


Continuous ring indicates
a well defined first-neighbours
distance d

Ring Ellipticity may be related
to different distances d_{\parallel} and d_{\perp}



Particule	$d_{\parallel} (\text{\AA})$	$d_{\perp} (\text{\AA})$
Pt 1	41,0	36,0
Pt-2	48,5	52,1



After fatty acid removal

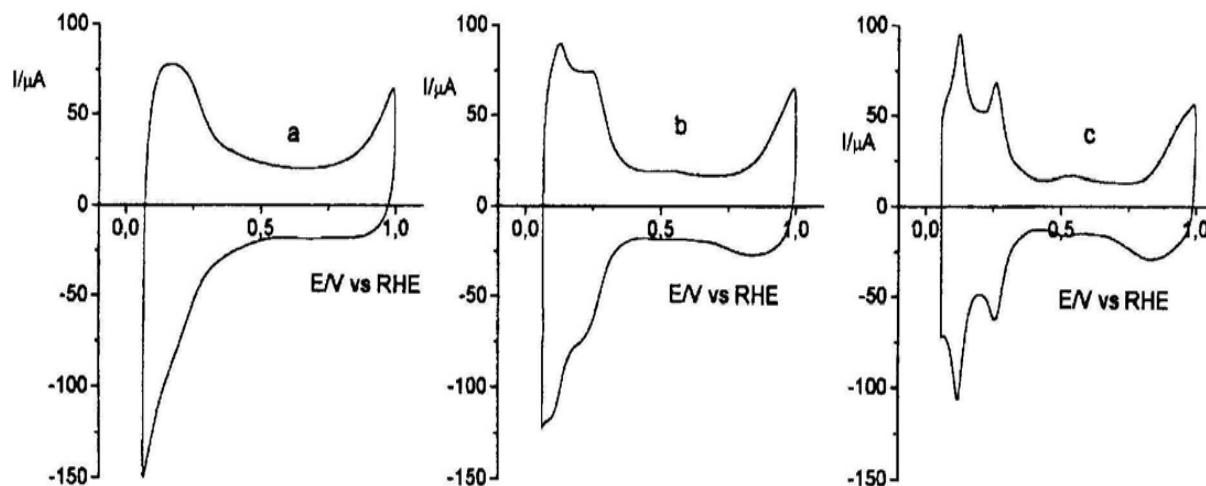
Particule	$d_{\parallel} (\text{\AA})$	$d_{\perp} (\text{\AA})$
Pt 1	40,4	35,3
Pt-2	49,6	40,8

INTRODUCTION

Capped or stabilized Platinum as electrocatalyst

- Control of platinum nanoparticle features versus electrochemical activity characterization

Controlled surface decontamination by lowering the oxydation potential ?



J. Solla-Gullon, V. Montiel, A. Aldaz, J Clavilier
J. Electroanal Chem. 491 (2000) 69

INTRODUCTION

Capped or stabilized Platinum as electrocatalyst

- Control of platinum nanoparticle features versus electrochemical activity characterization

→ Activation steps by thermal treatments :

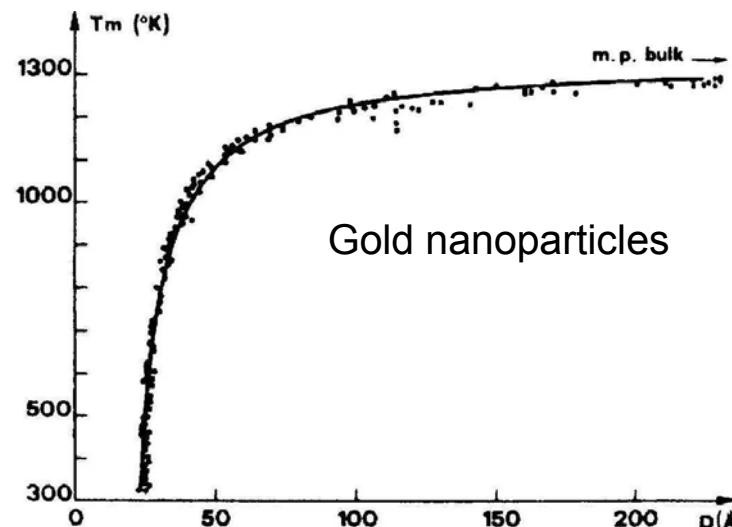


FIG. 6. Experimental and theoretical values of the

PH. Buffat and J-P Borel Phys. Rev. A 13 (1976) 2287

→ May change the features of low size nanoparticles !

INTRODUCTION

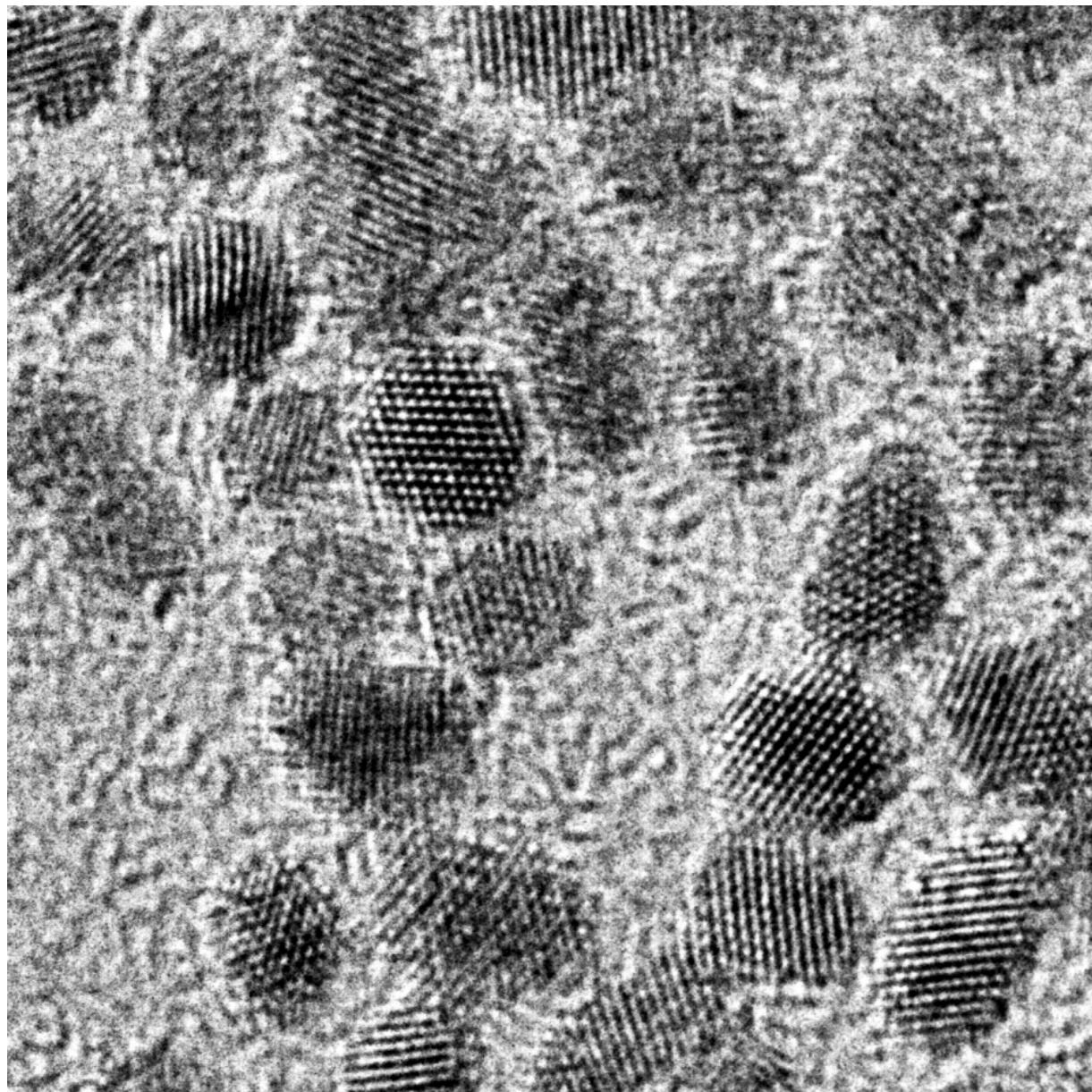
Capped or stabilized Platinum as electrocatalyst

→ Determination of electrocatalytical activity of capped/stabilized platinum nanoparticles raises many questions...

- Influence of capping or stabilizing agent on nanoscale nanoparticle features ?
- Does Hupd provide a reliable measurement of performances towards oxygen reduction in such a case ?
- What is the effect of changing the nanoscale scale environment on the electrochemical features ?



- Making capped platinum catalyst with different organic crowns well characterized (organic content)
- Control platinum loading in different kinds of nanostructures
- Characterize the electrocatalytical activity without changing the features of the catalyst
(No “activation” step !)



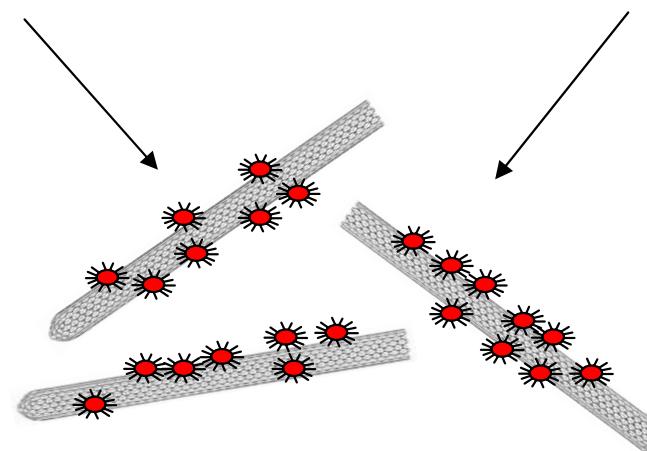
Part 3: Elaboration and properties of nanocomposite based on organically capped platinum nanoparticles and carbon nanotubes

Association of platinum nanoparticles and carbon nanotube through Bottom-up approach :

Capped platinum nanoparticle solution



Carbon nanotube dispersion

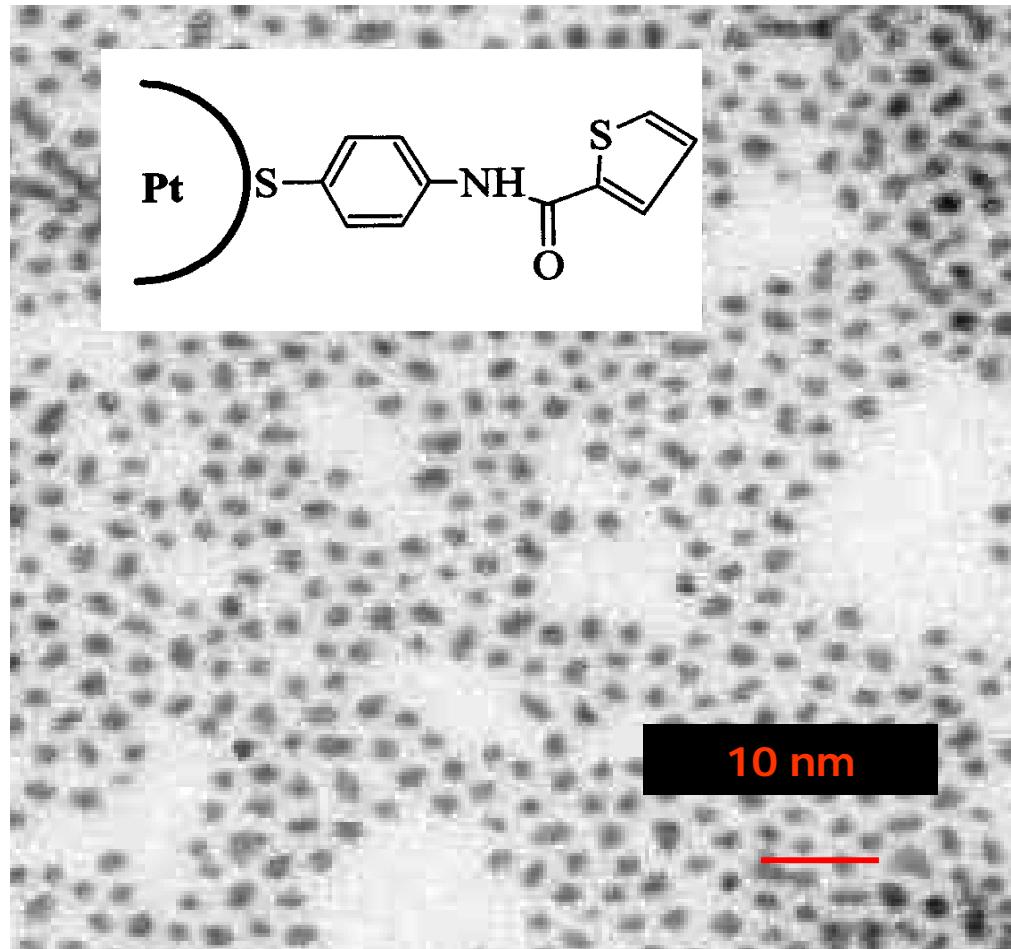


→ Controle of relative amount allows to form Nanocomposites liquid dispersion with controlled coverage of nanotube

Part 2: Elaboration and properties of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

Elaboration and features of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

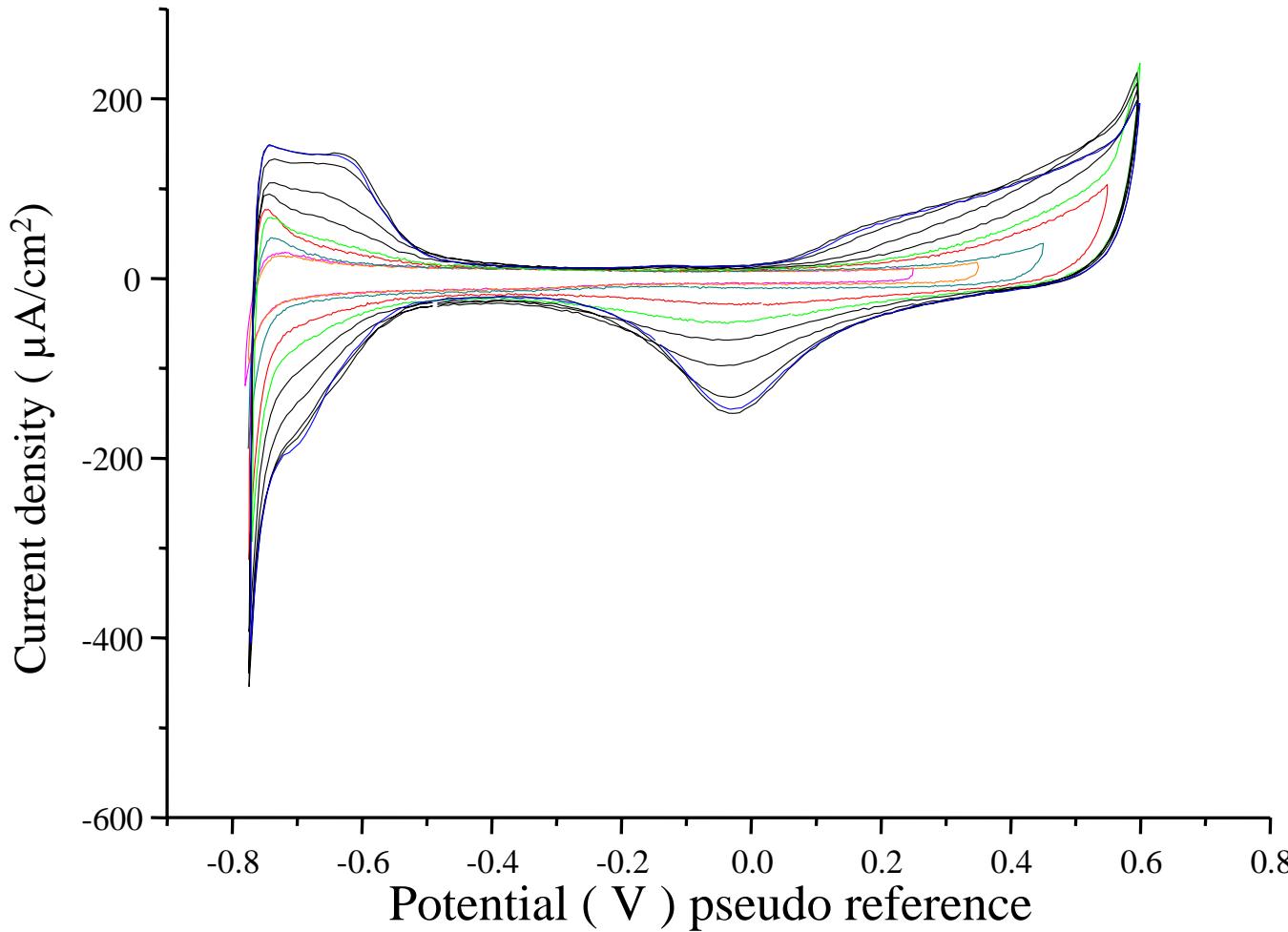
→ Transmission Electron Microscopy



Part 2: Elaboration and properties of Mixed Langmuir-Blodgett films based on organically capped platinum nanoparticles

Hydrogen underpotentiel deposition (charge of proton adsorption-desorption)

→ Scanning at higher and higher potential results in usual features



But modify the platinum core....

Part 3: Elaboration and properties of nanocomposite based on organically capped platinum nanoparticles and carbon nanotubes

→ Electrochemical characterization do not alter the organic crown