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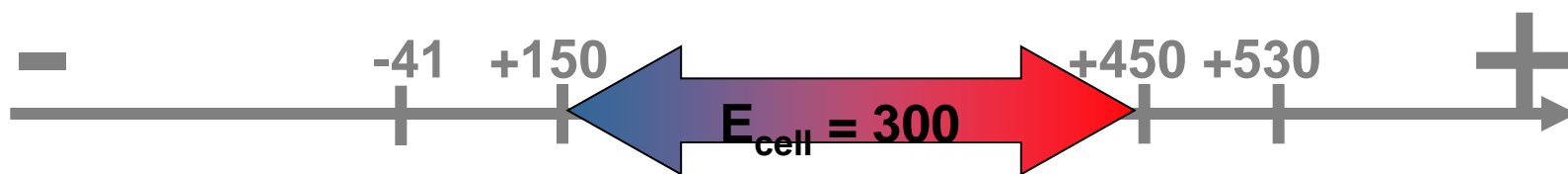
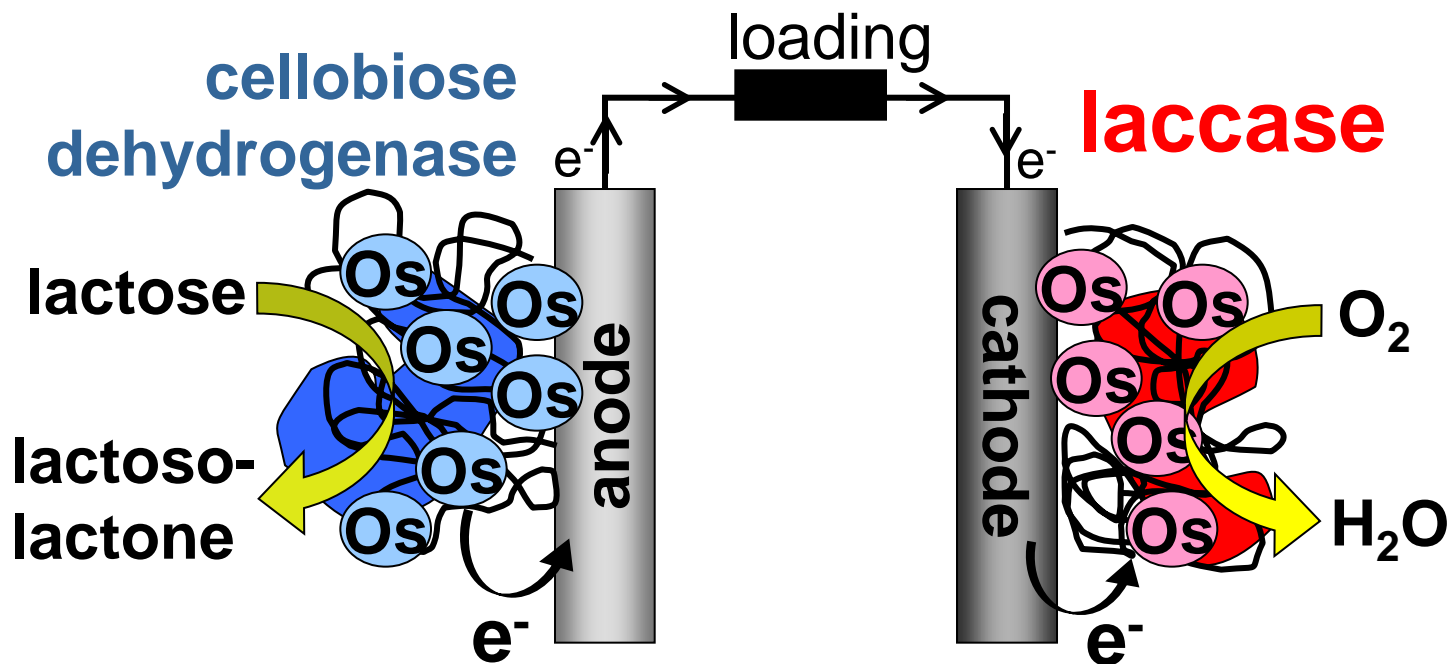
***Perspective pentru un nou biocatod de  
potențial ridicat – noi proprietăți ale  
enzimelor redox immobilizate pe nanostructuri  
compozite de grafit***

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# Concept of bienzymatic membrane-less biofuel cell (BFC)



 cellobiose dehydrogenase (CDH)

 laccase

Potential [mV] vs. Ag/AgCl 3M KCl

# Motivation for new material electrode

- High catalytic coverage:
  - large amount of **active enzyme**;
- Large **active** area of electrode:
  - using hierarchical carbonaceous materials two-generations CNT's
- Exploring specific properties of **bio-nano** interactions.

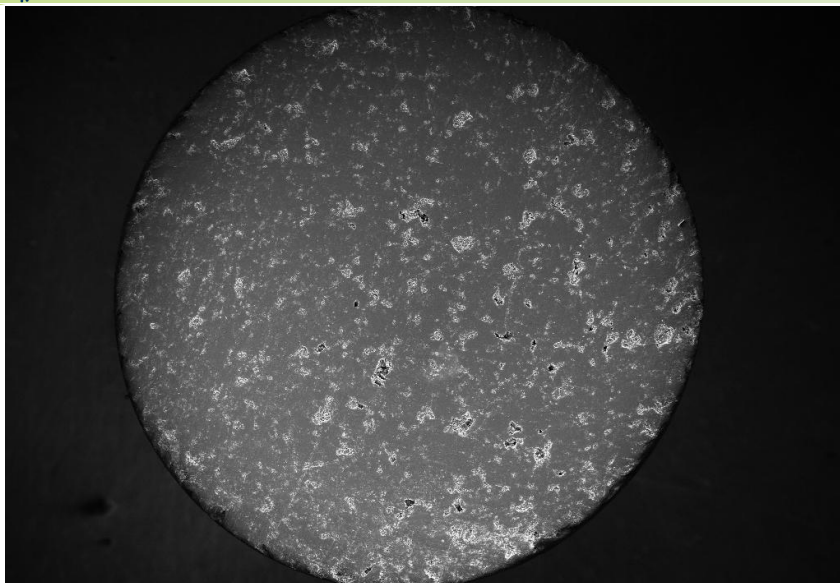
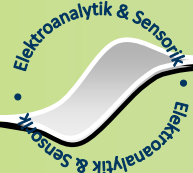
$$P_{\text{out}} = E \times I$$

$[E]; A; k_{\text{cat}}, n$

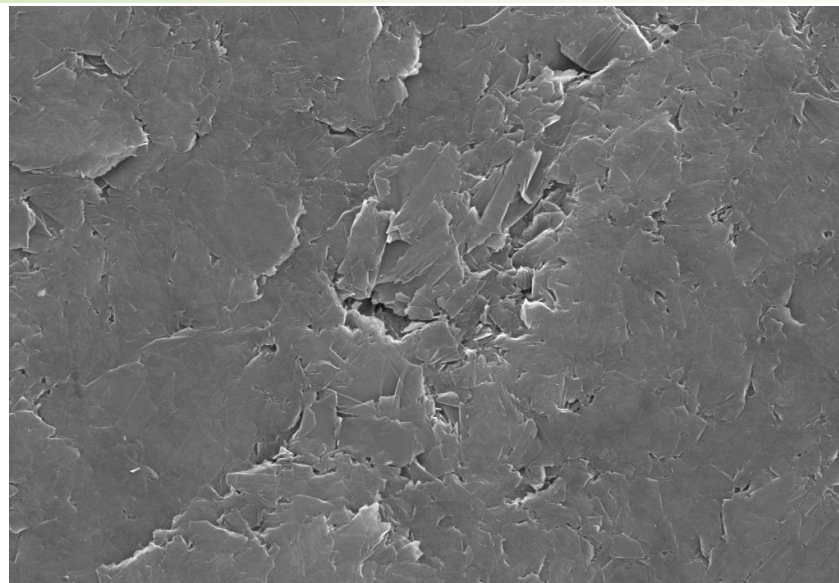
$E^{0'}$

# I. Large active area electrode

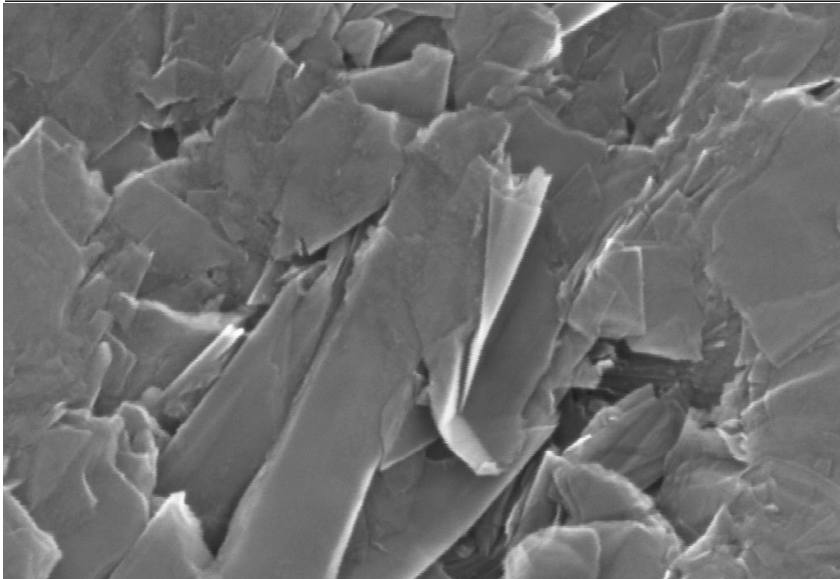
# Graphite electrode surface



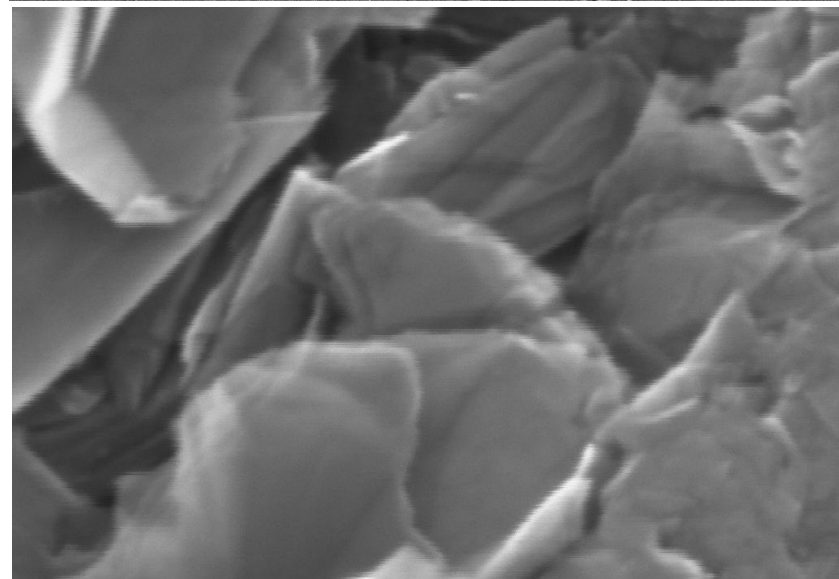
Ruhr-Universität-Bochum 200  $\mu$ m EHT = 10.00 kV Signal A = InLens Date :2 Apr 2009  
Zentrales REM WD = 8 mm Photo No. = 37 Mag = 74 X



Ruhr-Universität-Bochum 1  $\mu$ m EHT = 10.00 kV Signal A = InLens Date :2 Apr 2009  
Zentrales REM WD = 5 mm Photo No. = 38 Mag = 28.30 K X



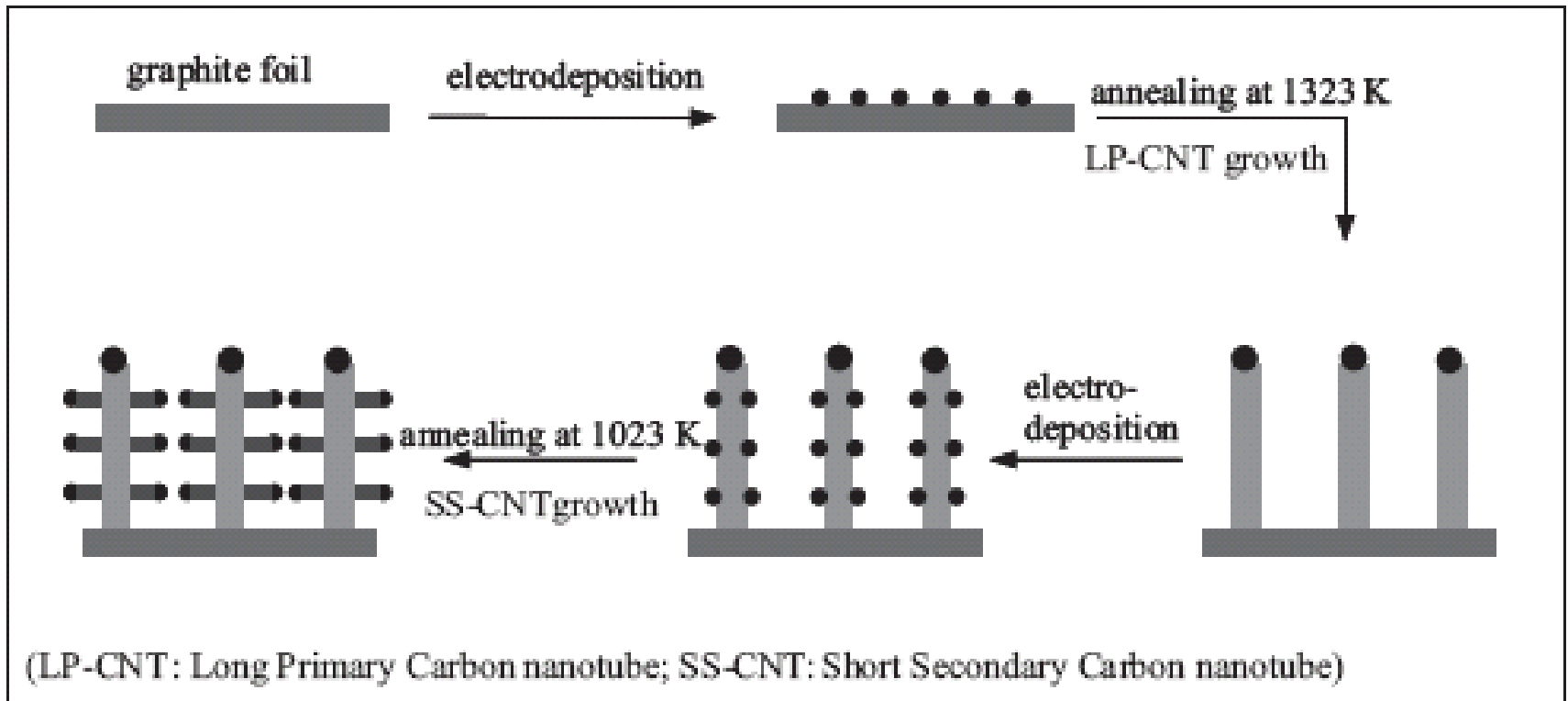
Ruhr-Universität-Bochum 200 nm EHT = 10.00 kV Signal A = InLens Date :2 Apr 2009  
Zentrales REM WD = 5 mm Photo No. = 39 Mag = 155.71 K X



Ruhr-Universität-Bochum 100 nm EHT = 10.00 kV Signal A = InLens Date :2 Apr 2009  
Zentrales REM WD = 5 mm Photo No. = 40 Mag = 394.18 K X

# Composite material: CNT/CMF onto carbon paper

## Preparation:



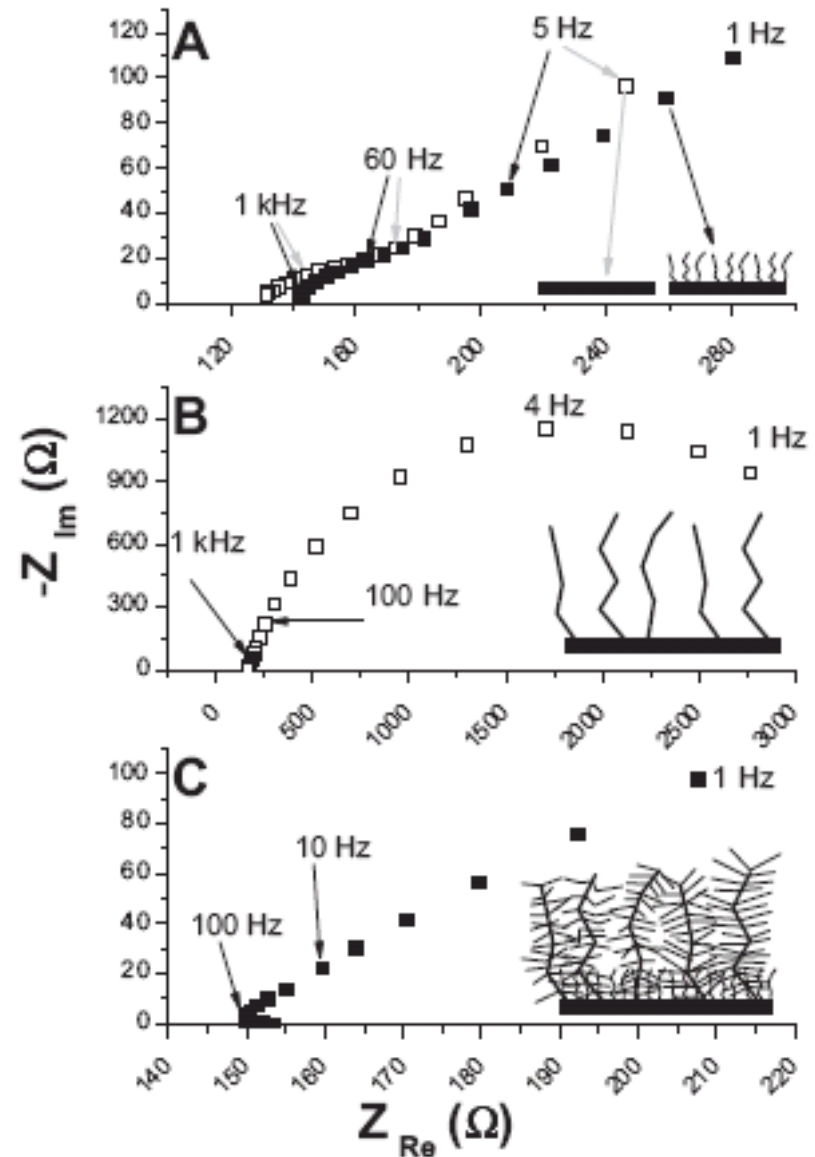
N. Li, X. Chen, L. Stoica, W. Xia, J. Qian, J. Aßmann, W. Schuhmann, M. Muhler

Adv. Mater. (2007), 19, 2957-2960

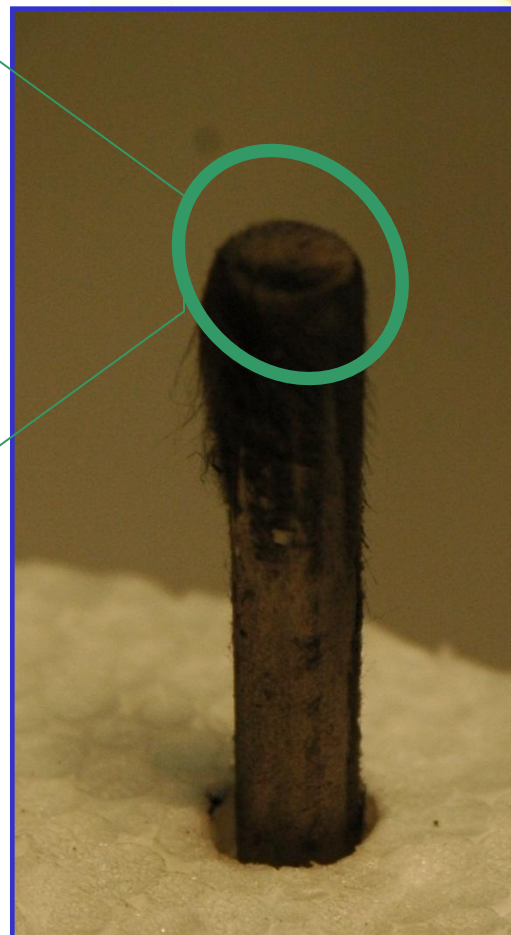
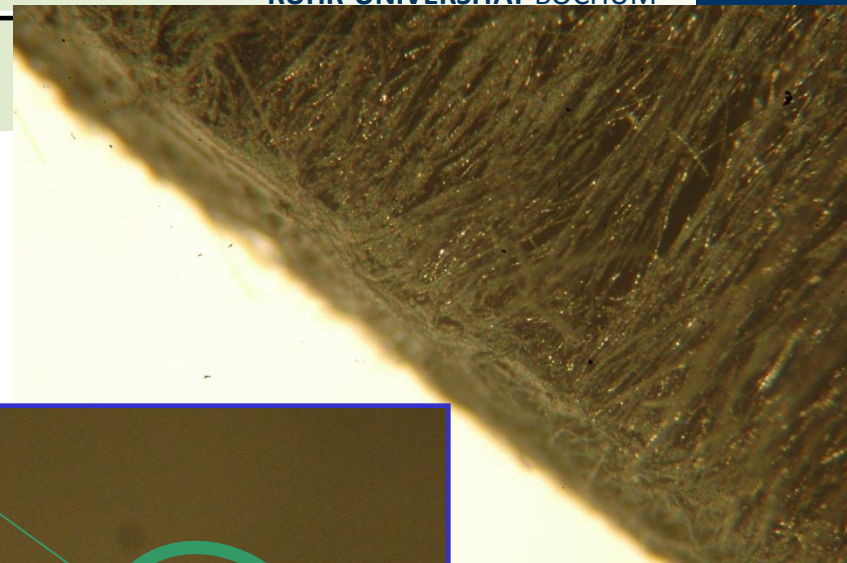
# EIS characterisation of CNT/CMF

## Properties:

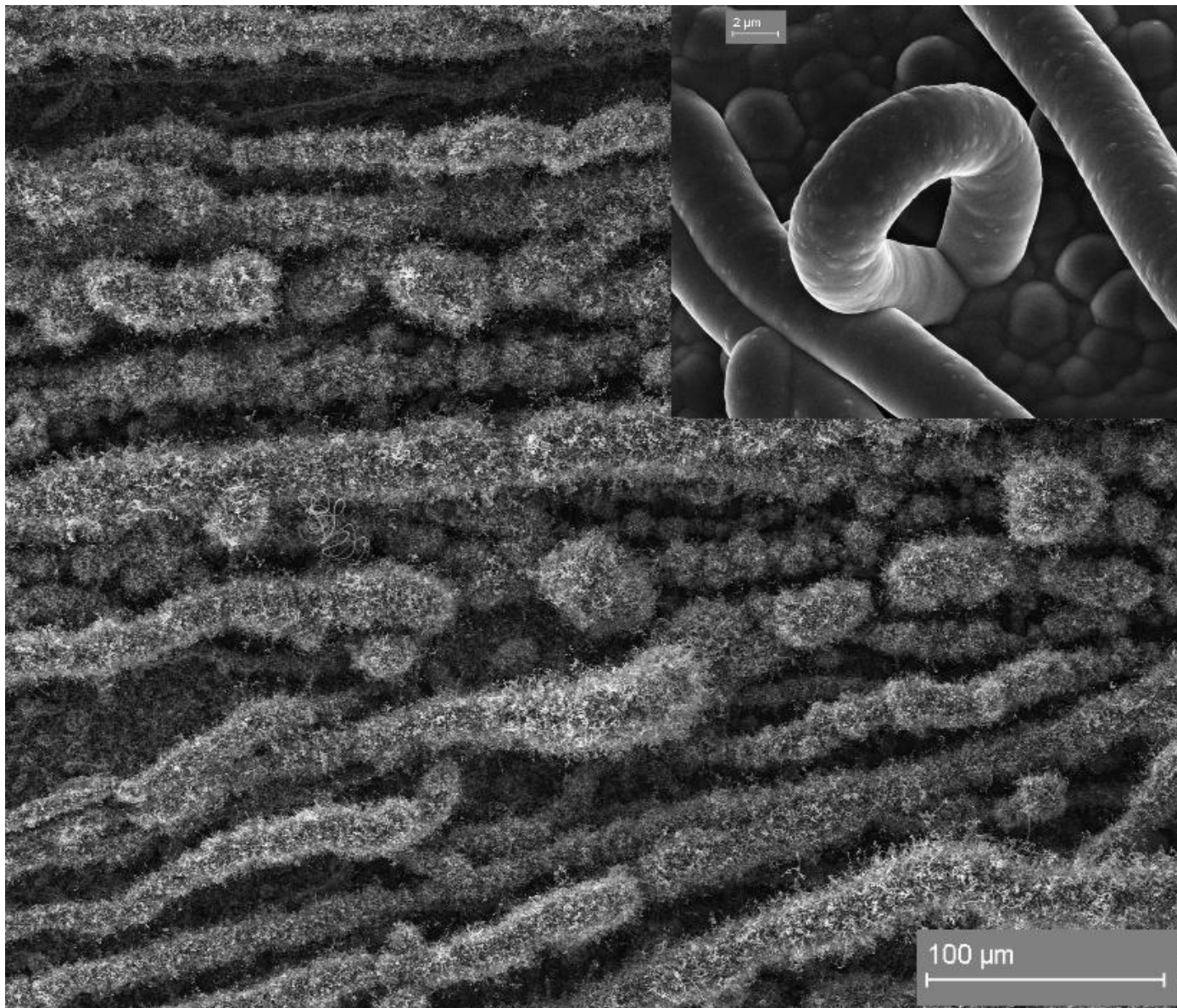
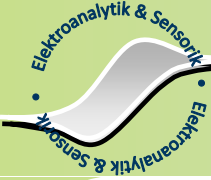
- Low ohmic resistance => no potential loss;
- Ratio active/geometric area=200;
- Non-restrictive diffusion of enzyme substrate.



# Various supports







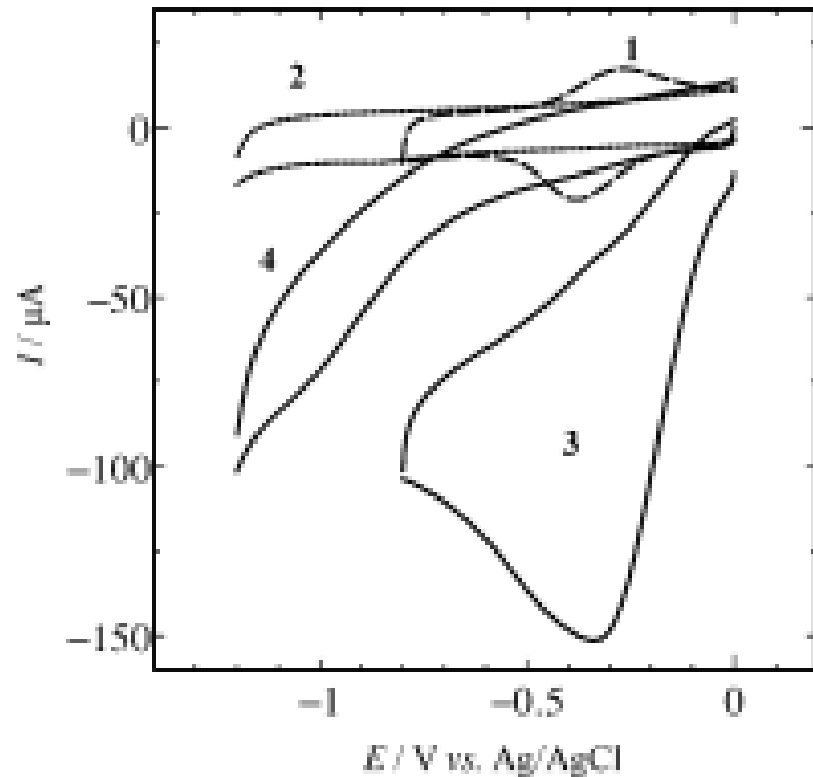
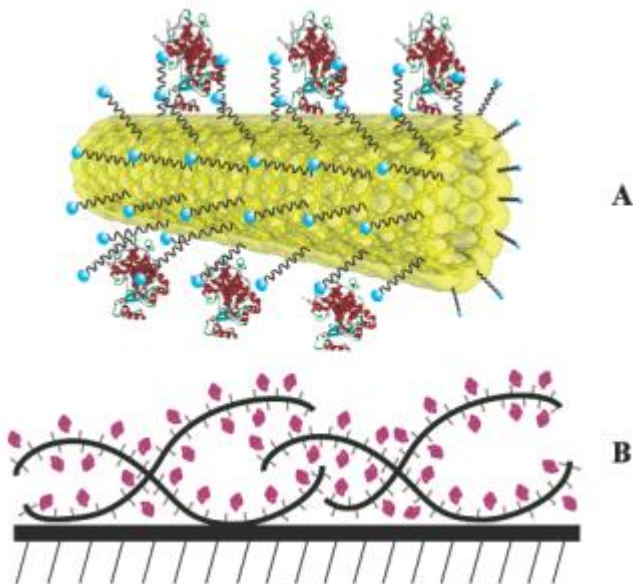
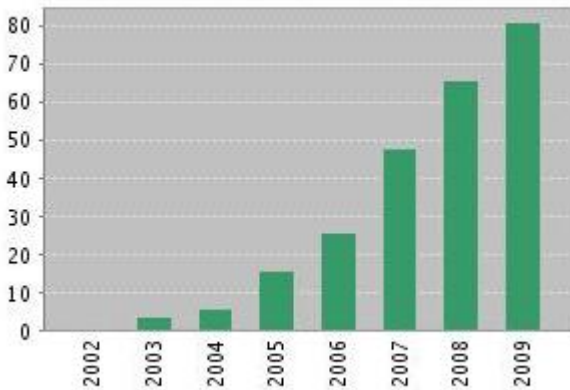
# II. Exploring specific bio-nano interactions

# HRP-CNT

250 results

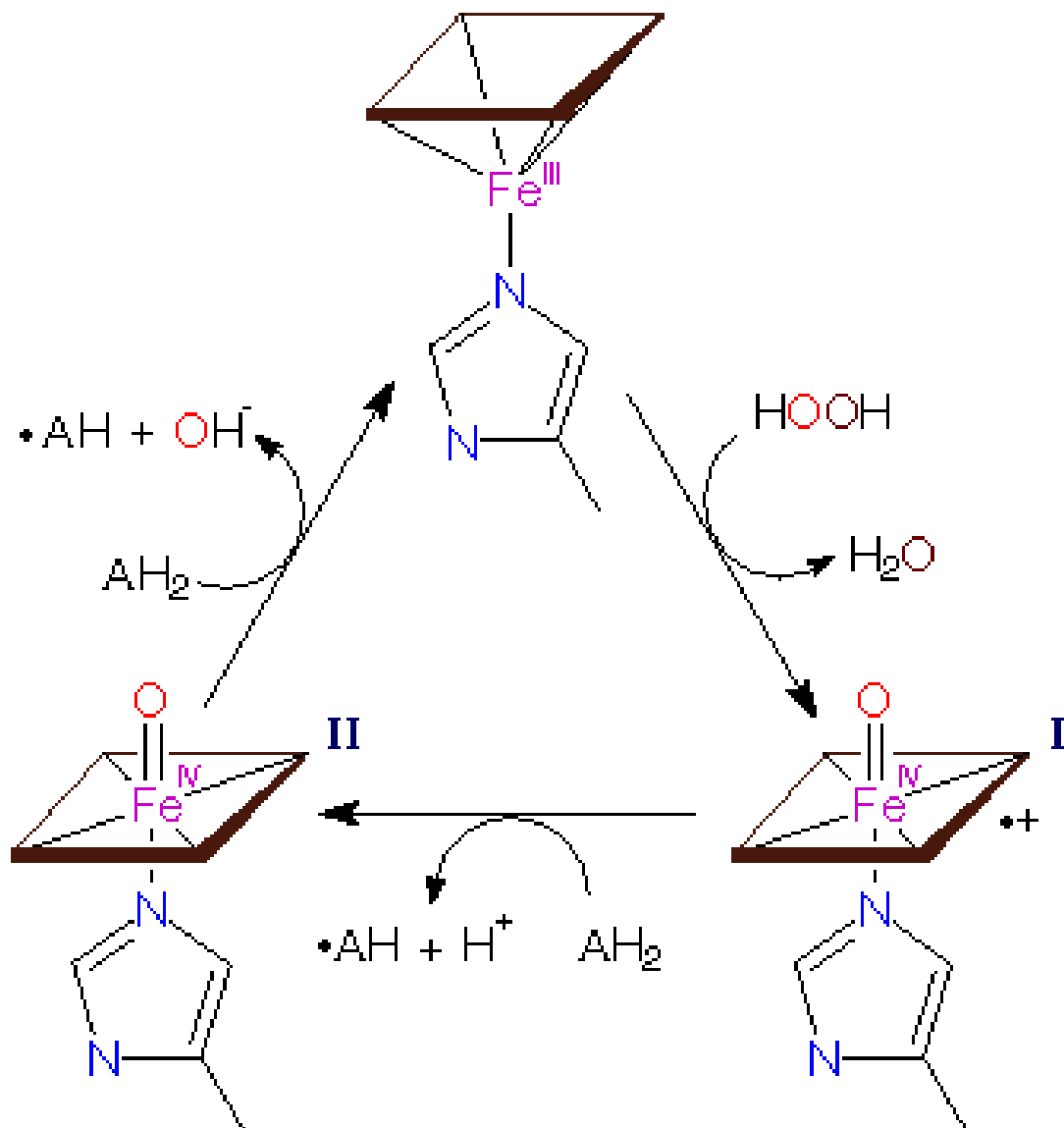
...only at low potentials!!

Published Items in Each Year



Y. Yan et al., Langmuir 2005, 21, 6560-6566

Resting enzyme



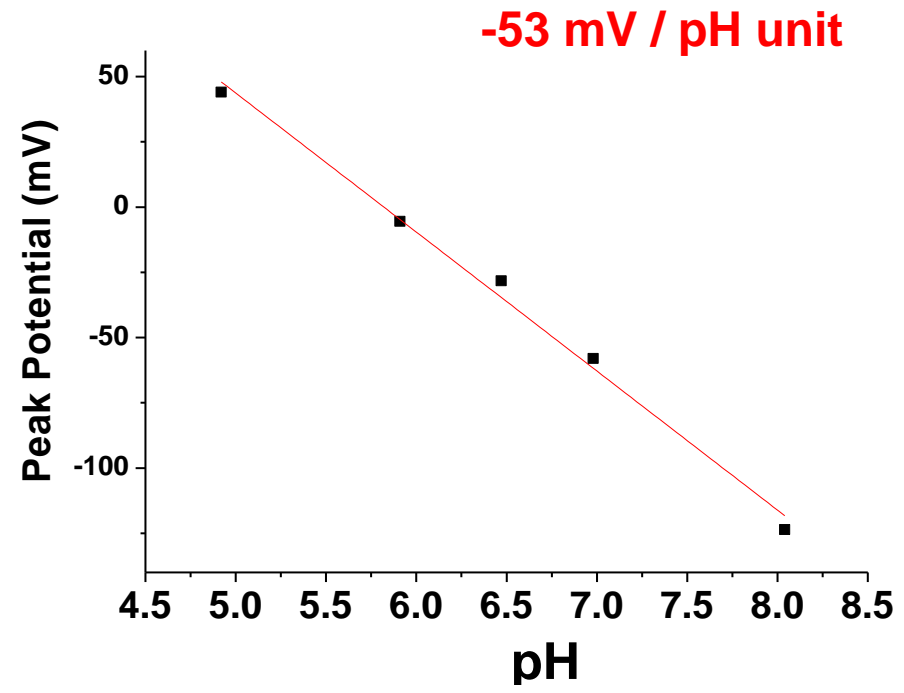
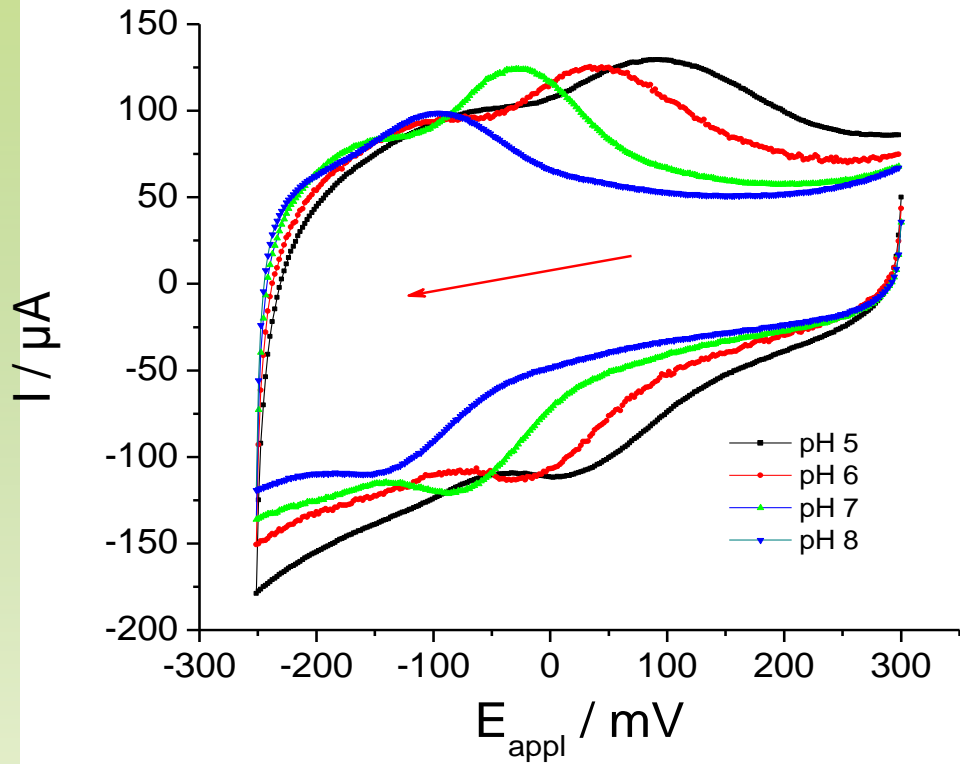
Thermodynamic potential for reduction = +750 mV

**Any**

**specific bioelectrochemistry of HRP**

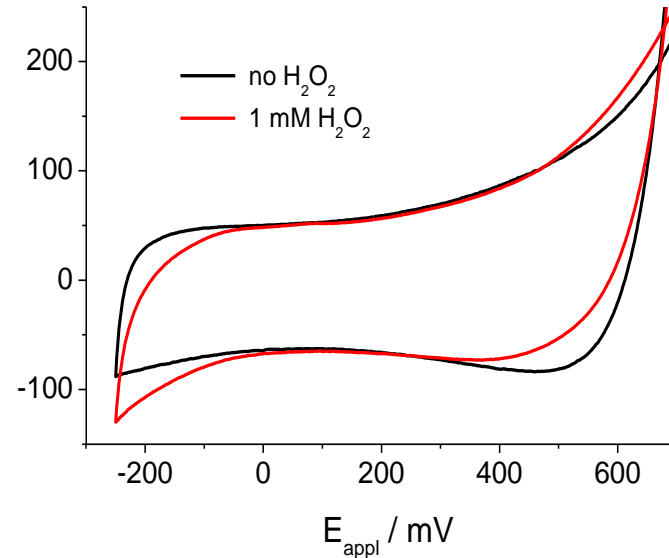
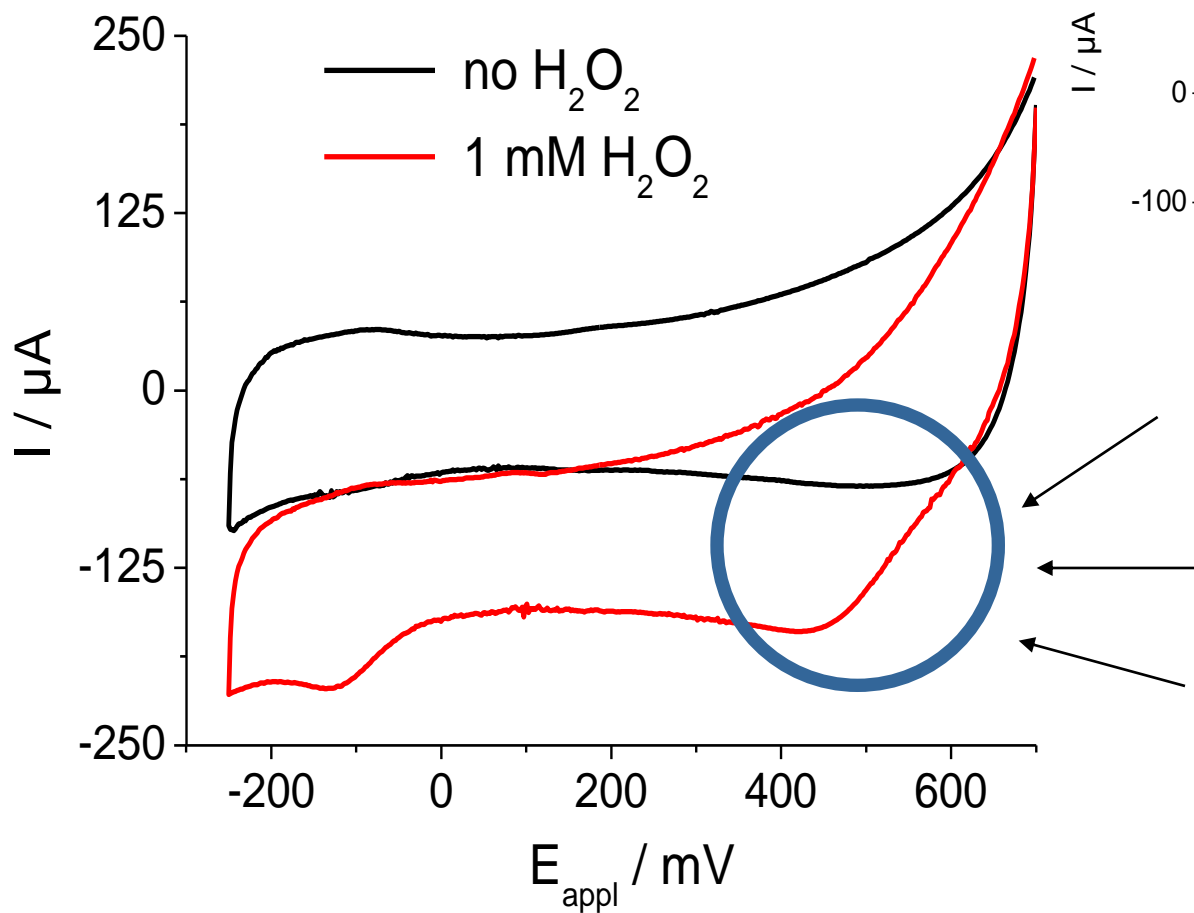
**@ these new materials?**

# Bioelectrochemistry of HRP-heme



PHA - pyrene-hexanoic acid

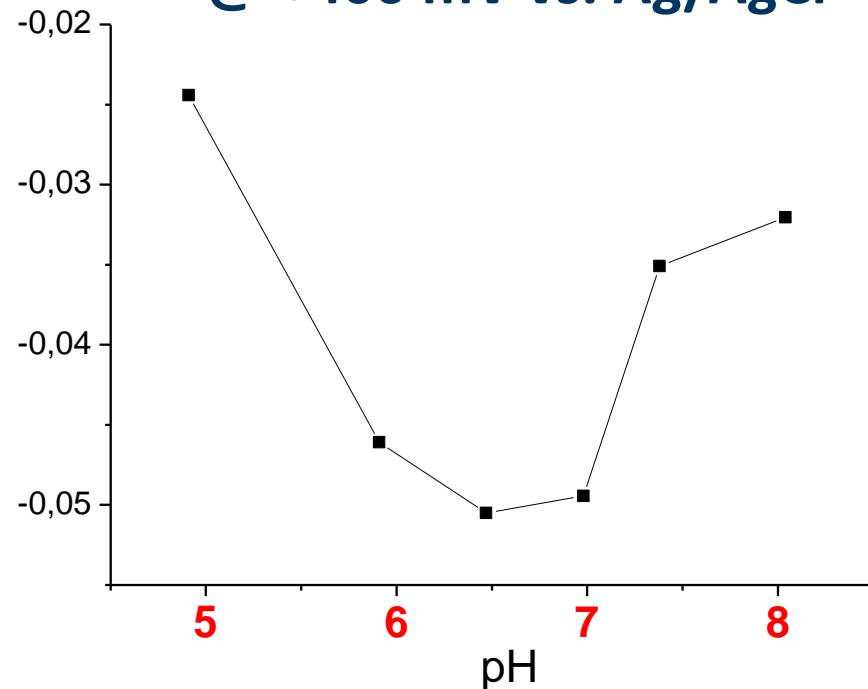
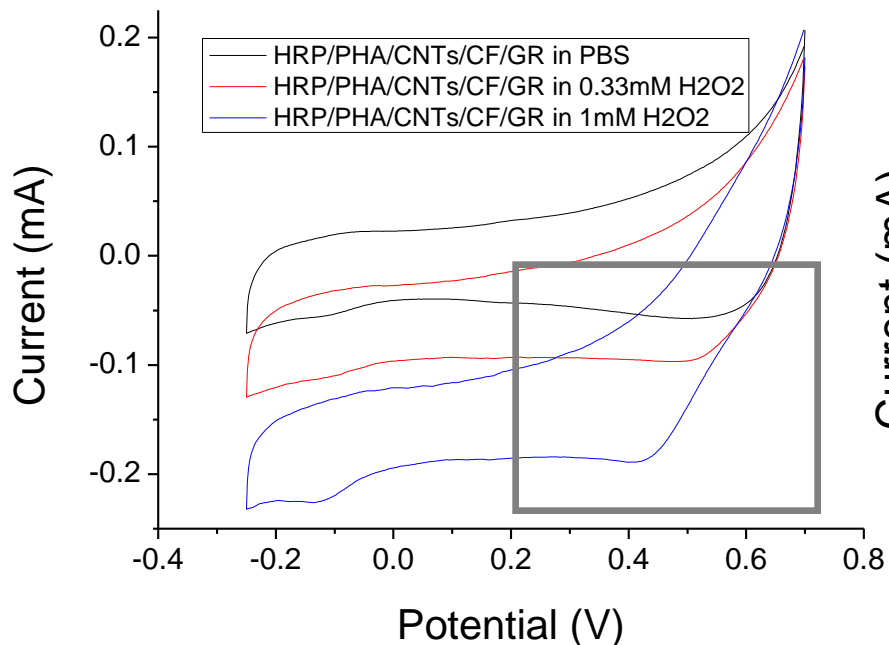
# Bioelectrocatalytic current for $H_2O_2$ reduction at +600 mV



# Bioelectrocatalytic current for $H_2O_2$ reduction at +600 mV

## Optimum pH

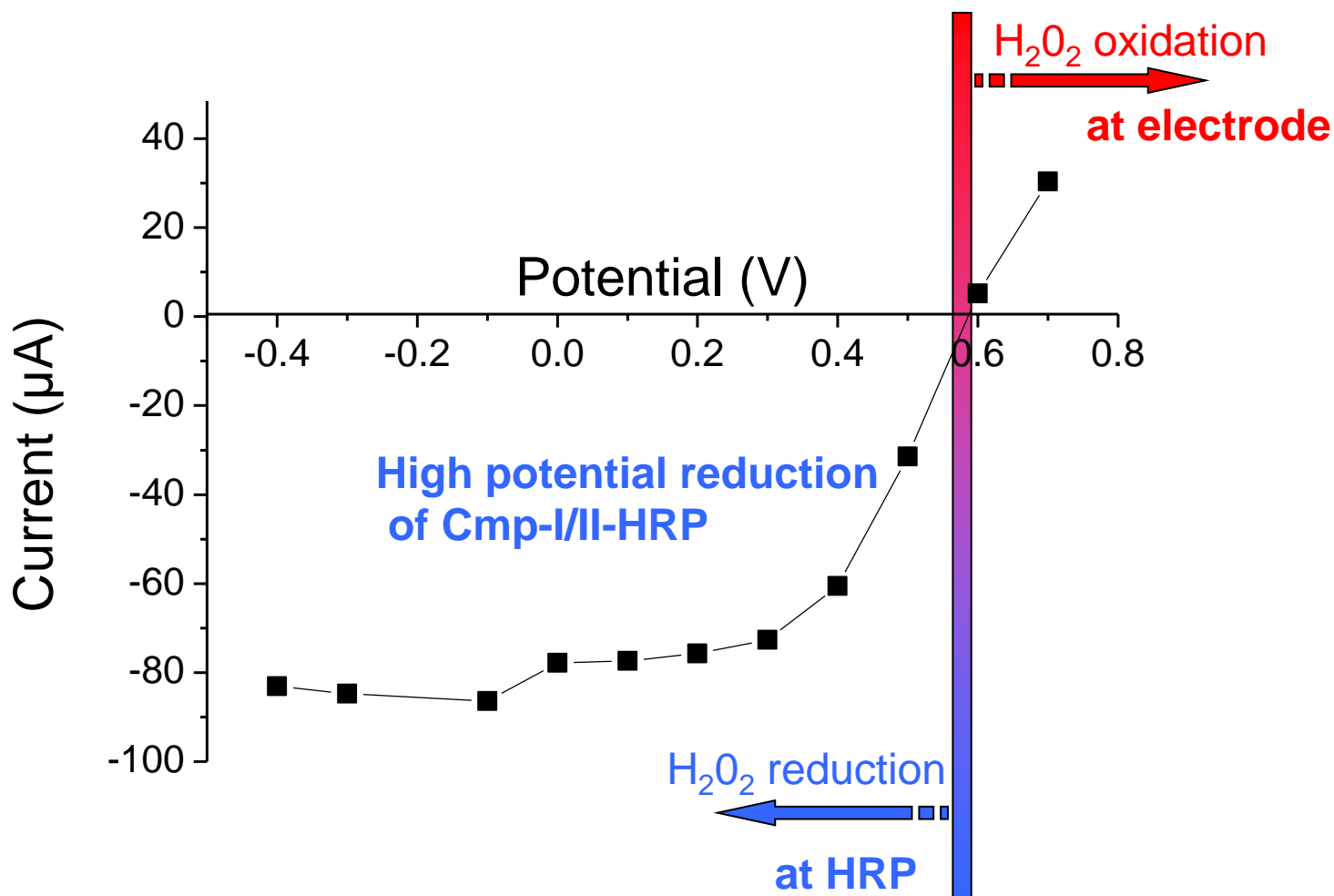
@ +400 mV vs. Ag/AgCl



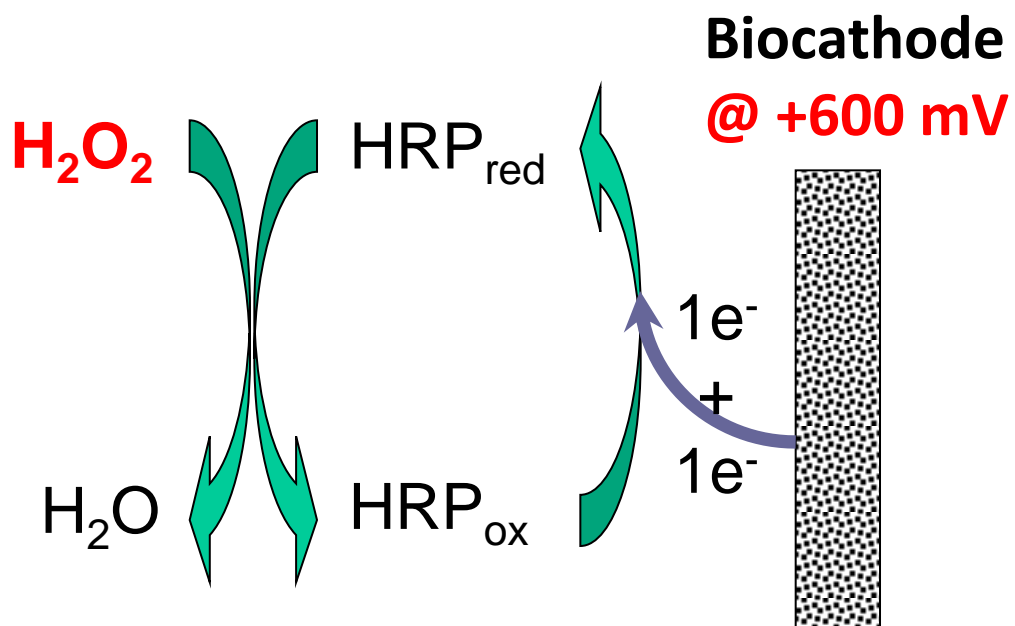
PHA - pyrene-hexanoic acid



# Hydrodynamic voltammogram



# Scheme of $\text{H}_2\text{O}_2$ involvement

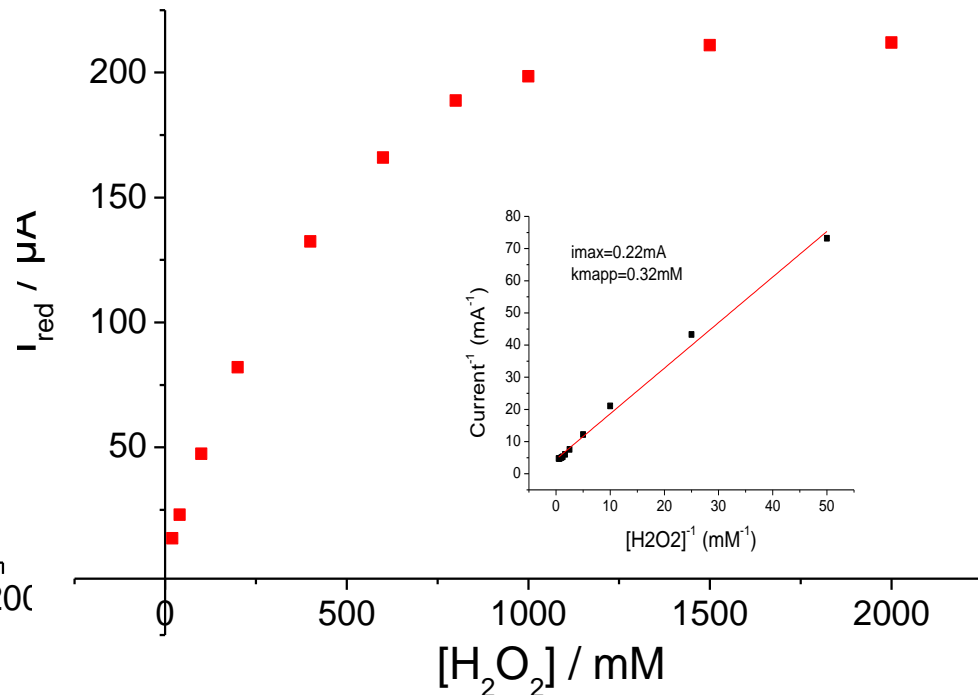
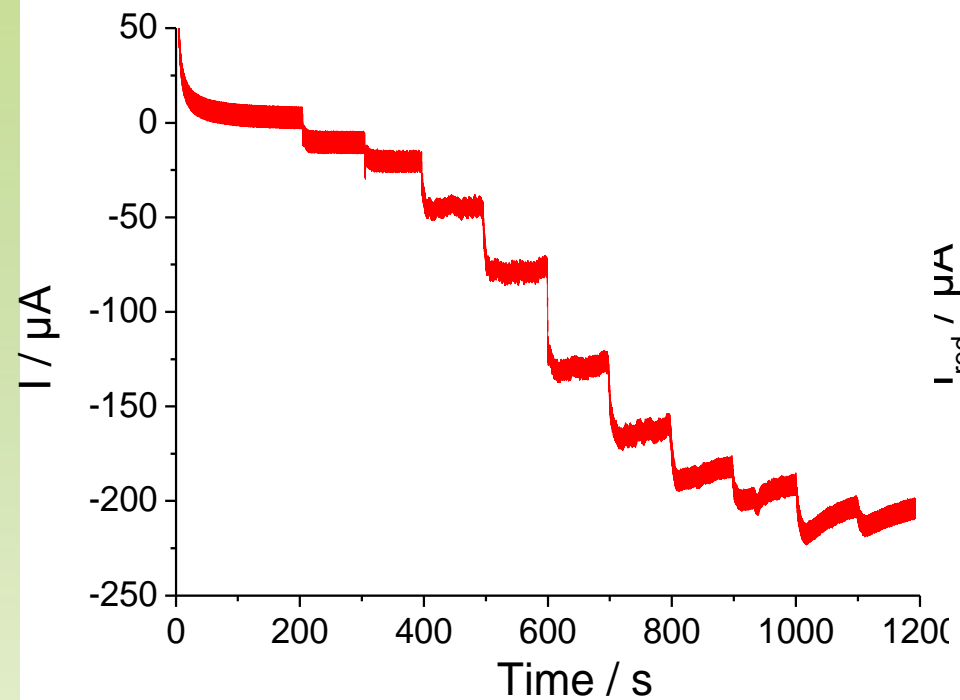


W. Jia, S. Schwamborn, C. Jin, W. Xia, M. Muhler, W. Schuhmann, L. Stoica *PCCP* **12** (2010) 10088.

# H<sub>2</sub>O<sub>2</sub> biosensor at +400 mV @ no O<sub>2</sub> involvement

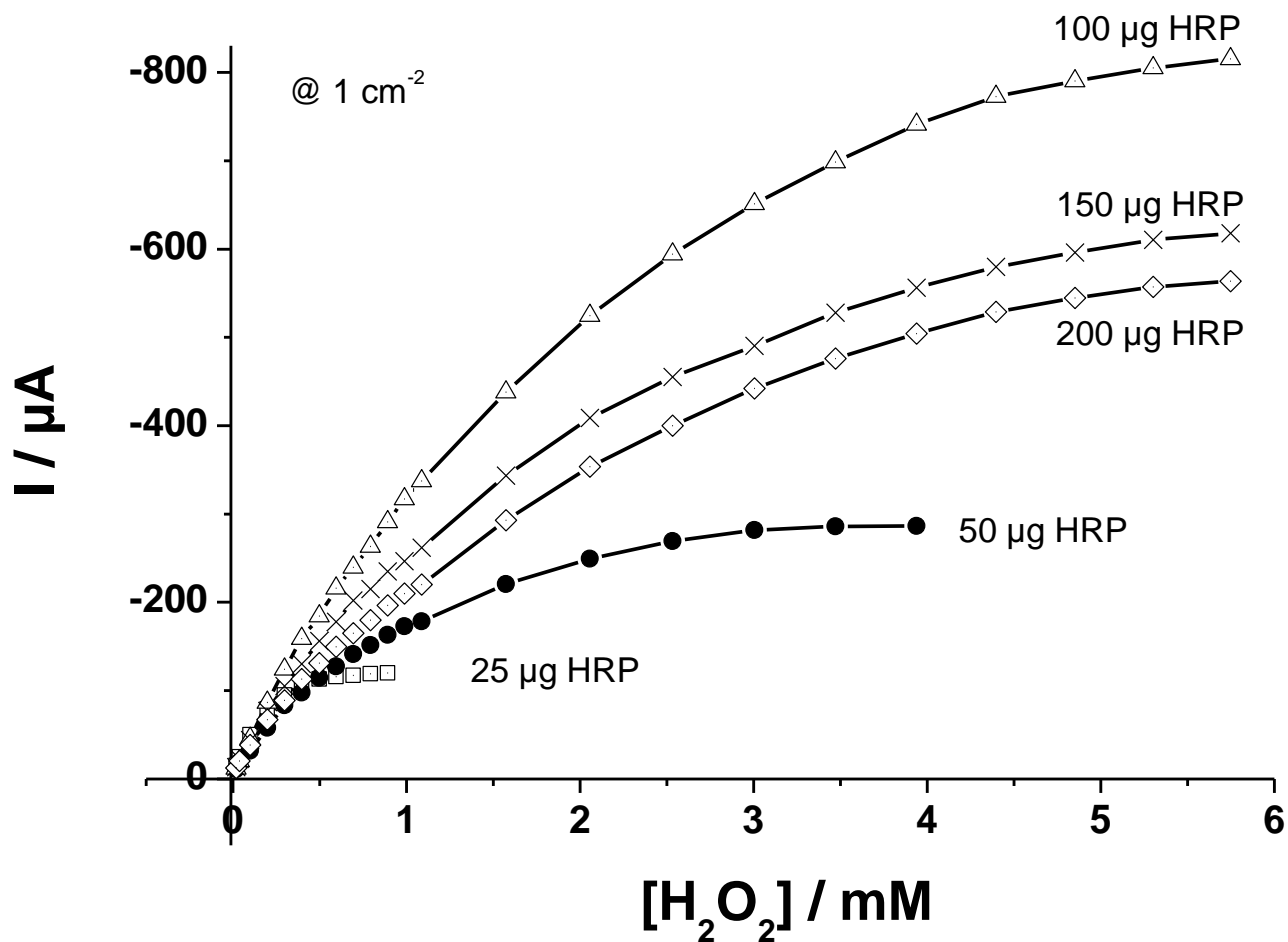
$I_{\max} = 220 \mu\text{A}$  ( $\sim 1.5 \text{ mM H}_2\text{O}_2$ )

$K_M = 320 \mu\text{M H}_2\text{O}_2$



Amperometric responses of the **HRP/PHA-CNTs/CF/GR** biosensor were recorded by additions of  $\text{H}_2\text{O}_2$  in  $\text{N}_2$ -saturated **PBS (pH 7.0) at +400 mV**

# HRP loading



$E_{\text{appl}} = +300 \text{ mV}$

# Is „glucose based cathode“ a promising candidate?

<i>Biocathodes based on...</i>	$E_{onset}$	$pH_{opt}$	$Cl^-$ inhibition	$e^- / O_2$ yield
<b>Laccase</b>	<b>+650</b>	<b>4</b>	<b>YES</b>	<b>4 e-</b>

$$P_{out} = E \times I$$

$$[E]; A; k_{cat}, n$$

$$E^{0'}$$

# Conclusions

## 3D-hierarchical carbon nanostructures:

- present excellent characteristics for large active area and enhanced/“novel” bioelectrocatalysis of known redox enzymes;

## Biocathode enzyme:

- Yes, indeed, high potential biocathode functioning on glucose/oxygen is feasible at *in-vivo* conditions (pH, Cl<sup>-</sup>)

# Acknowledgements go to...

- *EU-FP7 funds (project no. FP7-NMP-2008-SMALL-2 )*





**Thank you  
for your attention!**