



Noi biosenzori pe baza unui design rational al interfetei biomolecula-suport

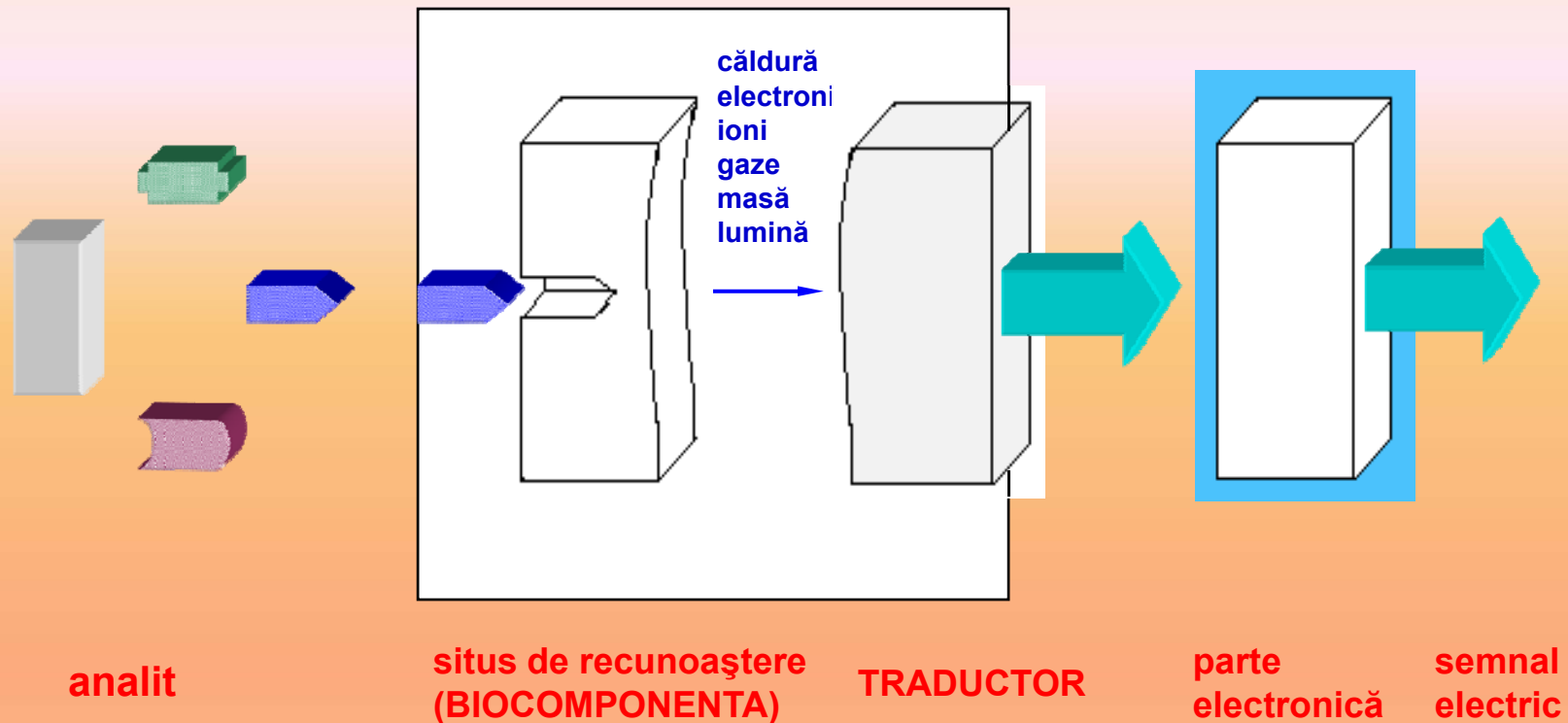
Camelia Bala

Department of Analytical Chemistry

Outlines

- ❖ **An introduction to biosensors**
- ❖ **CNT and CNF modified biosensors; food applications**
- ❖ **CNT-IL modified biosensors; environmental applications**
- ❖ **Conclusions**

Biosensors



- A **biosensor** is a **self-contained integrated device**, which is capable of providing specific quantitative or semi-quantitative analytical information using a **biological recognition element** (biochemical receptor) which is retained in **direct spatial contact with a physical transduction element**.

BIOSENSORS

```
graph TD; A[BIOSENSORS] --> B[BIOAFFINITY]; A --> C[BIOCATALYTIC]; B --> D[ANTIBODY]; B --> E[BIOLOGICAL RECEPTORS]; B --> F[DNA]; C --> G[ENZYMES]; C --> H[CELLS]; C --> I[TISSUES]
```

BIOAFFINITY

ANTIBODY

BIOLOGICAL
RECEPTORS

DNA

BIOCATALYTIC

ENZYMES

CELLS

TISSUES

Features and Characteristics of Biosensors

Targeted
Specificity



Biosensors can be designed to detect either a single analyte with high specificity or a whole group of analytes

Electronic
Processing



Data can be processed, stored, exported and displayed in many different ways

Integration into other devices allows actions to be taken automatically

Continuous
Measurement



Immediate remedial actions are possible in fields such as medical diagnostic and industrial process control

Selected measurement
in complex samples



Sample may not need preparation prior analysis

Direct measurements in blood, foods, waste water, etc. are possible

Fast
measurement



Waiting times for test results
acceptably short

High sample through-put can
be achieved in automated
analysers

Small size

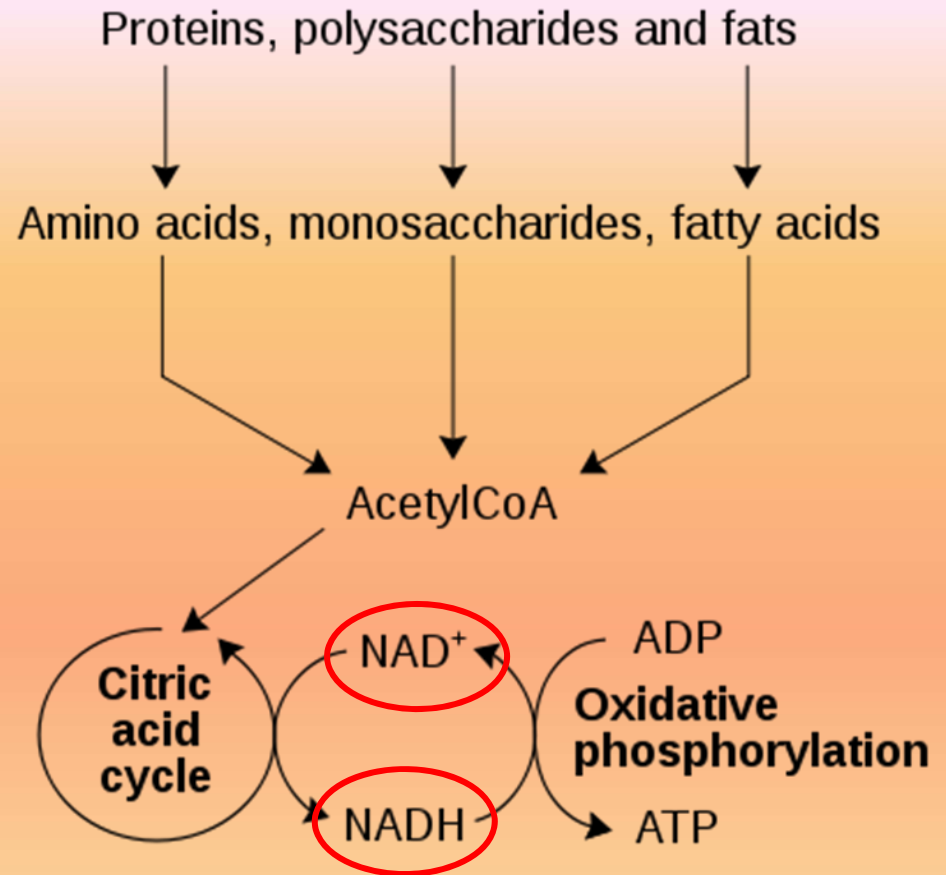
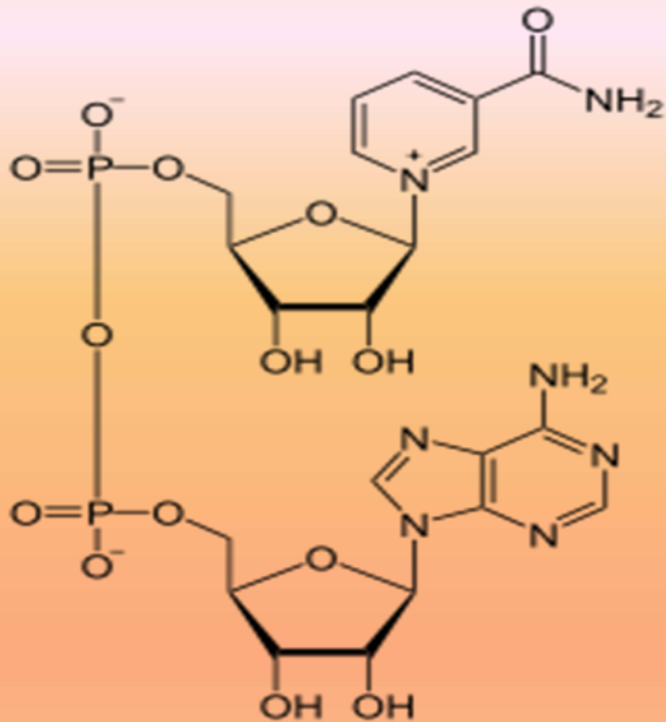


Compact designs for “field
use” are possible

Use in confined places such
as needles and catheters *in
vivo* is possible

Can measure multiple
analytes in a small sample

Nicotinamide Adenine Dinucleotide

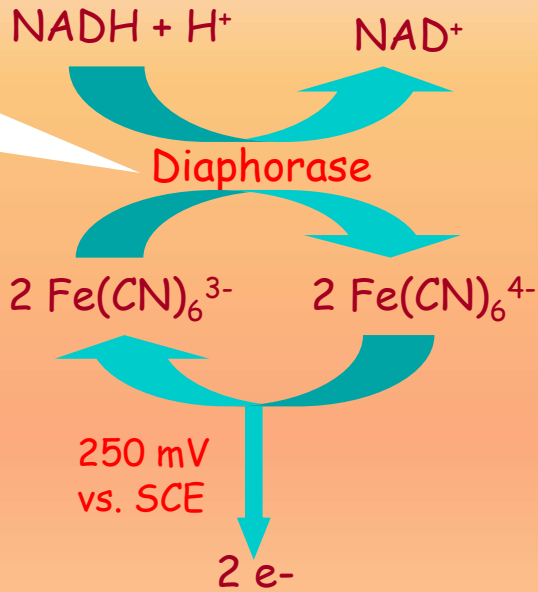


- coenzyme found in all living cells.
- natural carriers of electrons;
- participate to redox processes in cells;
- act as coenzymes for ~500 oxidoreductases

Redox metabolism

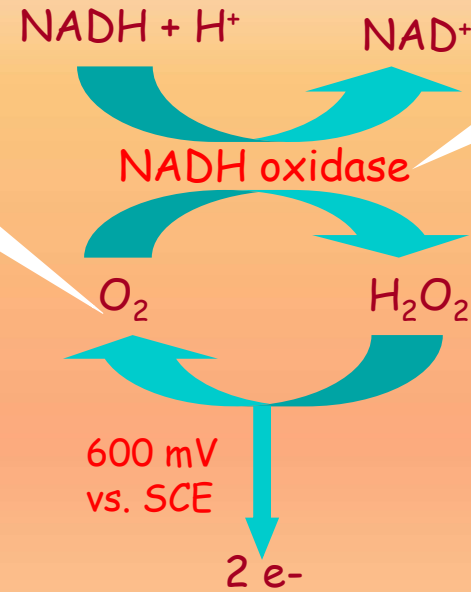
DH-BASED BIOSENSORS

Commercially available
Low cost



Low stability of diaphorase
Necessary addition of
ferricyanide in the medium

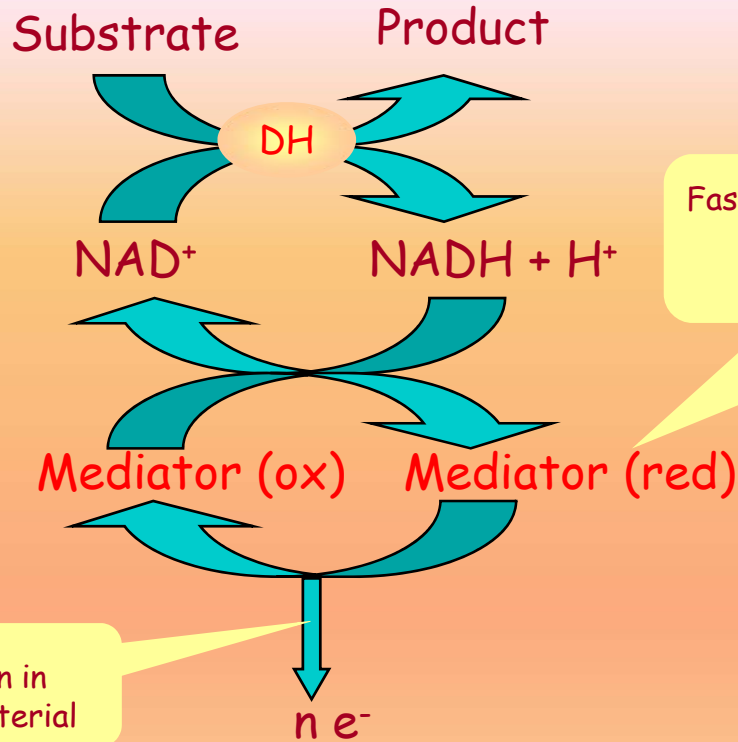
No additional mediator



High stability

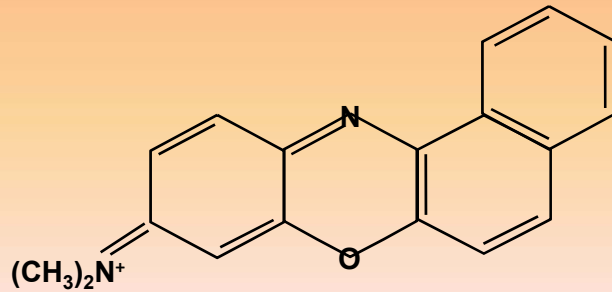
High overvoltage for H_2O_2 oxidation

DH-BASED BIOSENSORS

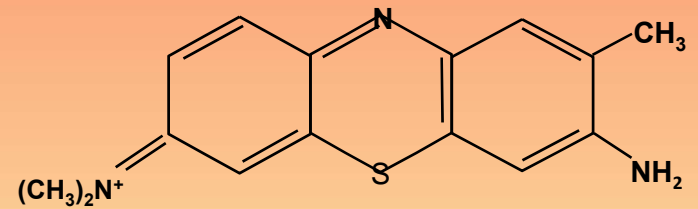


Fast electron transfer rate with NADH

Low incorporation in the electrode material



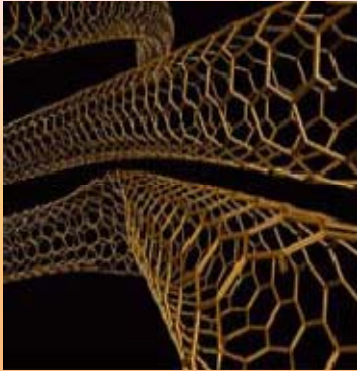
Meldola Blue



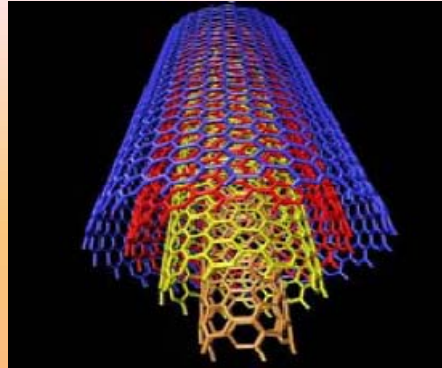
Toluidine Blue

Carbon Nanotubes (CNT)

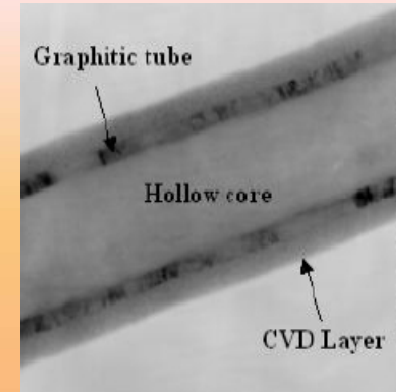
SWCNT



MWCNT



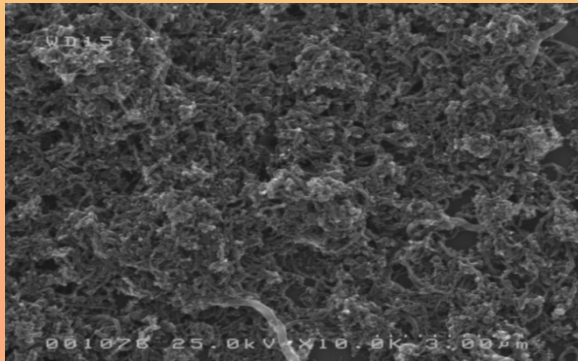
CNF



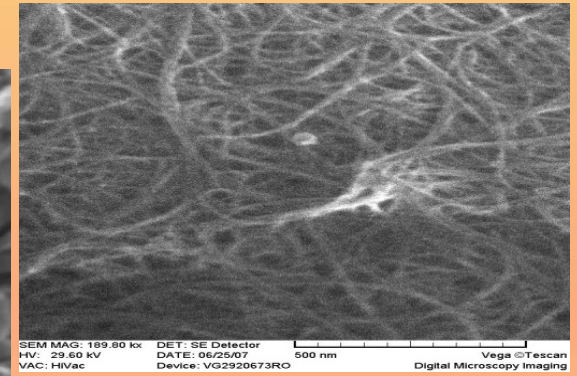
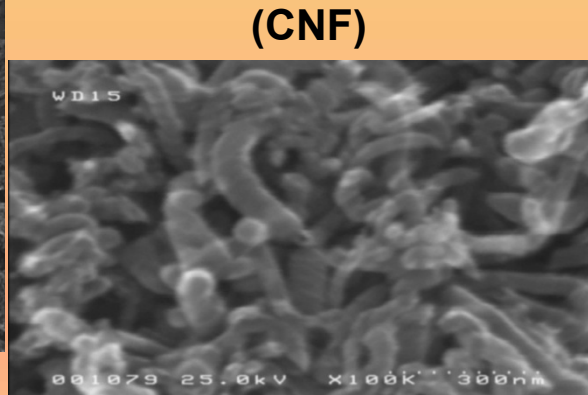
- High surface area
- High electrical conductivity (six orders of magnitude higher than copper)
- Good chemical stability
- Can be easily functionalized through the attachment of other chemical groups (the functionalization takes place at ends cap and defects existing on the wall)
- Can be easily assembled in different composite matrices or pastes

NADH oxidation using carbon nanofibers and nanotubes based sensors

- Morphologic characterization of carbon nanofibers/nanotubes layer



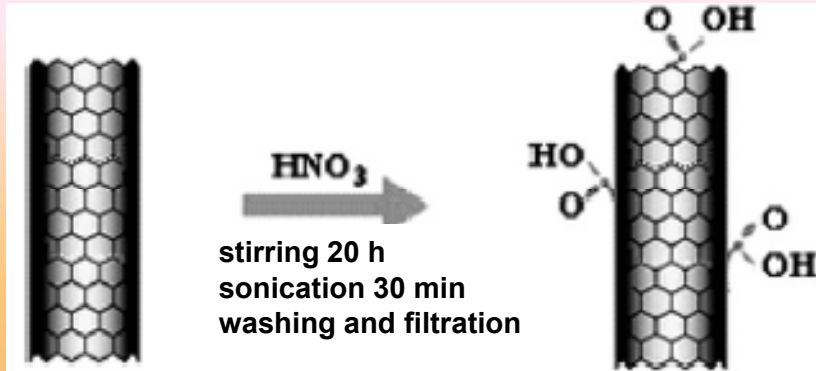
(CNF)



(SWNT)

Improving the sensitivity and selectivity

• Modification of CNT by oxidation

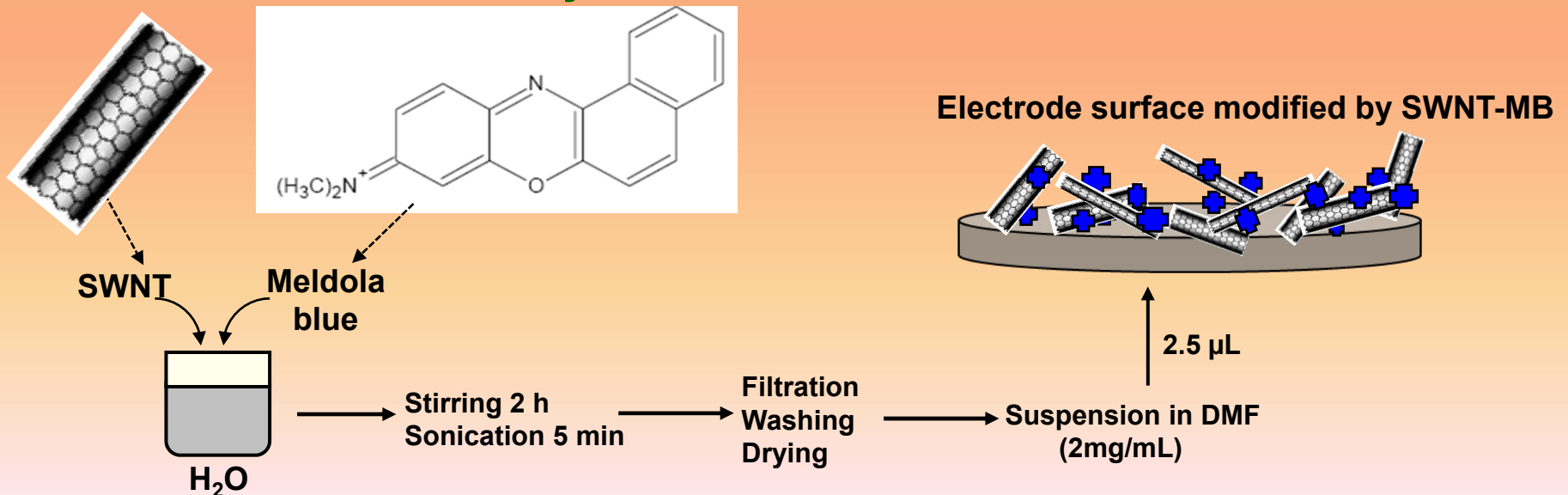


- ✓ Oxidation peak of NADH shifts to lower value for oxidized SWNT (from 300 mV to 220 mV)
- ✓ Specific sensitivity: $67.46 \text{ mA/M} \times \text{cm}^2$
- Linear range: 0.015 - 2.5 mM
- Limit of detection: $12 \mu\text{M}$ (S/N=3)

inferior to those of GC electrode modified with untreated SWNT

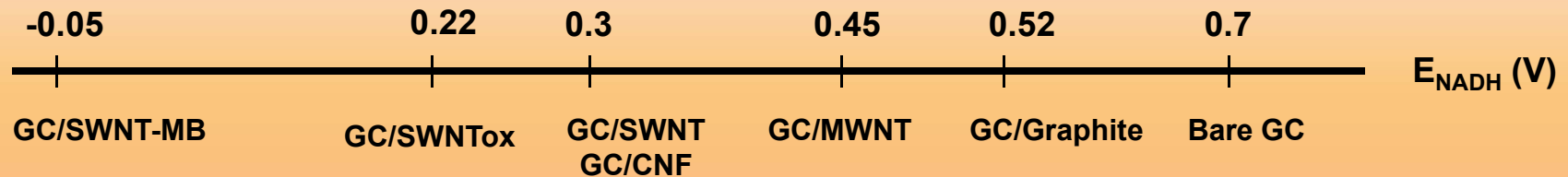
➡ The decrease of oxidation potential by only 80 mV is not sufficient to eliminate the interference of easily oxidable compounds

• Modification of CNT by redox mediator



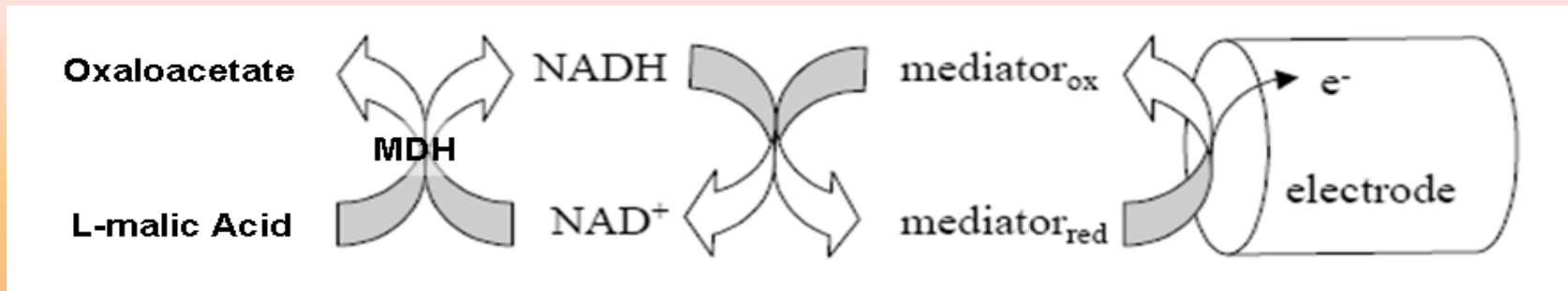
Benefits

- By modifying the glassy carbon electrode with CNF and CNT (treated or untreated) is possible to obtain a porous surface, able to oxidize the NADH cofactor at lower potential values



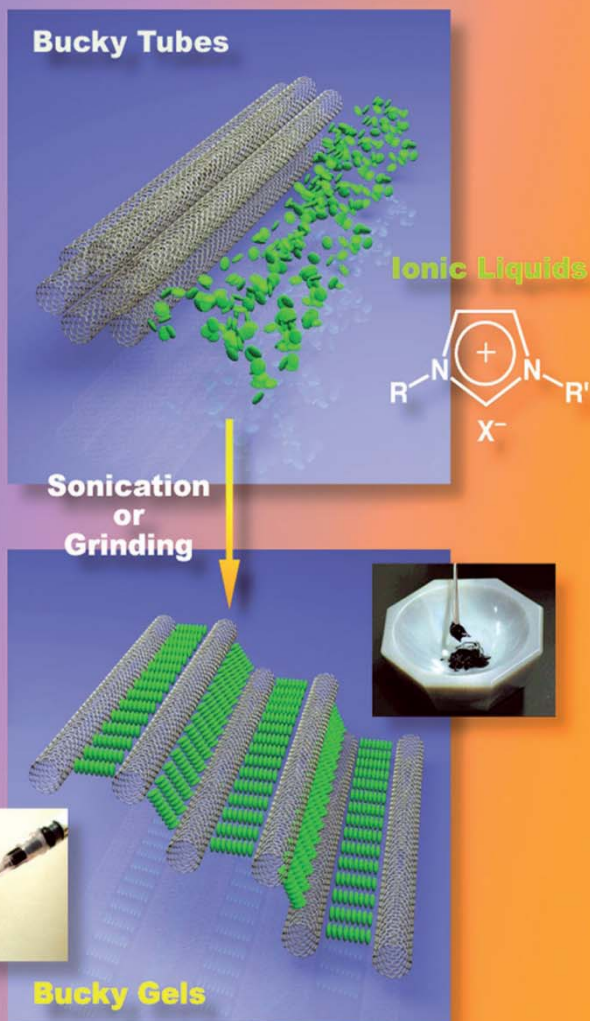
- Increased sensitivity
- Shorter response time
- Smaller limits of detection
- Good stability
- Functionalization of SWNT with redox mediator totally eliminates the interferences
- Improved detection of NADH could offer a great possibility to assemble low-potential biosensors based on dehydrogenases for important substrates detection.

Low-potential detection of malic acid with SWNT-MB



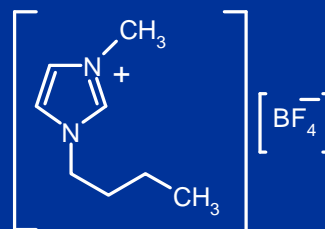
- L-malic acid - predominant acid in many fruits**
- serves as principal indicator of fruit maturity**

Carbon Nanotubes Encounter Ionic Liquids to Create New Soft Materials

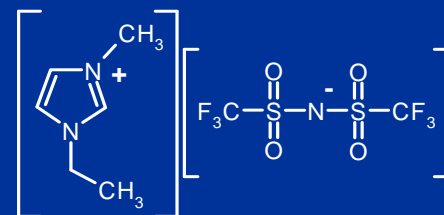


Imidazolium-ion-based Ionic Liquids

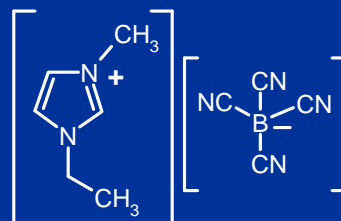
- electrical conductivity
- electrochemical stability
- dispersants for CNTs



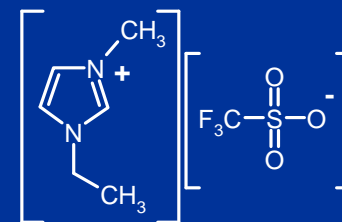
[BMIM][BF₄]



[EMIM][NTF₂]

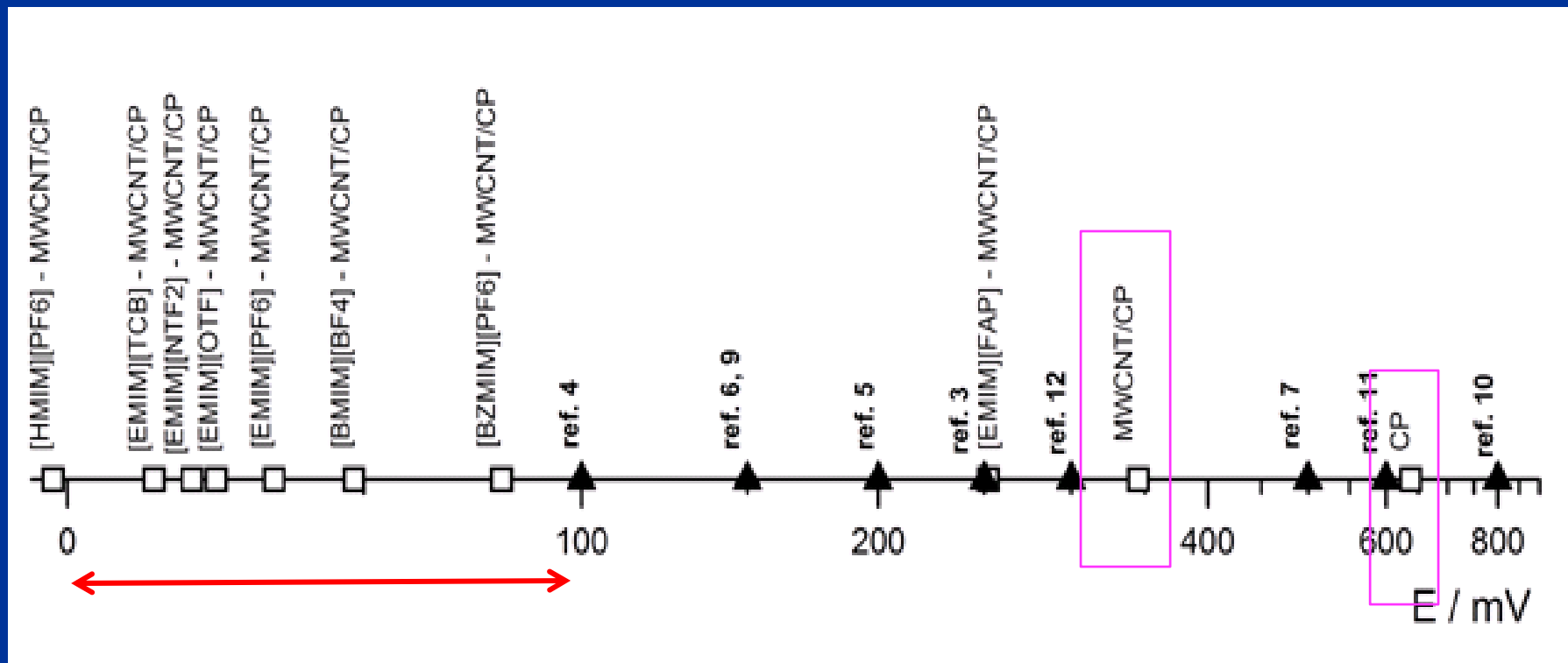


[EMIM][TCB]



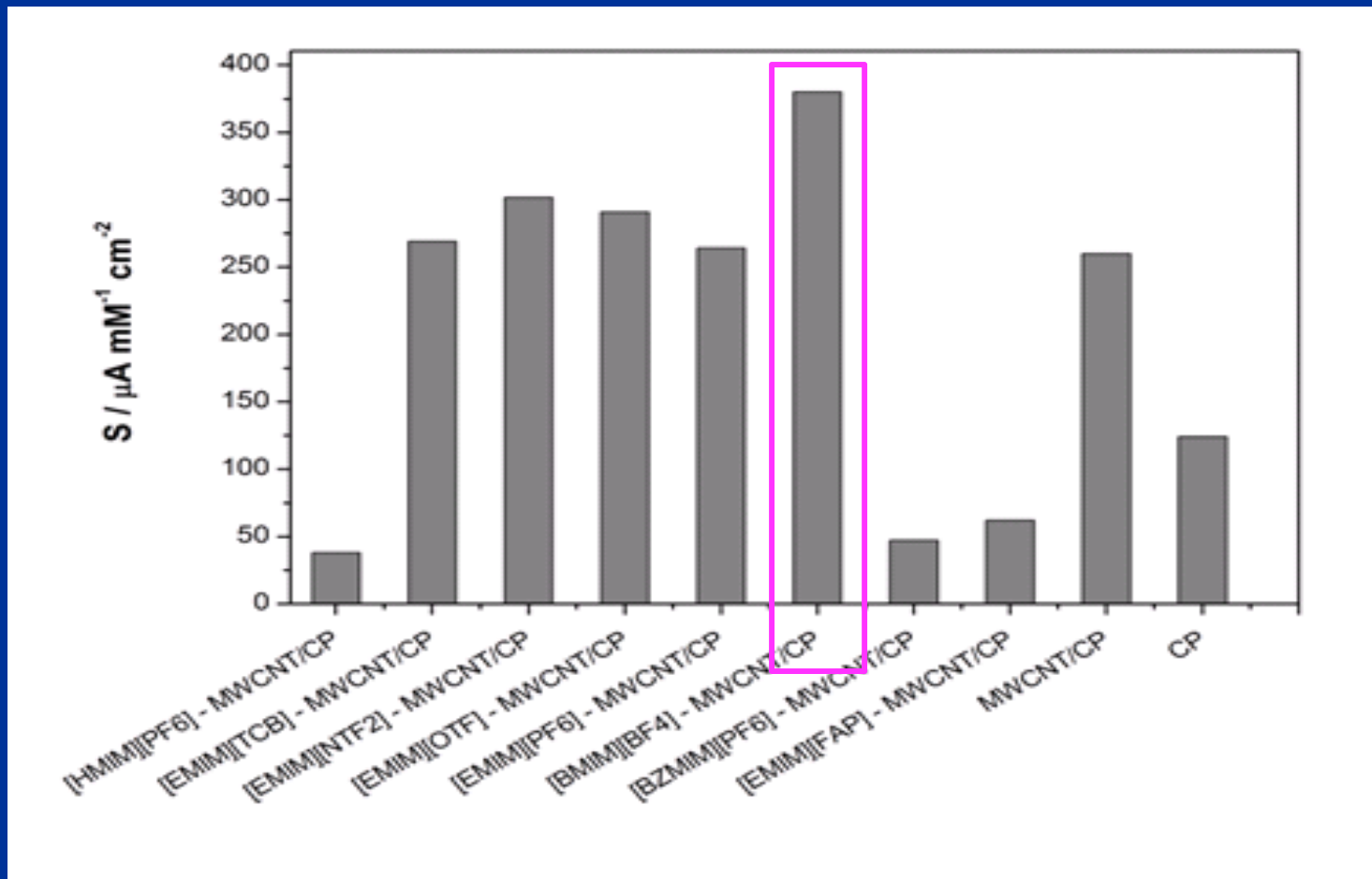
[EMIM][OTF]

Main characteristics of thiocholine sensors



(A) Thiocholine oxidation potential for IL-MWCNT based sensors and other reported sensors;

Main characteristics of thiocholine sensors



B) Sensitivity of the thiocholine sensors

Four gel modified electrodes present better sensitivity compared with MWCNT/CP electrode, the highest being obtained with [BMIM][BF₄]-MWCNT gel

Conclusions

- Analytical parameters of biosensors (limit of detection, linear range, stability) were improved through optimization of the immobilization matrix of enzyme.
- The functionalization of SWNT with redox mediator results in significant improvement for analytical characteristics of developed biosensor.
- Amperometric biosensors developed were used for simple and fast determination of some analyts.
- Sensitivity can increase due to better conduction properties, the limits of detection can be lower, very small quantities of samples can be analysed, direct detection is possible without using labels, and some reagents can be eliminated.