ET-1039: Nanotechnology

UNIVERSITAT JAUME•I

Chapter 4: Applications with organic, inorganic and hybrid materials

4.1 solar cells

4.2 Photocatalysis

4.3 electronic and optoelectronic devices

4.4 biosensors & enzymatic fuel cells

4.5 Batteries and supercapacitors

4.6 Graphene

4.7 Piezo electrics

4. Applications with organic, inorganic and hybrid materials

4.4 Sensors

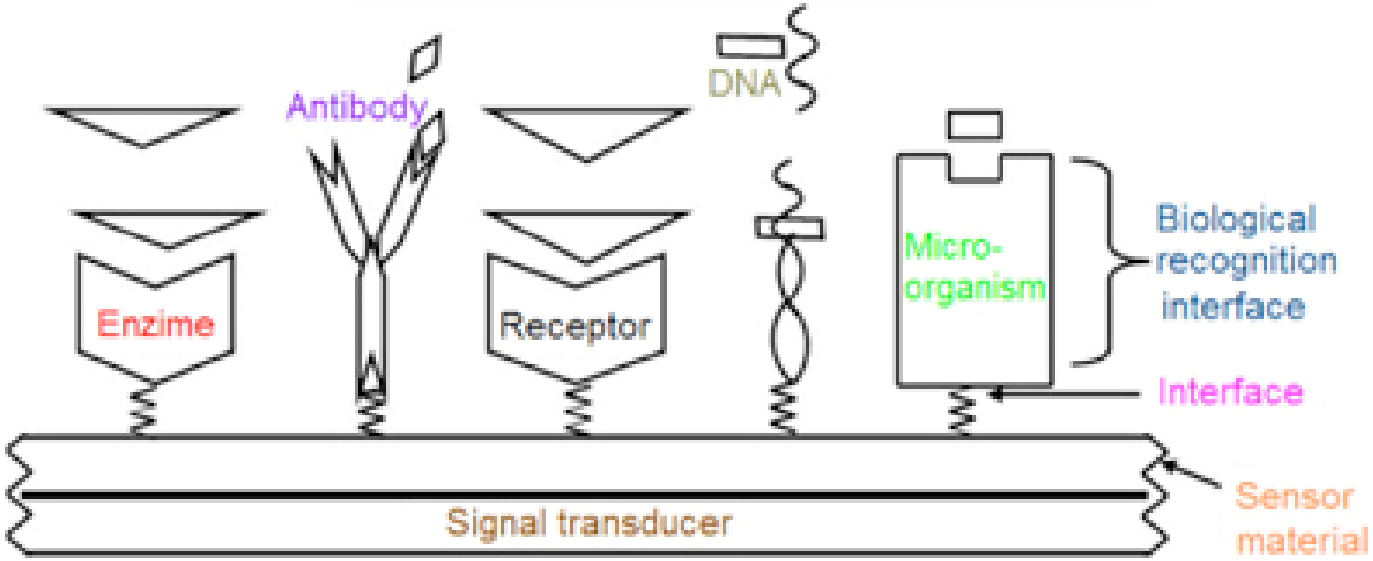


Figure 1. Schematic representation of nanobiosensor components (modified from Topal).[20]

J. Braz. Chem. Soc. vol.23 no.1 São Paulo Jan. 2012
http://dx.doi.org/10.1590/S0103-50532012000100004

4. Applications with organic, inorganic and hybrid materials

4.4 Sensors

Enzimatic sensors:

Enzymes are molecules designed to produce (catalize) a specific chemical reaction.

i.e. Glucose oxidase oxidizes Glucose to obtain high energy electrons and produce protrons which later on will be used in cell metabolic reactions. In other words, this is a reaction that basically provides energy to living cells.

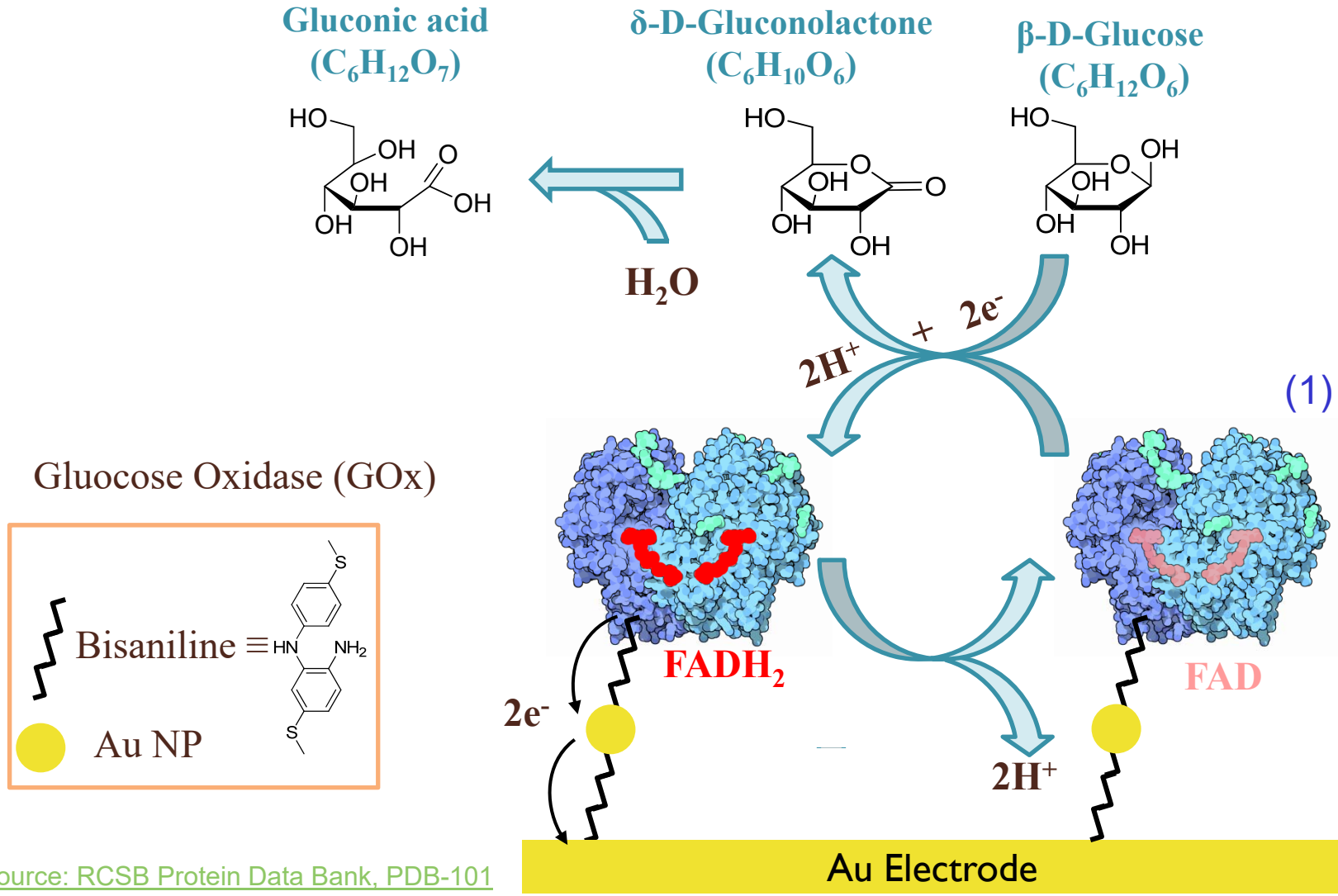
Fixing glucose oxidase to a conducting electrode, both glucose sensors and enzymatic fuel cells may be obtained.

How it works: When glucose hits a glucose oxidase enzyme it is directed and positioned upon one of its active centers (FAD) . The FAD takes 2 protons and 2 electrons (2 hidrogen atoms) from glucose that is transformed into glucolactone. If Glucose oxidade is wired to an electrode, we can extract these electrons (obtaining current), and the FAD delivers the two protons to the solution, so that it can start again. The current obtained is proportional to the amount of glucose in the solution.

In enzymatic fuell cells, the protons are combined with oxigen at a cathode with another enzyme (Lacasse) to complete the cycle.

4. Applications with organic, inorganic and hybrid materials

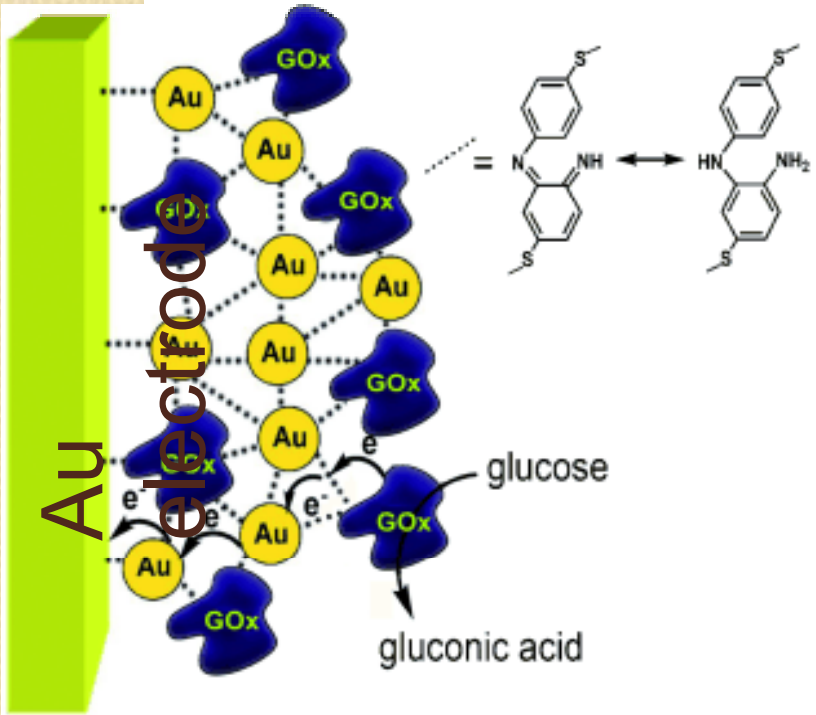
4.4 Sensors

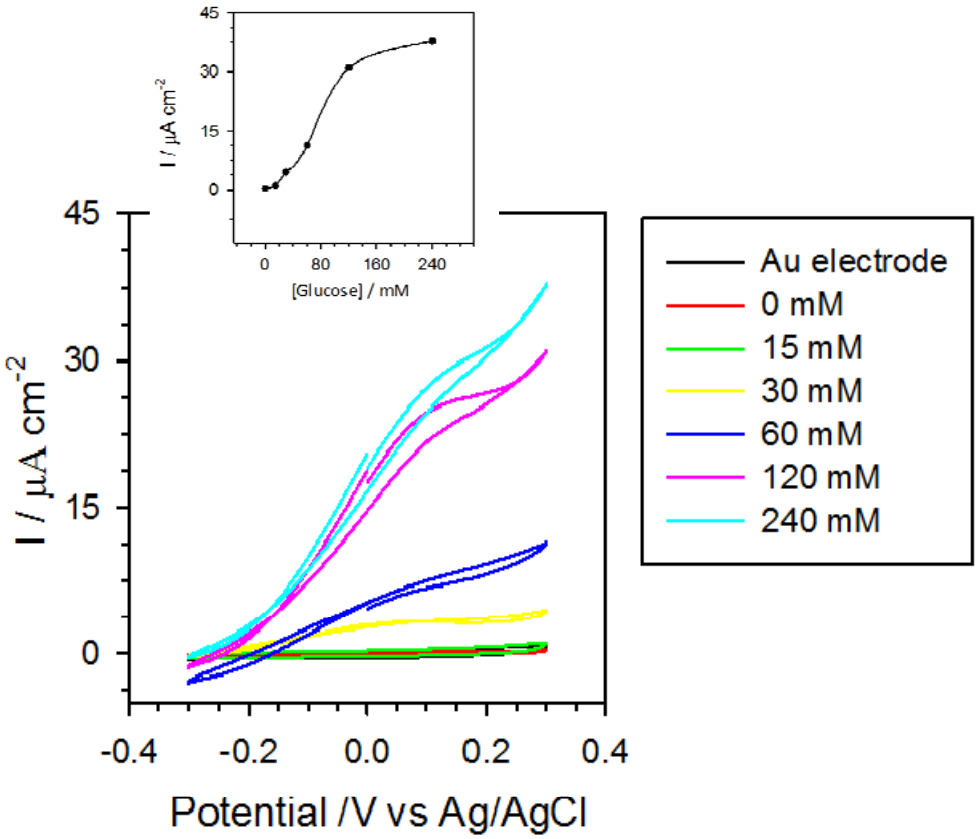


(1) Image Source: RCSB Protein Data Bank, PDB-101

4. Applications with organic, inorganic and hybrid materials

4.4 Sensors





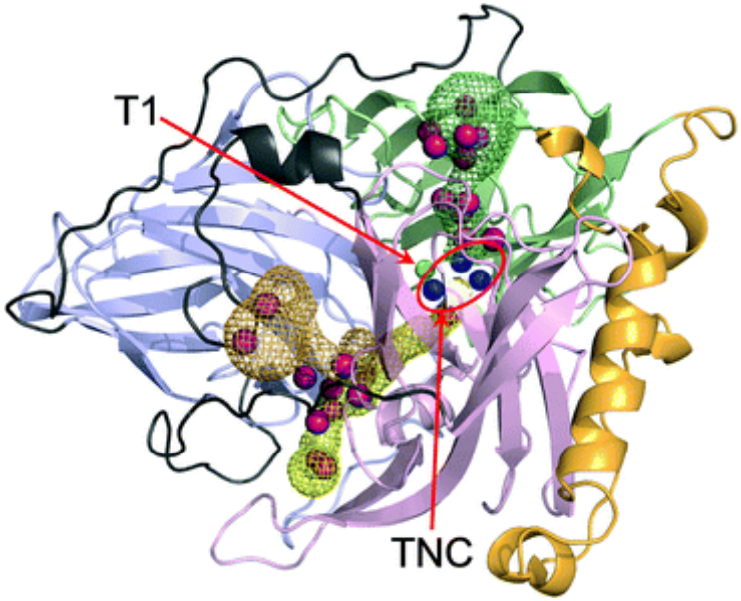
Cejudo et al. To be published

4. Applications with organic, inorganic and hybrid materials

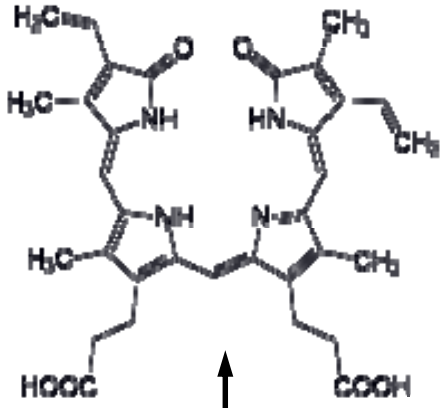
4.4 Sensors

$C_{33}H_{34}N_4O_6$ (biliverdina)

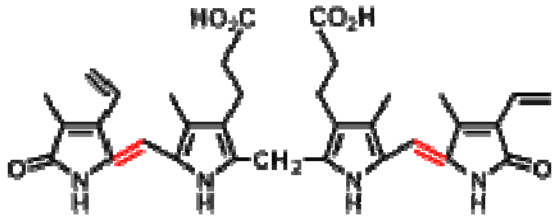
Bilirubina oxidasa (BOD)



H_2O +



½ O_2



$C_{33}H_{36}N_4O_6$ (Bilirubina)

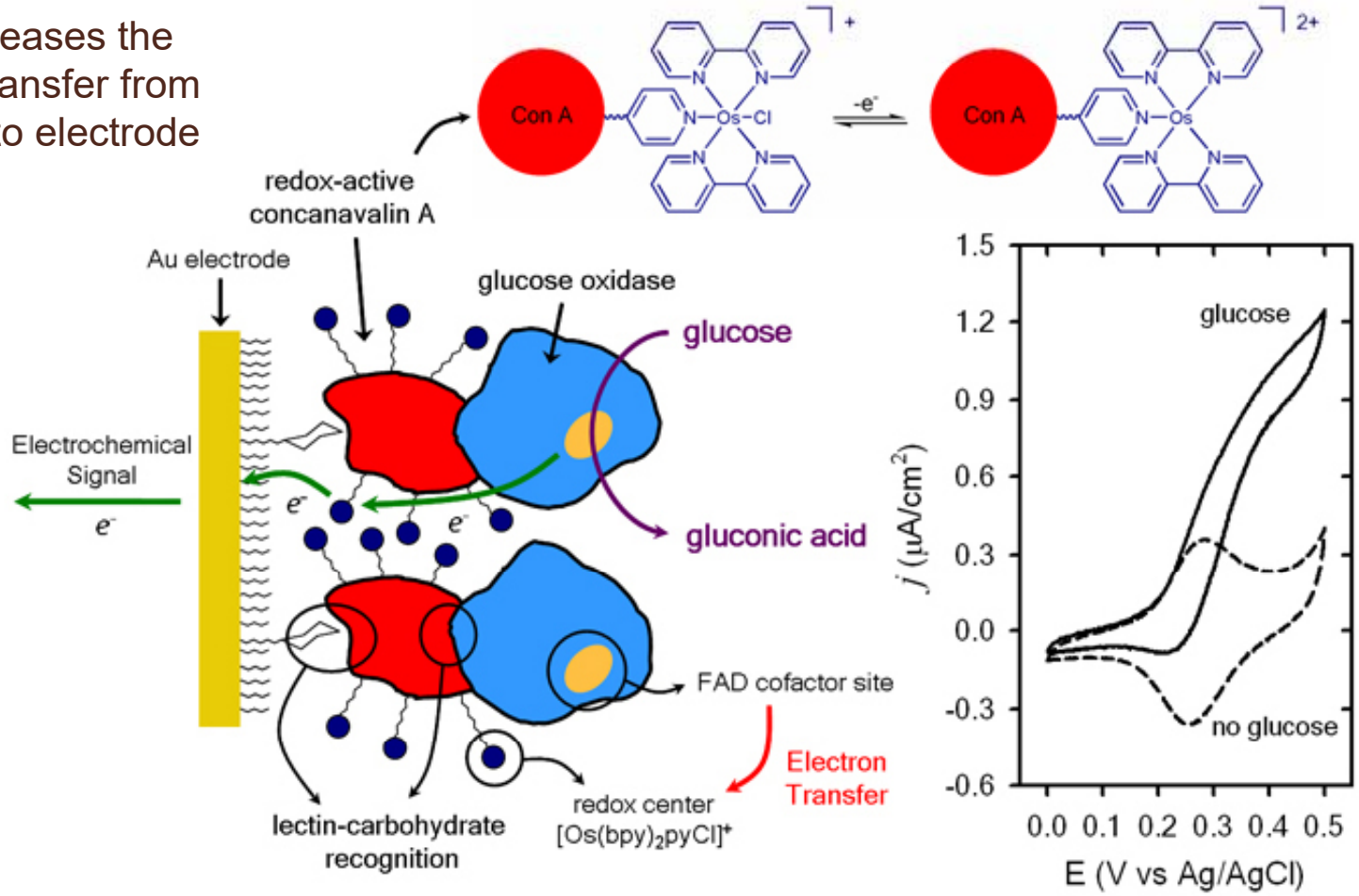
Cracknell et al. Dalton Trans., 2011 **4, 40**, 6668-6675

4. Applications with organic, inorganic and hybrid materials

4.4 Sensors

Osmium based Glucose sensors

Osmium eases the charge transfer from enzyme to electrode

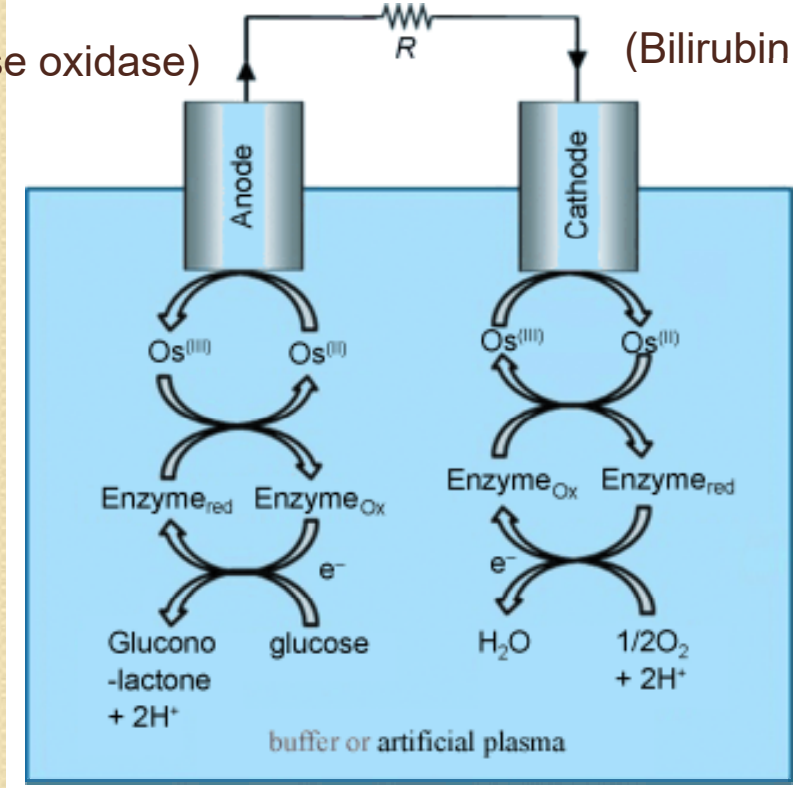


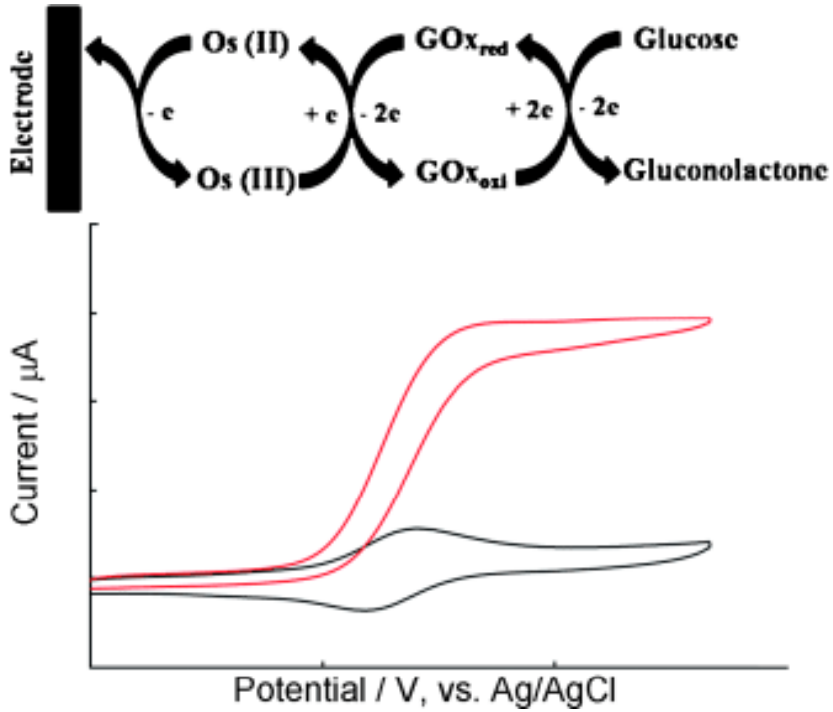
4. Applications with organic, inorganic and hybrid materials

4.4 Sensors

(Glucose oxidase)

(Bilirubin oxidase)

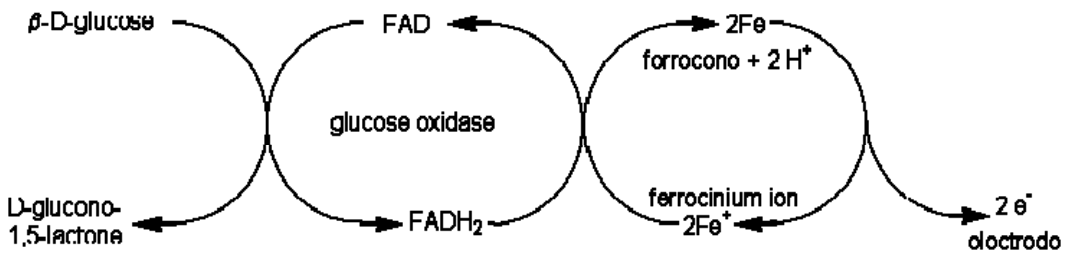


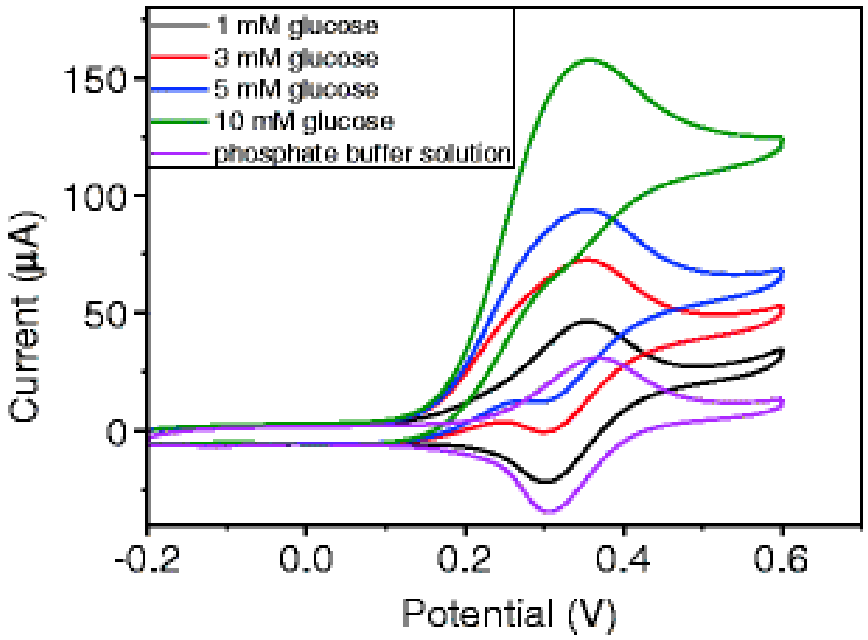


ChemPhysChem (2013) 14, 2302–2307 & 2343–2347

4. Applications with organic, inorganic and hybrid materials

4.4 Sensors



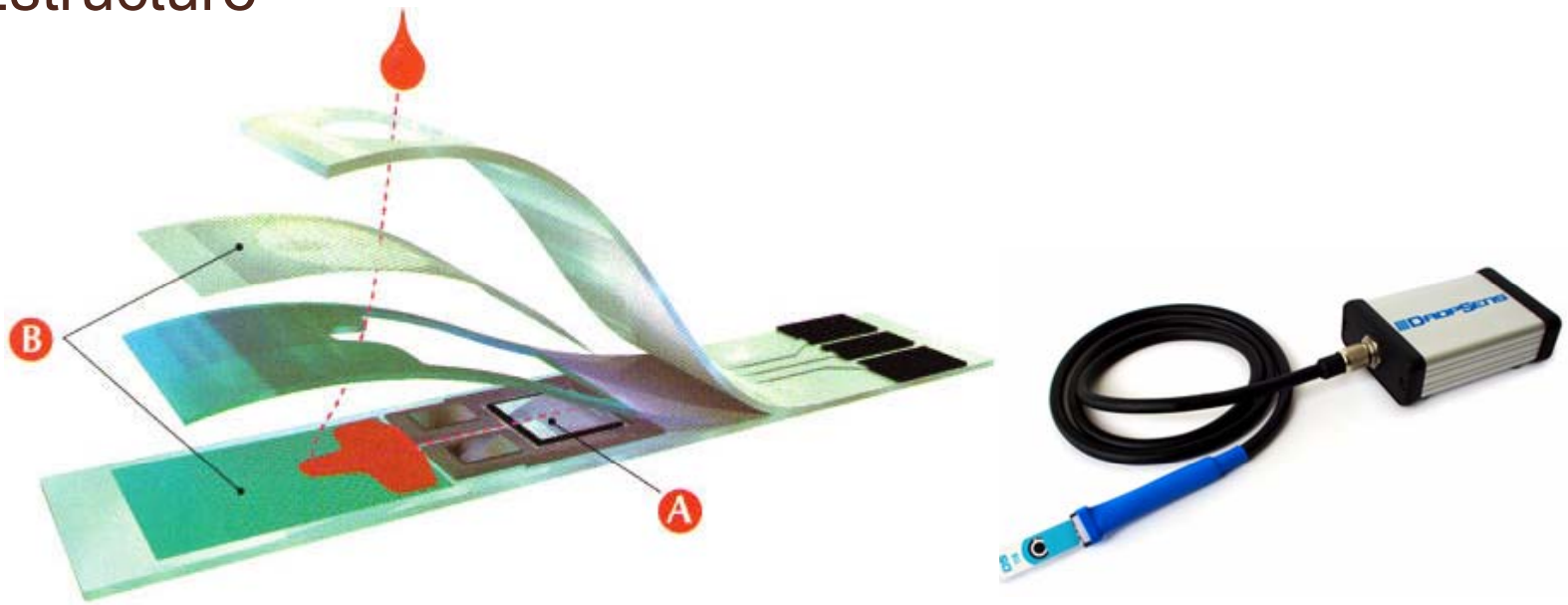


Microchimica Acta 2011, 174, pp 281-288

4. Applications with organic, inorganic and hybrid materials

4.4 Sensors

Estructure



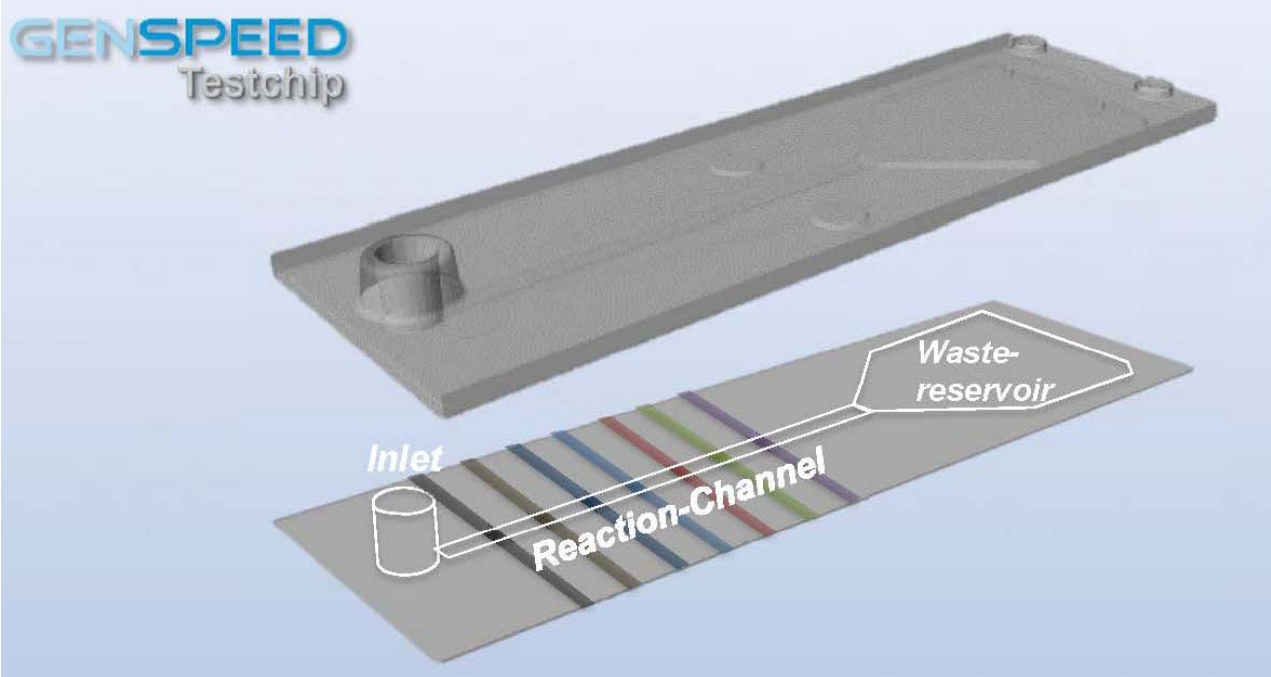
Cross section of a commercial strip for self-testing of blood glucose (based on the Precision biosensor manufactured by Abbott Inc.): (A) electrode system; (B) hydrophobic layer (drawing the blood)

J. Wang, Chemical Reviews, 2008, **108**, 814 − 825
http://www.dropsens.com

4. Applications with organic, inorganic and hybrid materials

4.4 Sensors

Estructure



- Microfluidic top part is bonded to plastic foil
- Microfluidcs with *Inlet – Reaction channel – Waste reservoir*
- Core: Reaction channel with 7 different - analyte specific- reaction sites
- Waste-reservoir also serves as capillary pump

4. Applications with organic, inorganic and hybrid materials

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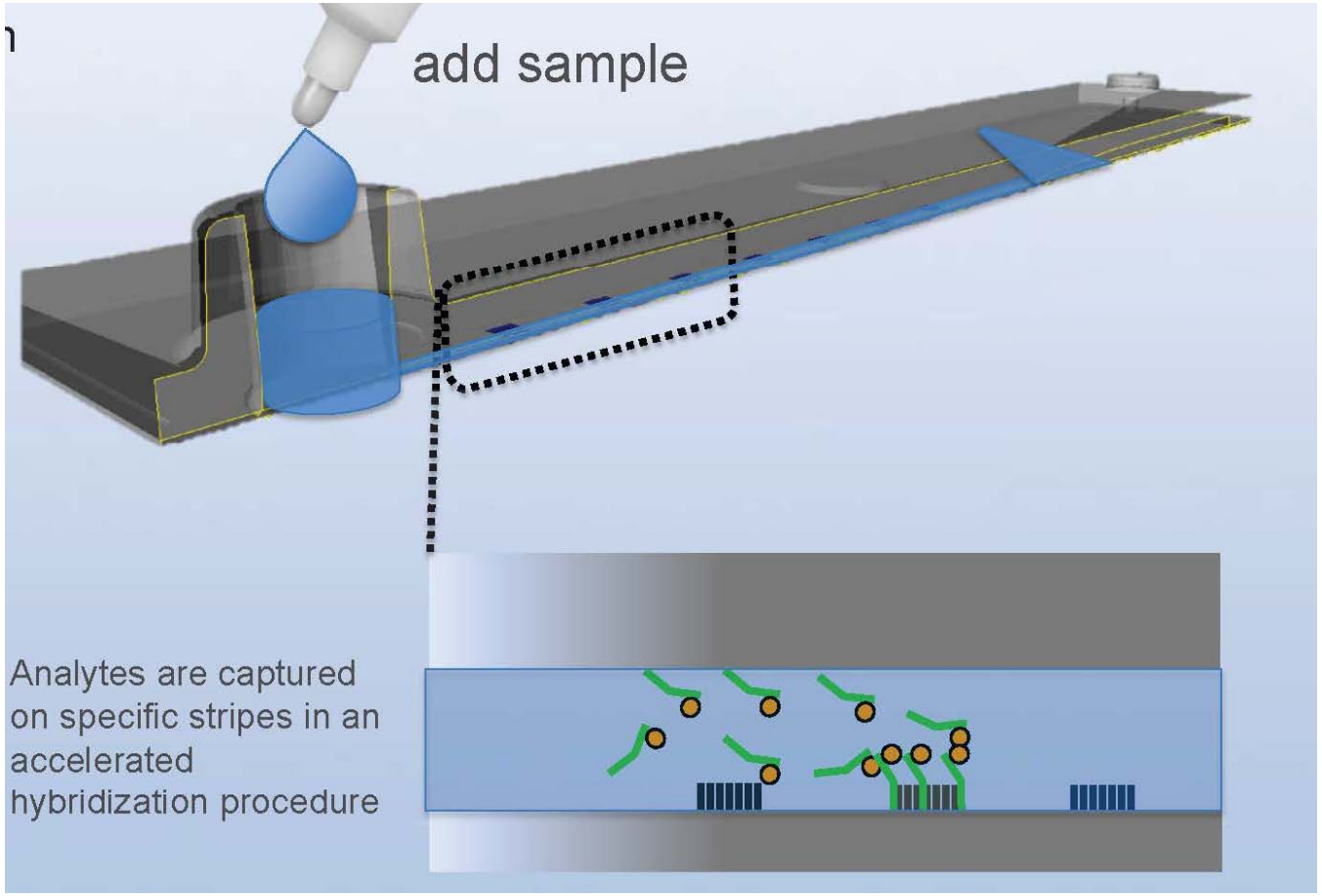
Estructure



www.**greinerbioone**.com

4. Applications with organic, inorganic and hybrid materials

4.4 Sensors

Final product

www.**greinerbioone**.com

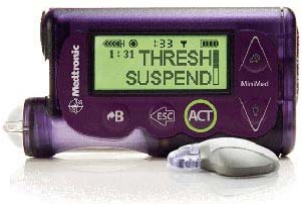
4. Applications with organic, inorganic and hybrid materials

4.4 Sensors

Manufacturer (2010)	Brand	Assay method	Minimal sample volume (uL)	Test time (second)	Assay range (mg/dL)	Hematocrit range (%)	Memory (results)
Abbott	FreeStyle Freedom	GDH-PQQ	0.3	−5	20–500	15–65	400
AgaMatrix	WaveSense KeyNote	GOD	0.5	4	20–600	20–60	300
Arkray	Glucocard X-meter	GDH	0.3	5	10–600	30–52	360
Bayer	Ascensia Contour	GDH-FAD	0.6	5	10–600	0–70	480
Bionime	Rightest GM300	GOD	1.4	8	20–600	30–55	300
Diabestic Supply of Suncoast	Advocate Redi-Code*	GOD	0.7	7	20–600	20–60	450
Diagnostic Devices	Prodigy Autocode	GOD	0.6	6	20–600	20–60	450
LifeScan	OneTouch UltraLink	GOD	1.0	5	20–600	30–55	500

4. Applications with organic, inorganic and hybrid materials

4.4 Sensors

Companies	Guardian REAL-Time Continuous Glucose Monitoring System	Dexcom G4 Platinum	MiniMed® 530G with Enlite
Availability	FDA approved in June 2006 (monitor) and February 2007 (MiniLink Transmitter) and available for purchase	STS system FDA approved in March, 2006. Upgraded since and available for purchase	FDA approved in September 2013
			
Weight	2.8 oz	2.4 oz	4 oz
Screen Size	approx 1.8" x 0.75"		522/722 screen
Monitor Size	3" x 2"	4" x 1.8" x 0.5"	No Monitor, displays on pump
Transmitter/ Sensor Size	1.64" x 1.4" x 0.37"		2" x 1.5" / 0.75" diameter
Sensor Life	3 days	7 days	6 days
Sensor Canula size	14 mm	13 mm	8.75 mm

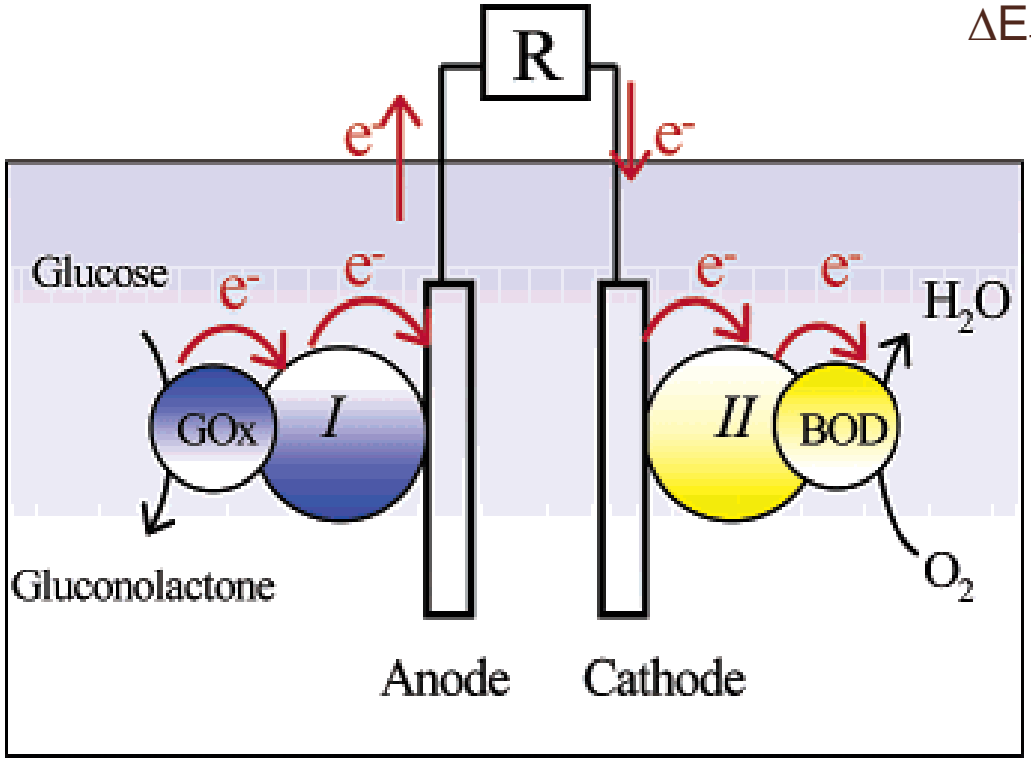
4. Applications with organic, inorganic and hybrid materials

4.4 Sensors

$FADH_2 \leftrightarrow FAD + 2H^+ + 2e^-$ $E^0 = -0.180$ V

$BOD + 1/2O_2 + 2H^+ + 2e^- \leftrightarrow BOD + H_2O$ $E^0 = 0.816$ V

$\Delta E_{teo} = 0.996$ V



Enzymatic Fuel cell

Mano et al, J. Am. Chem. Soc. 2003, 125, 6588-6594
Zayats et al, Electroanalysis 20, 2008, No. 6, 583 – 601

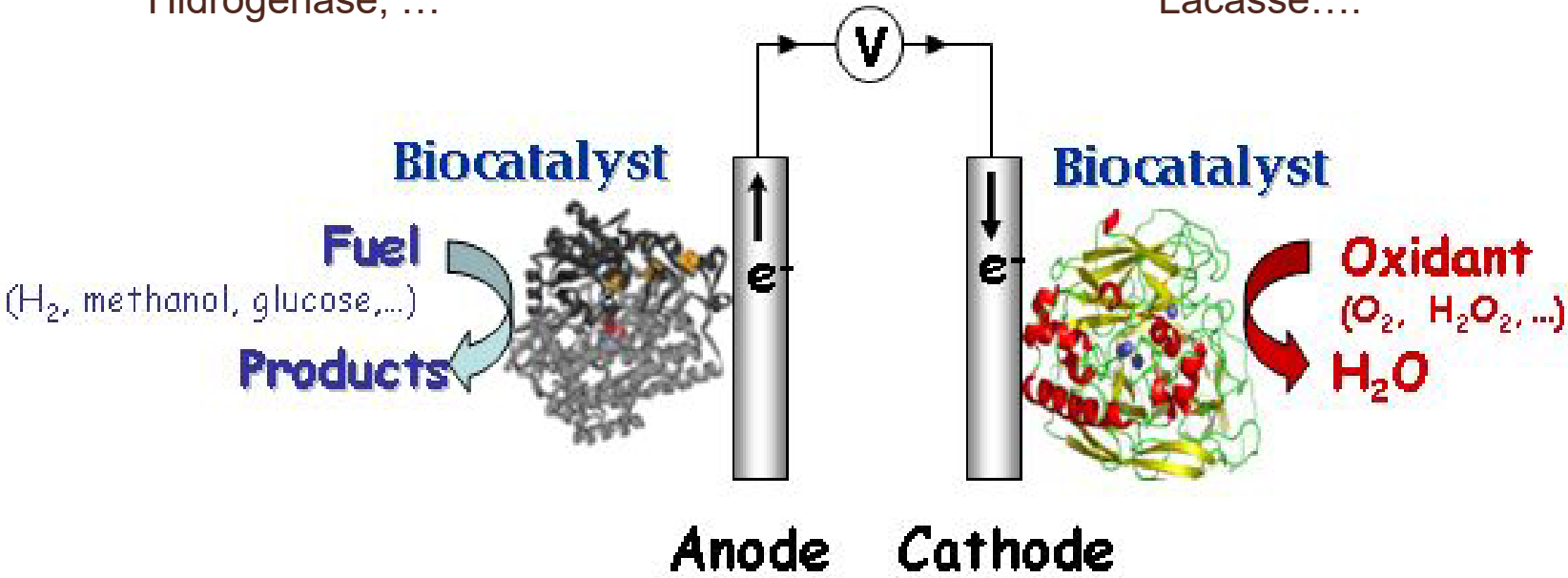
4. Applications with organic, inorganic and hybrid materials

4.4 Sensors

Enzymatic Fuel cell

Glucose Oxidase,
Hidrogenase, …

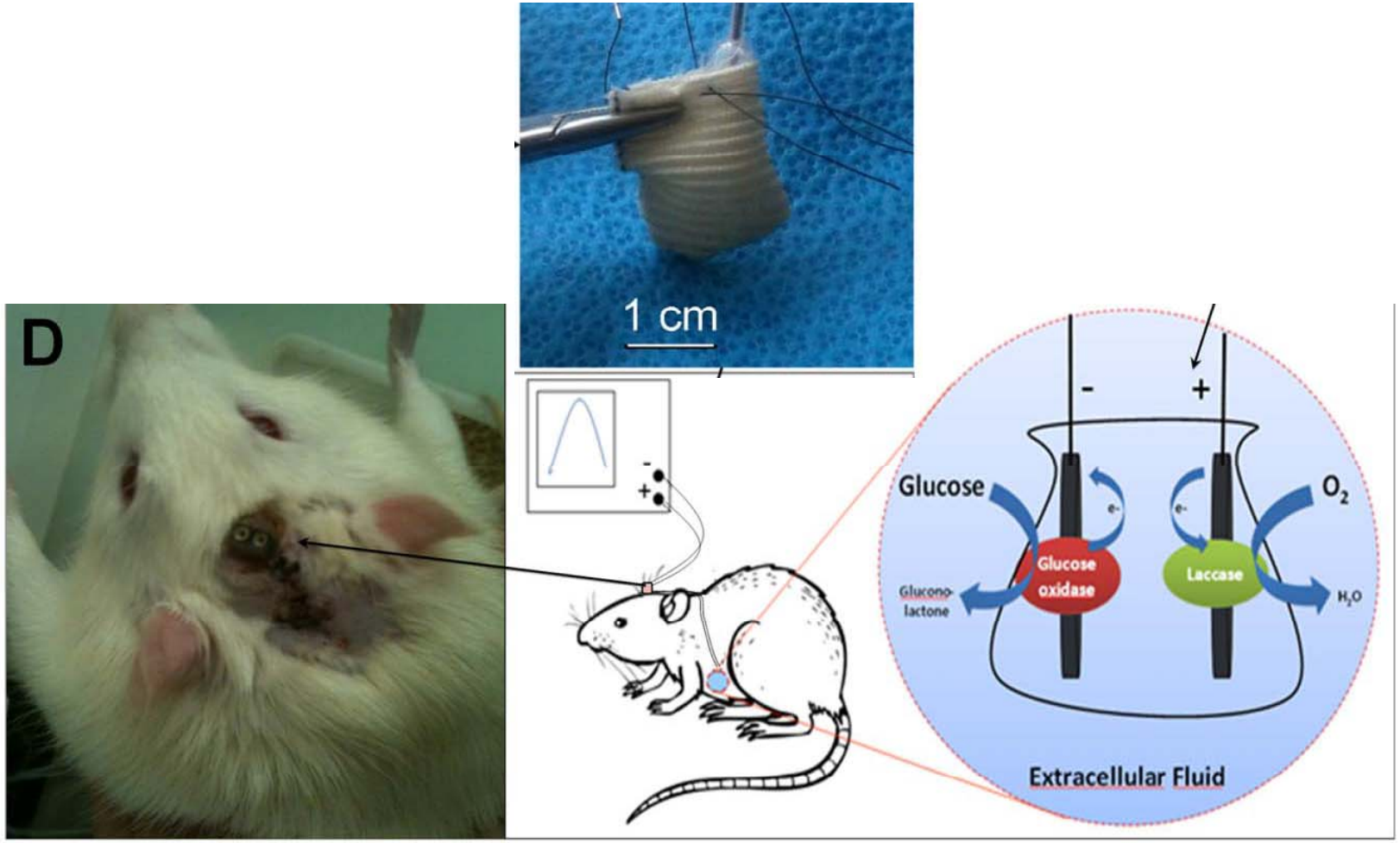
Bilirubin oxidase
Lacasse….



Nanotechnology and Nanomaterials » "Syntheses and Applications of Carbon Nanotubes and Their Composites"
Chapter 19, Carbon Nanotube-Enzyme Biohybrids in a Green Hydrogen Economy, De Poulpiquet et al.

4. Applications with organic, inorganic and hybrid materials

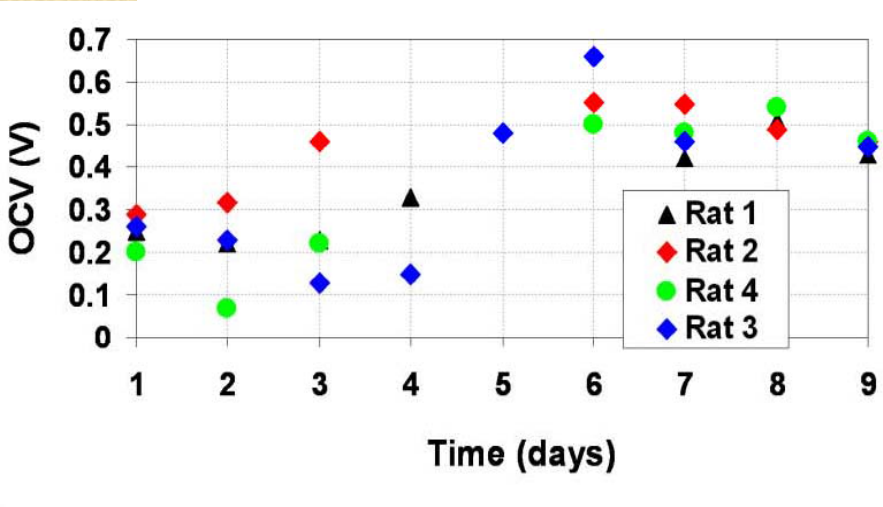
4.4 Sensors

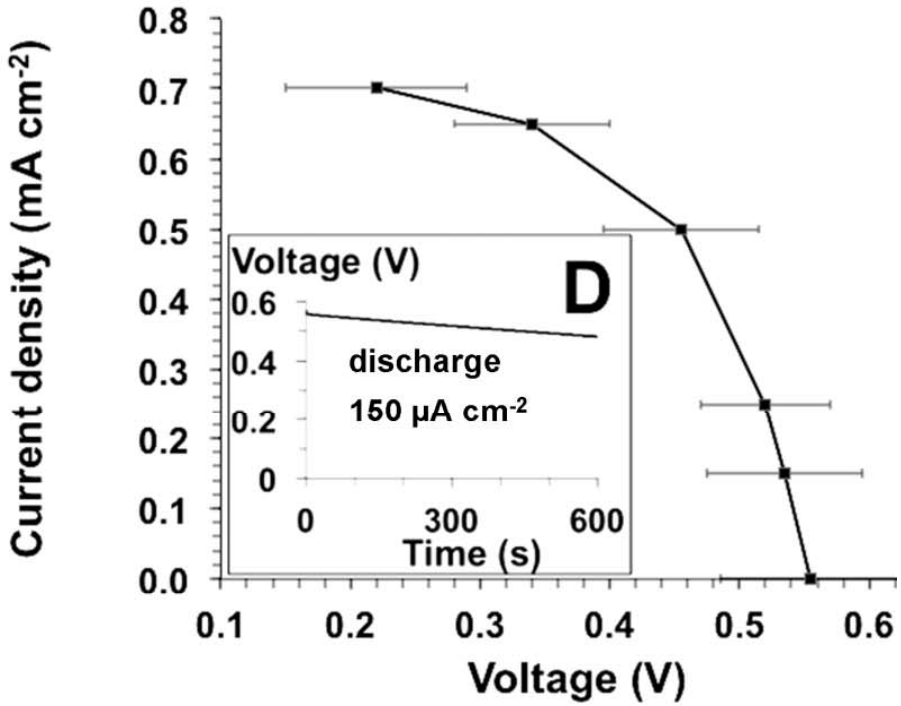


Zebda et al. Nature. Scientific Reports. 3 : 1516. DOI: 10.1038/srep01516

4. Applications with organic, inorganic and hybrid materials

4.4 Sensors

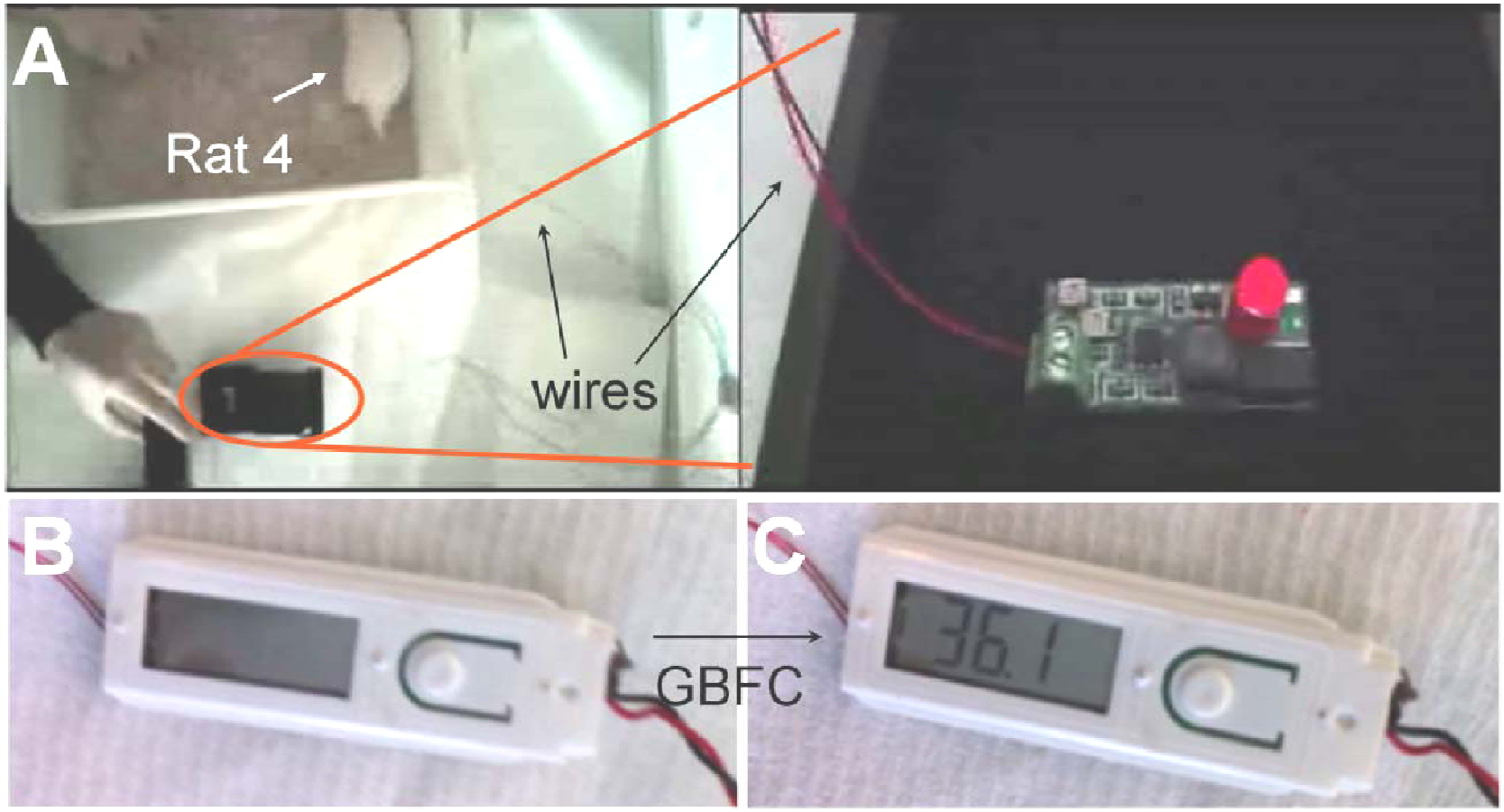




Zebda et al. Nature. Scientific Reports. 3 : 1516. DOI: 10.1038/srep01516

4. Applications with organic, inorganic and hybrid materials

4.4 Sensors



Zebda et al. Nature. Scientific Reports. 3 : 1516. DOI: 10.1038/srep01516

4. Applications with organic, inorganic and hybrid materials

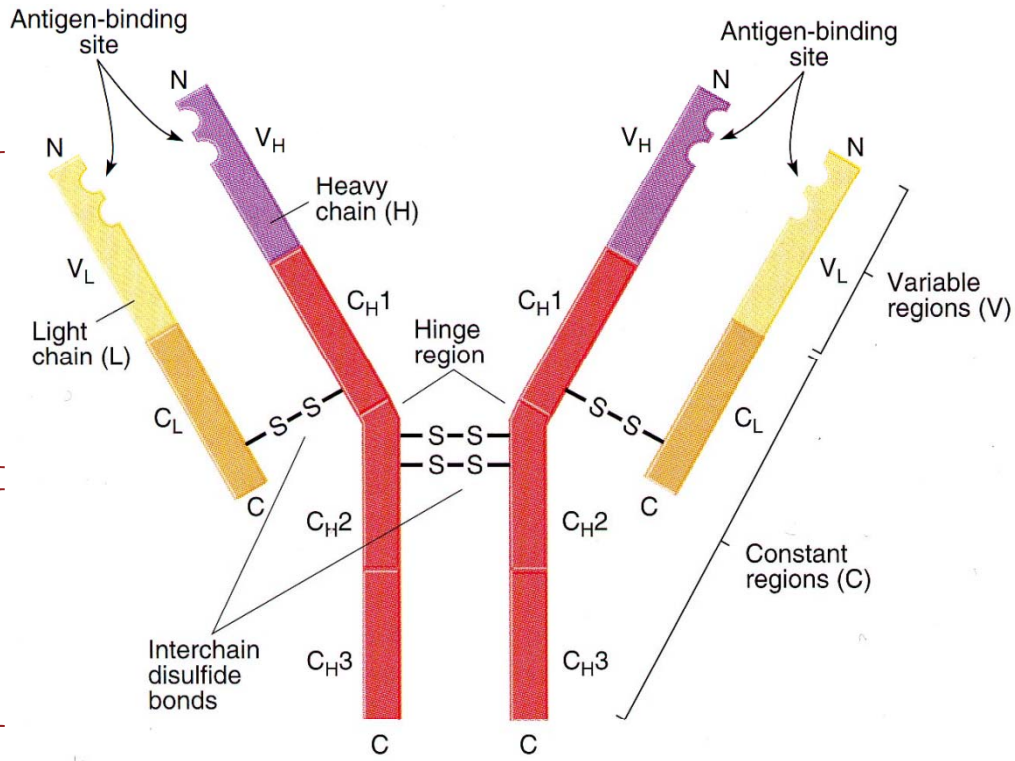
4.4 Sensors

Antigen – antibody recognition

Antibody structure

Fab
(fragment antigen binding)

Fc
(Fragment, crystallizable)



http://www.bioatla.com/antibody-structure/

4. Applications with organic, inorganic and hybrid materials

4.4 Sensors

Antigen – antibody recognition

Antibody structure

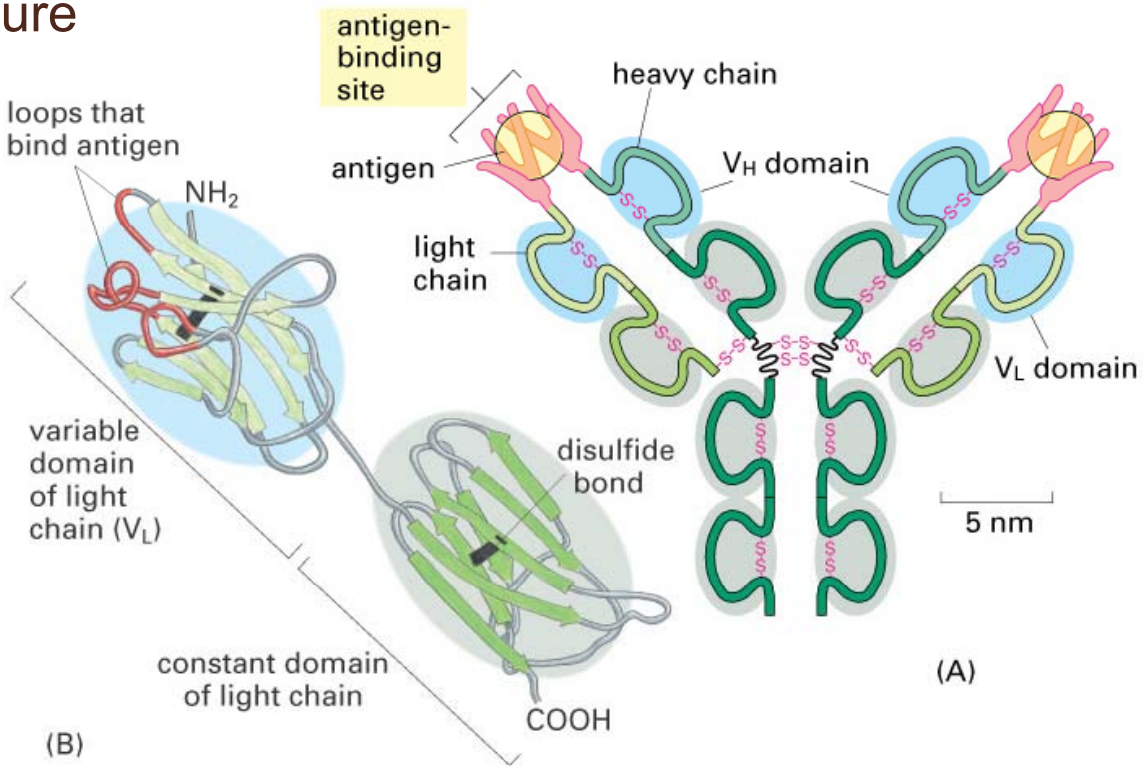


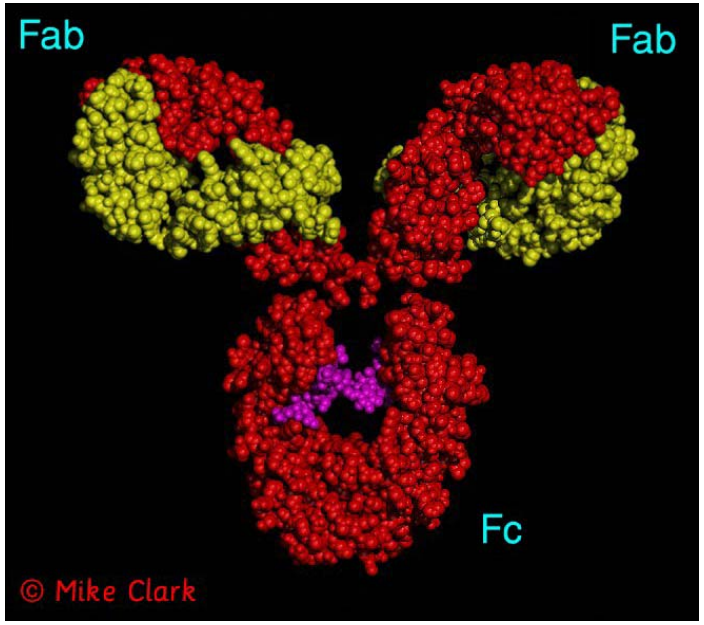
Figure 4-32 Essential Cell Biology, 2/e. (© 2004 Garland Science)

http://www.accessexcellence.org/RC/VL/GG/ecb/antibody_molecule.php

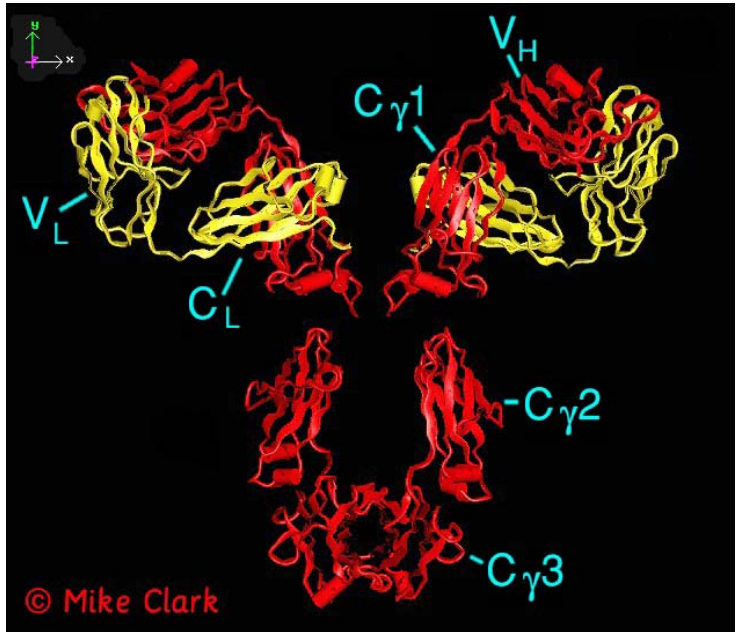
4. Applications with organic, inorganic and hybrid materials

4.4 Sensors

Antigen – antibody recognition



Raytraced image of the model of human IgG1 showing the two heavy chains in red, the two light chains in yellow and the carbohydrate attached to the heavy chains in purple.



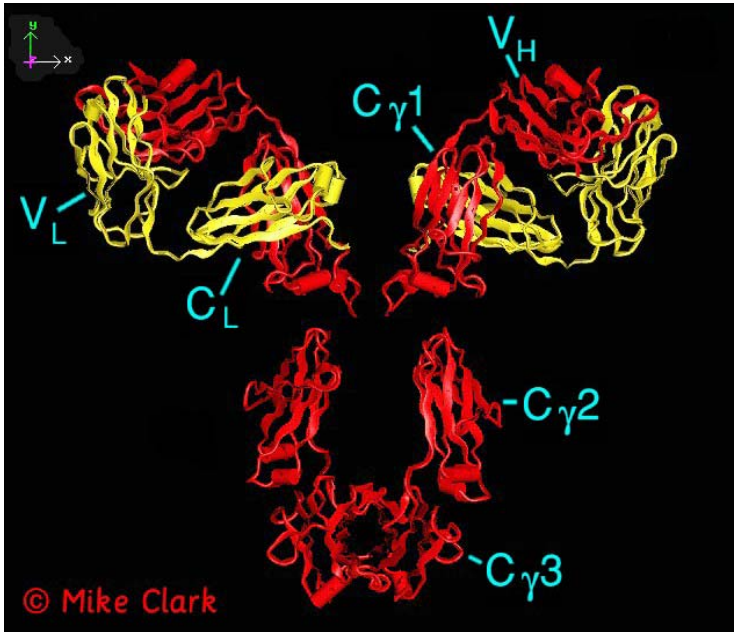
Representation of the same model in which the secondary structure of the alpha-carbon backbone trace is shown. The beta strands are indicated as ribbons and can be clearly seen.

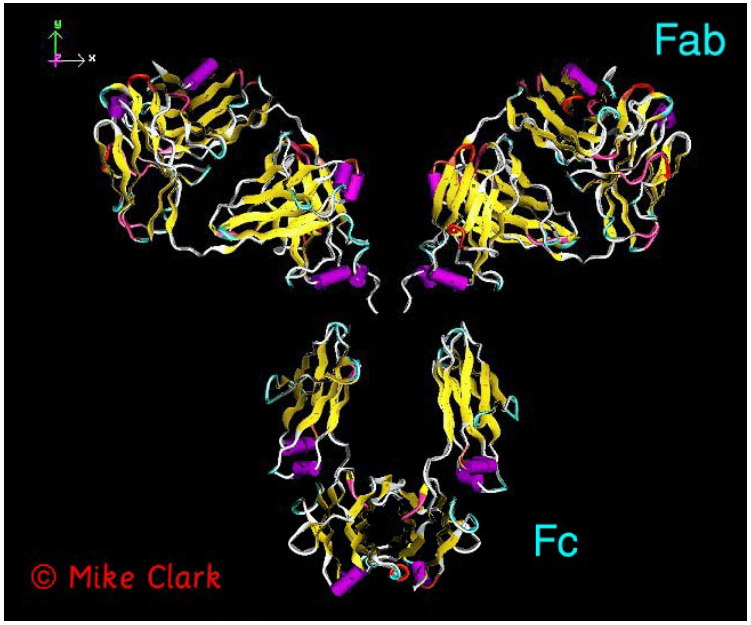
http://www.path.cam.ac.uk/~mrc7/igs/mikeimages.html

4. Applications with organic, inorganic and hybrid materials

4.4 Sensors

Antigen – antibody recognition



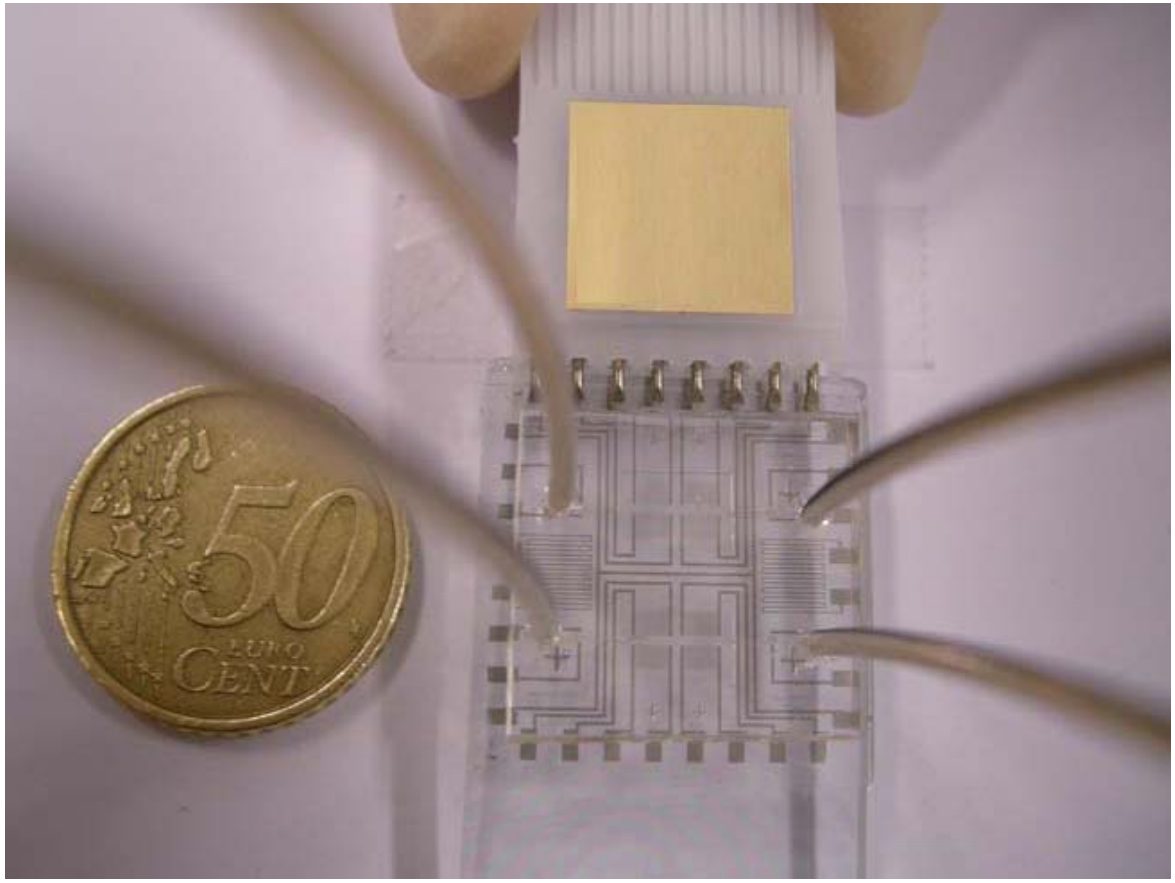


Model of human IgG1 in which the secondary structure within the model is indicated by both shape and colour. The conserved beta barrel structures making up each immunoglobulin domain along with the beta turns and helical turns at the ends of the beta strands can clearly be identified. If you look carefully you will see that the domain structures for the heavy and light chain V-regions is different from the constant region domains

4. Applications with organic, inorganic and hybrid materials

4.4 Sensors

Antigen – antibody recognition



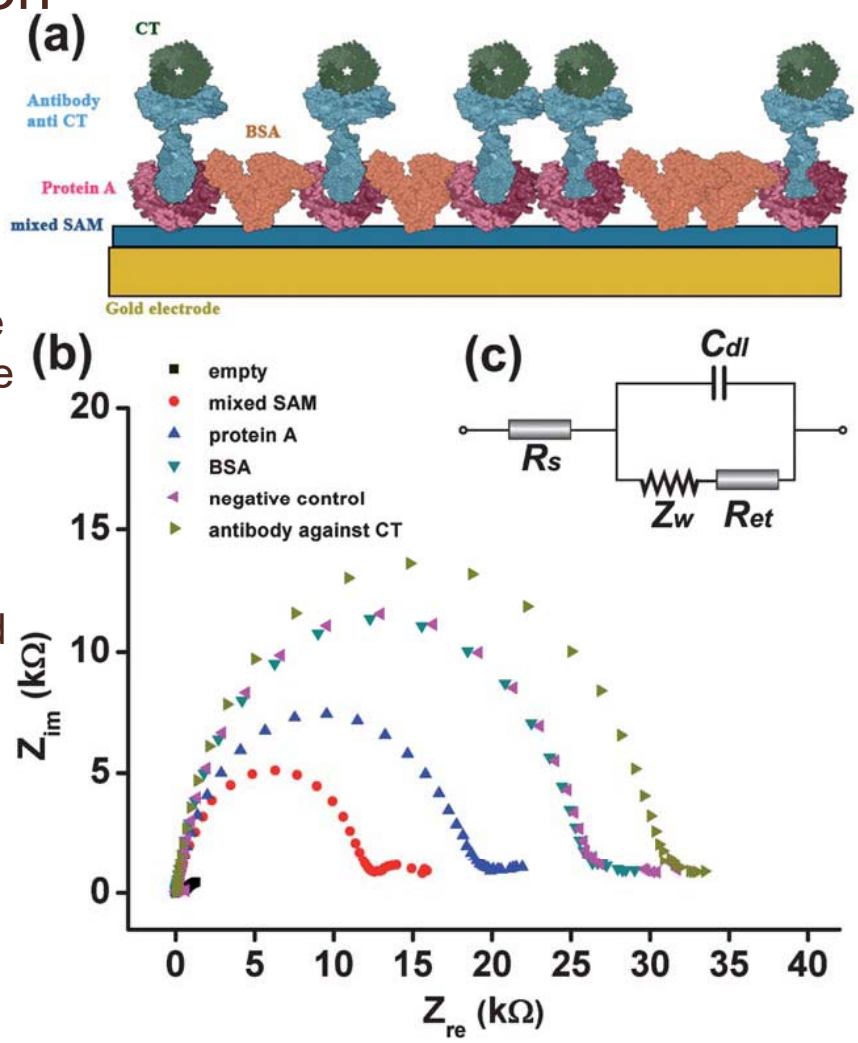
Lab Chip, 2011, 11, 658–663
Toxins 2014, 6, 1325-1348

4. Applications with organic, inorganic and hybrid materials

4.4 Sensors

Antigen – antibody recognition

(a) Schematic representation of electrode functionalization.
(b) Nyquist spectra corresponding to the different functionalization steps.
After each step, an increasing in impedance values is observed, except in the case of the negative control (cyan curve).
(c) Equivalent circuit for impedance spectroscopy measurements. The circuit includes ohmic resistance of the electrolyte solution R_s, Warburg impedance Z_w resulted from the ionic diffusion of the electrolyte, double layer capacitance C_{dl} and electron transfer resistance R_{et}.



Lab Chip, 2011, 11, 658–663
Toxins 2014, 6, 1325-1348

4. Applications with organic, inorganic and hybrid materials

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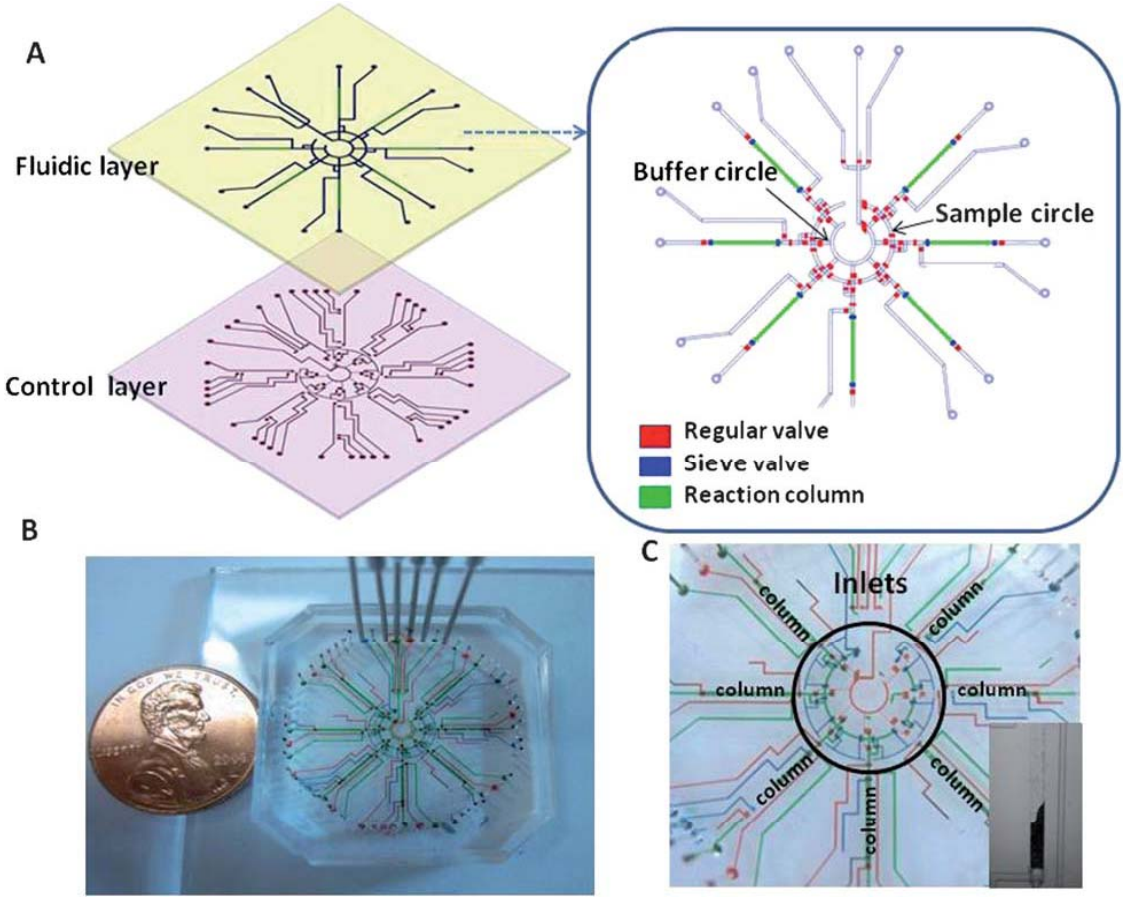
Antigen – antibody recognition



Lab Chip, 2011, 11, 3516–3522
Toxins 2014, 6, 1325-1348

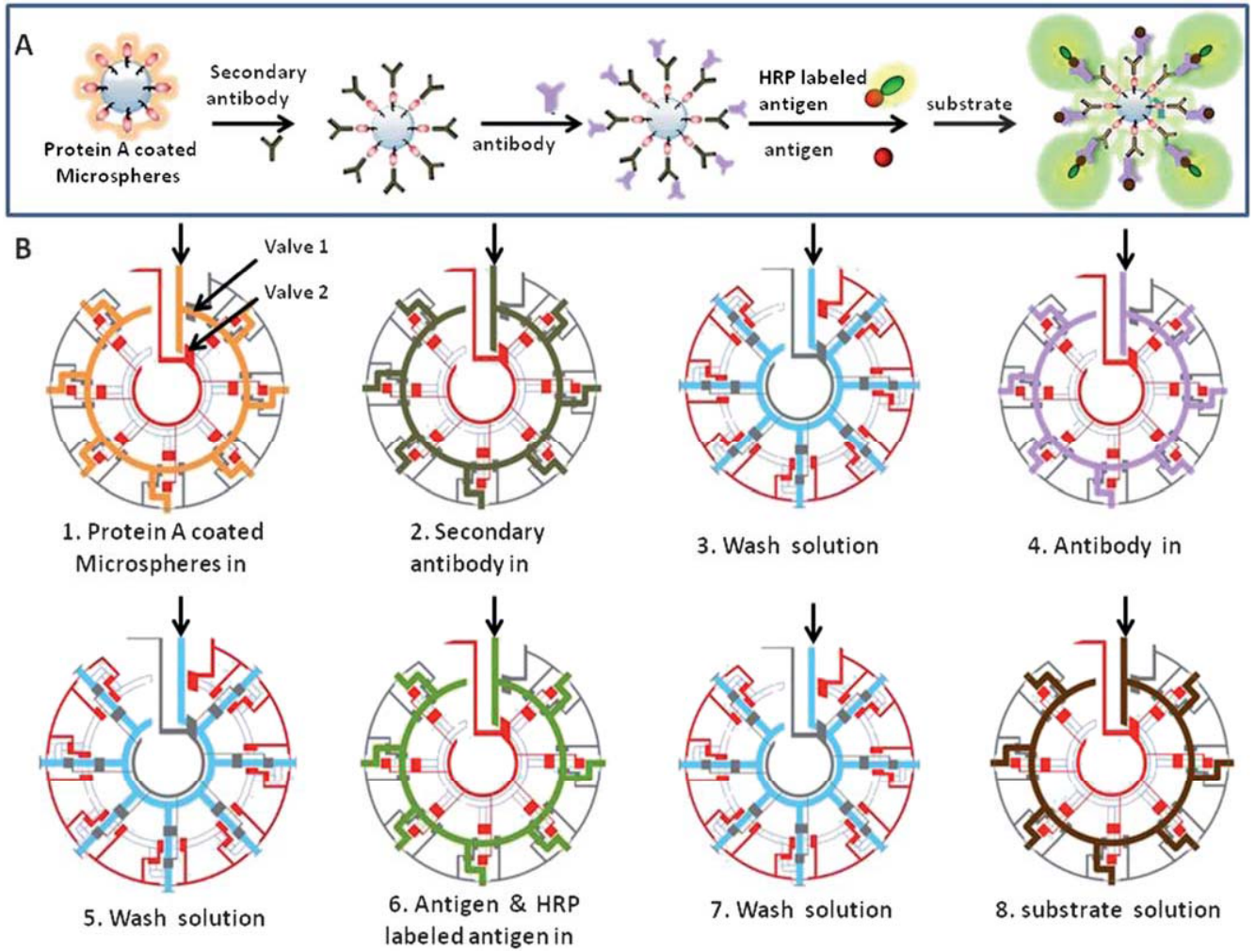
4. Applications with organic, inorganic and hybrid materials

4.4 Sensors

Antigen – antibody recognition

(A) Schematic diagram of the competitive immunoassay in the immune-reaction columns.

(B) Illustration of the chip operations to complete the immunoassay. The center circle area of the chip is graphical shown: each process of the reagent loading was controlled by two valves (Valve 1 and Valve 2). Status of the valves is clarified by different colours: red for action; gray for inaction.



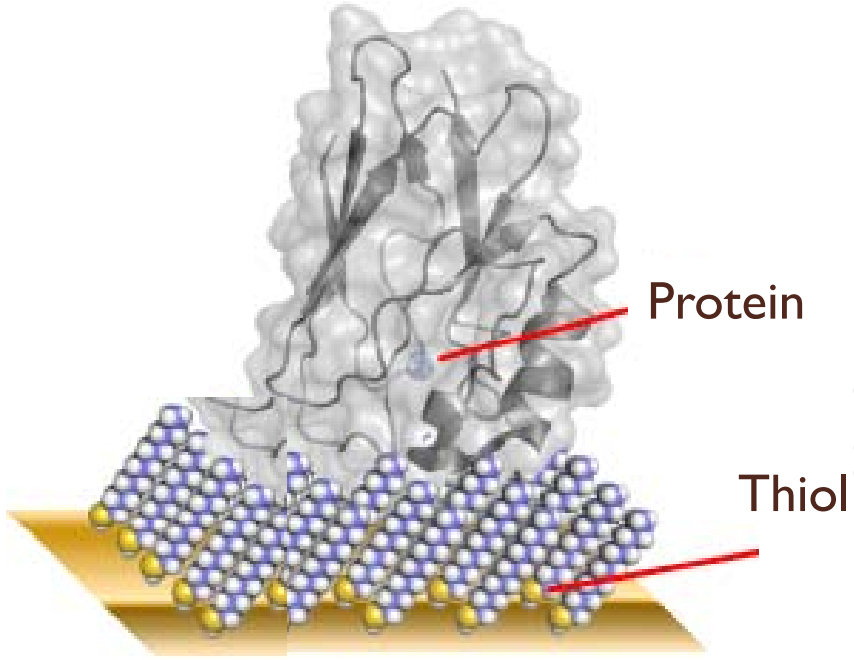
Lab Chip, 2011, 11, 3516–3522
Toxins 2014, 6, 1325-1348

4. Applications with organic, inorganic and hybrid materials

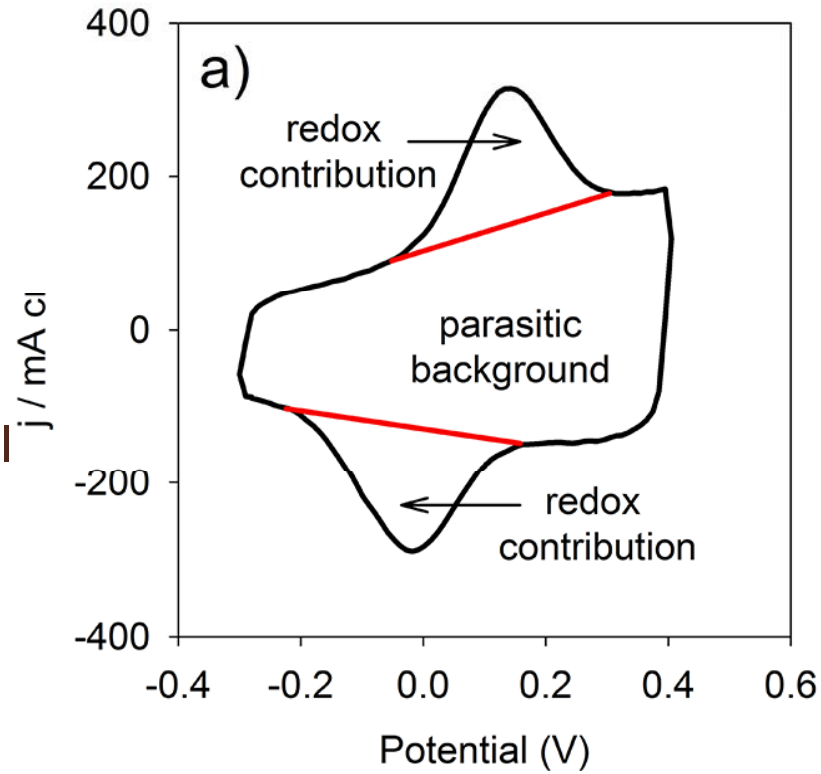
4.4 Sensors

Detection procedures

Redox protein



Voltametric analysis

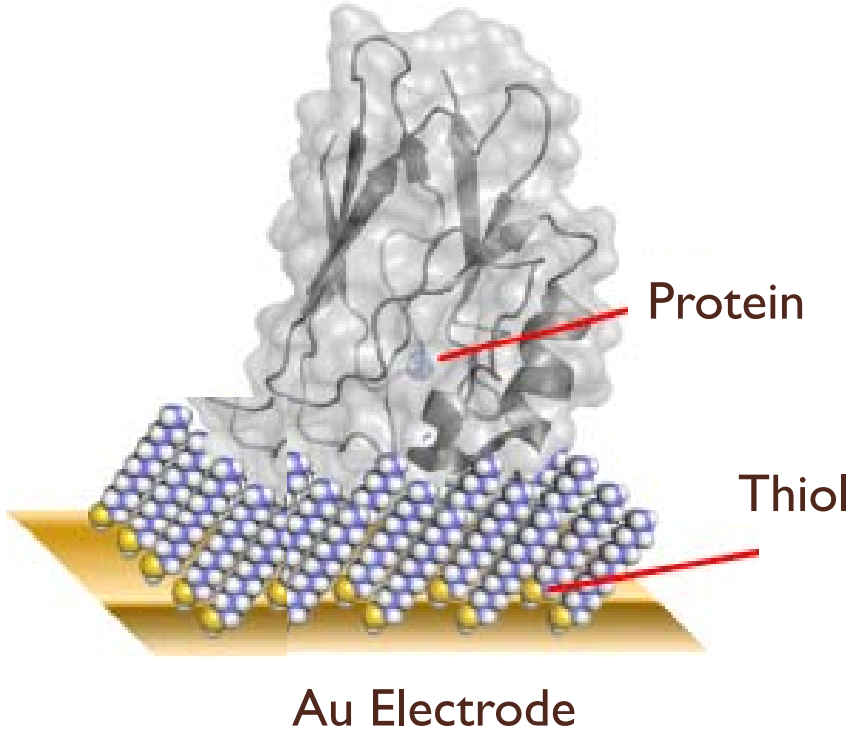


Anal. Chem. 2013, 85, 411−417

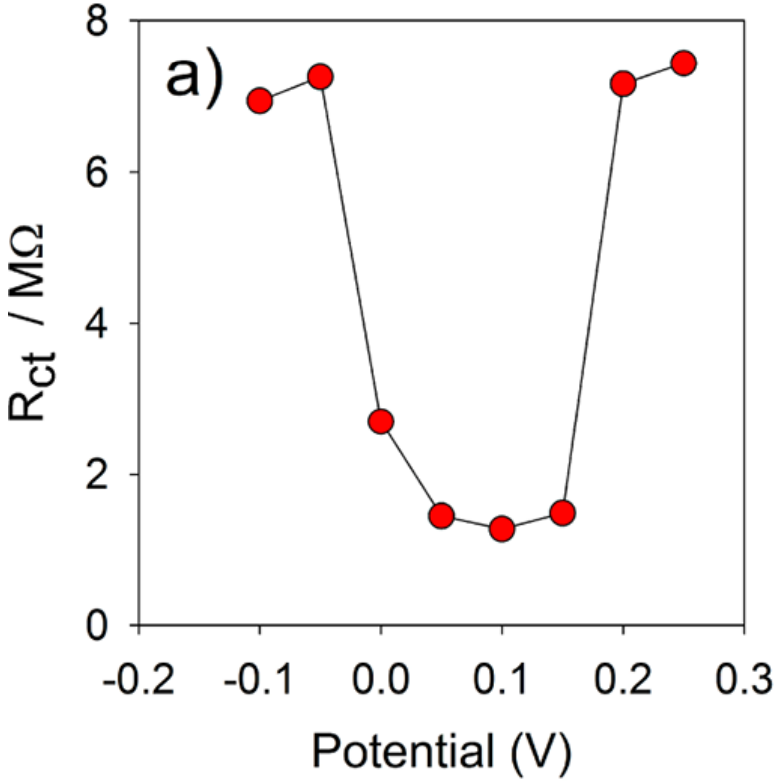
4. Applications with organic, inorganic and hybrid materials

4.4 Sensors

Detection procedures



Impedance analysis (resistance)



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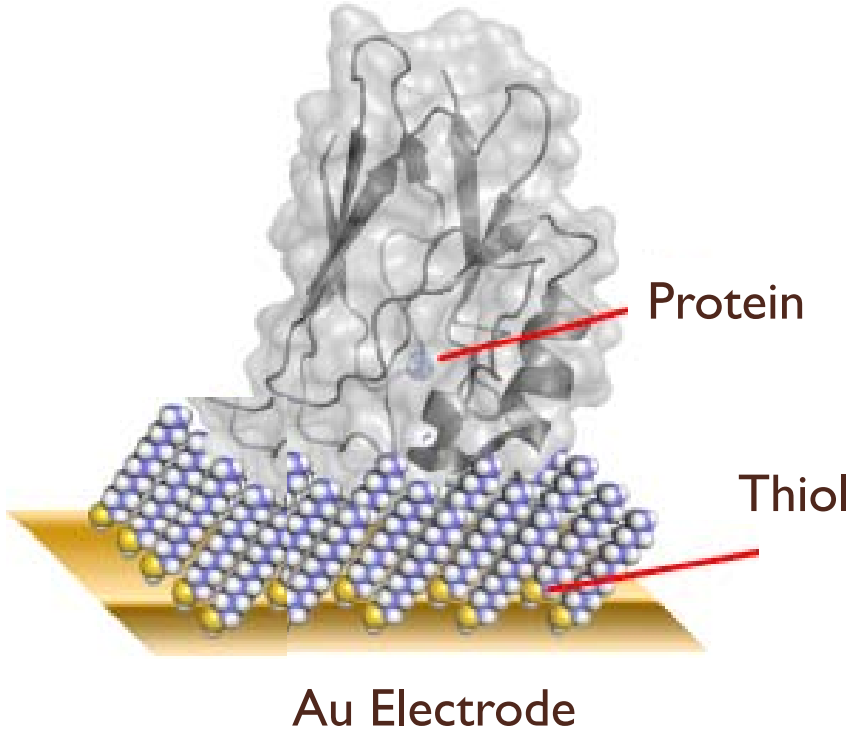
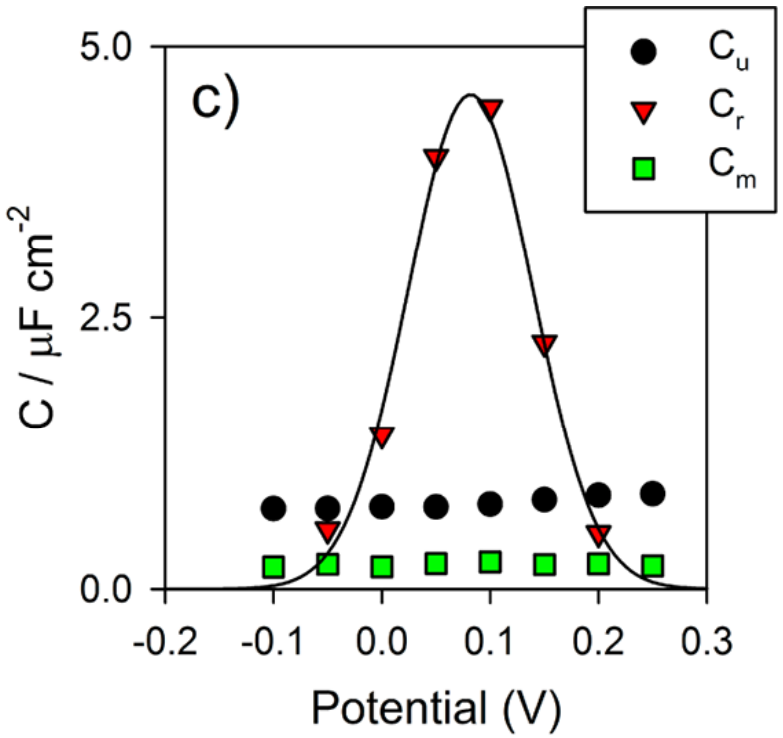
4. Applications with organic, inorganic and hybrid materials

4.4 Sensors

Detection procedures



Impedance analysis (capacitance)



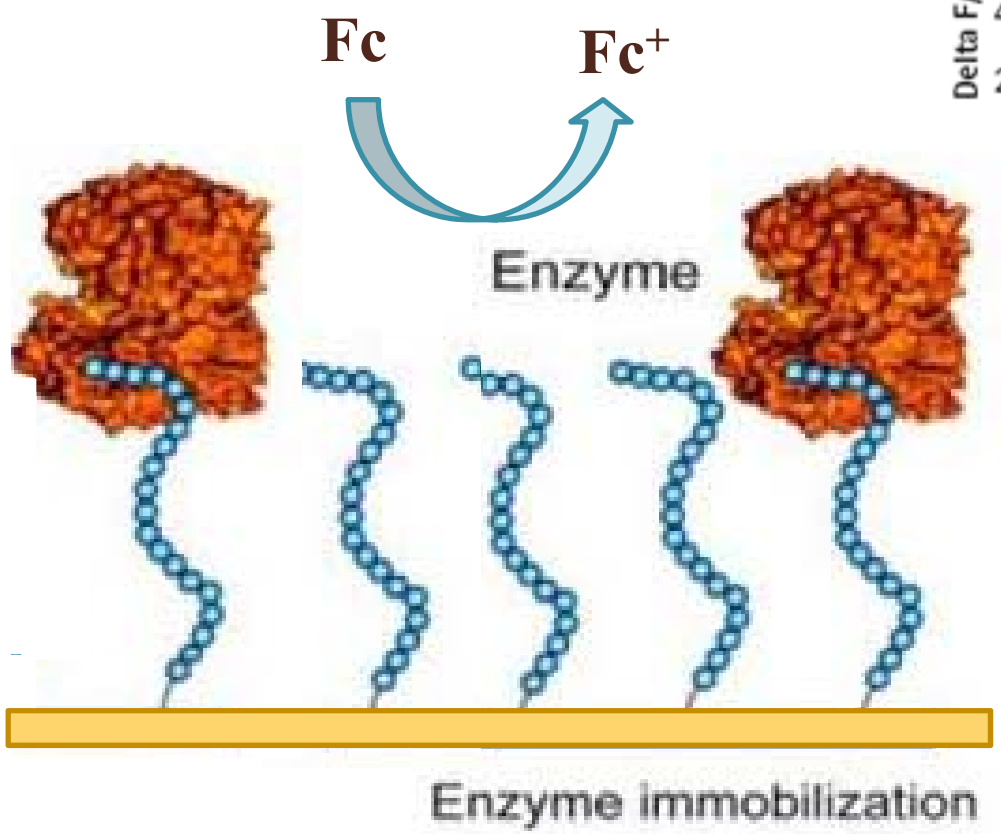
Anal. Chem. 2013, 85, 411−417

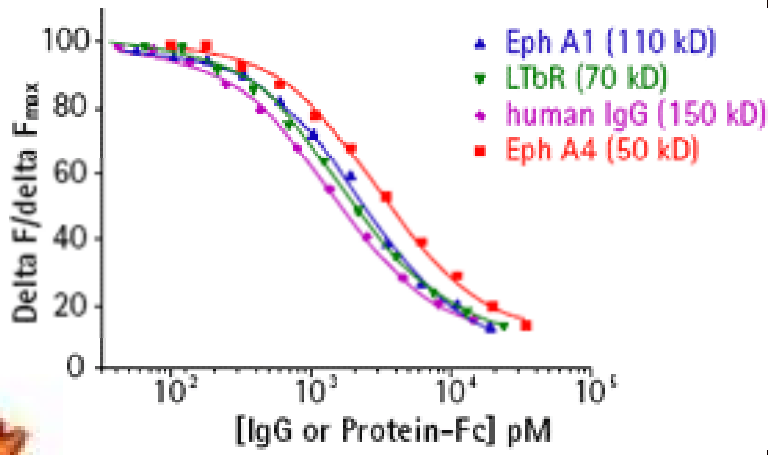
4. Applications with organic, inorganic and hybrid materials

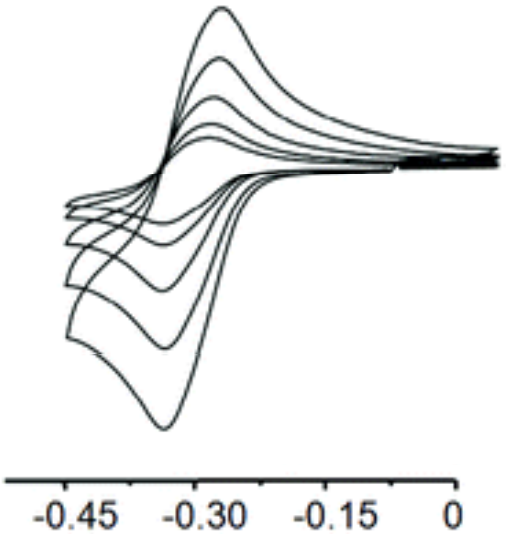
4.4 Sensors

Detection procedures

No Redox protein→ Redox labels





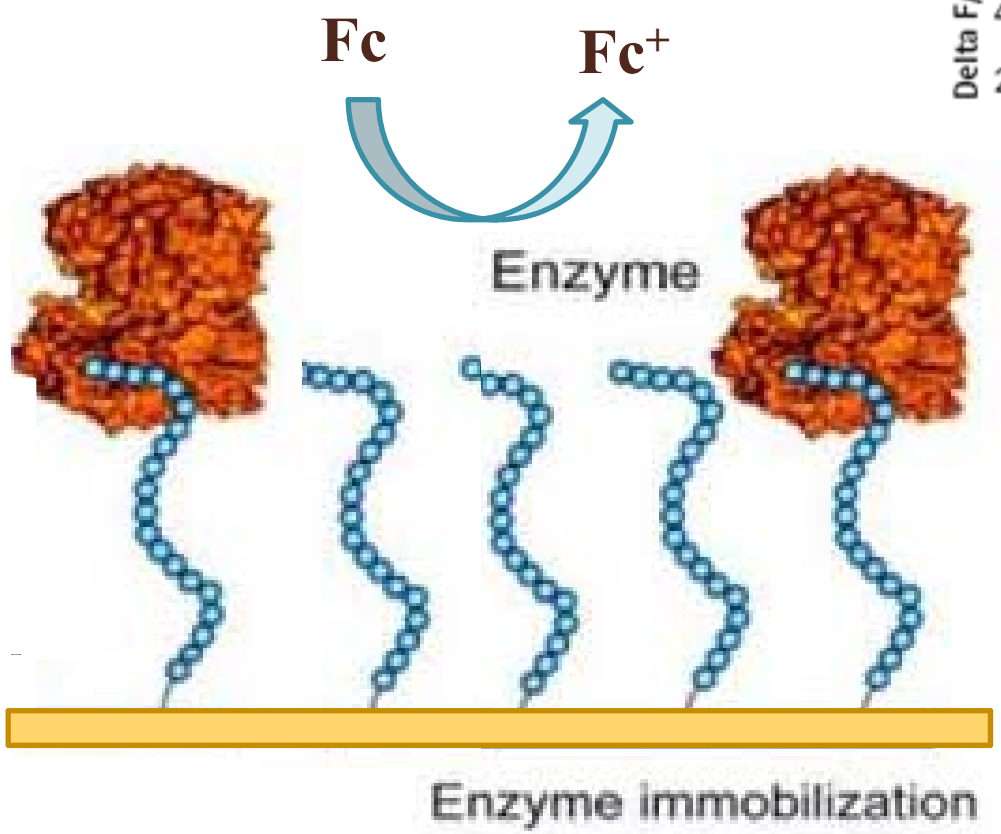


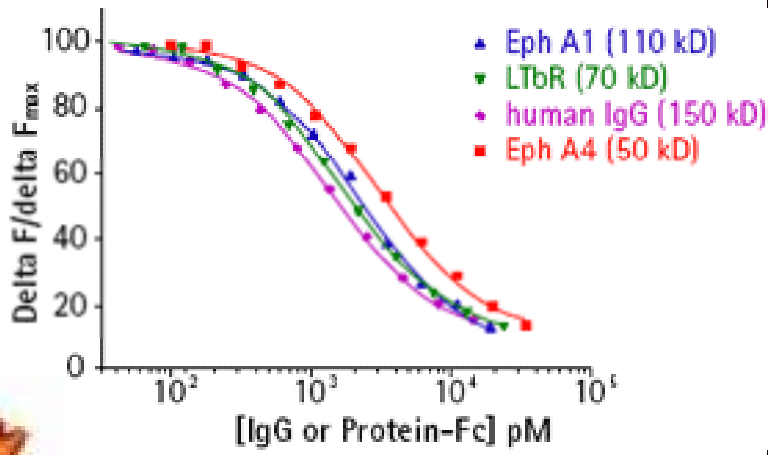
4. Applications with organic, inorganic and hybrid materials

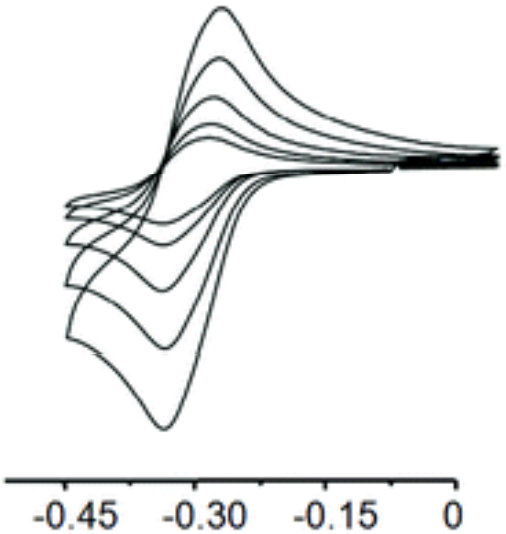
4.4 Sensors

Detection procedures

No Redox protein→ Redox labels







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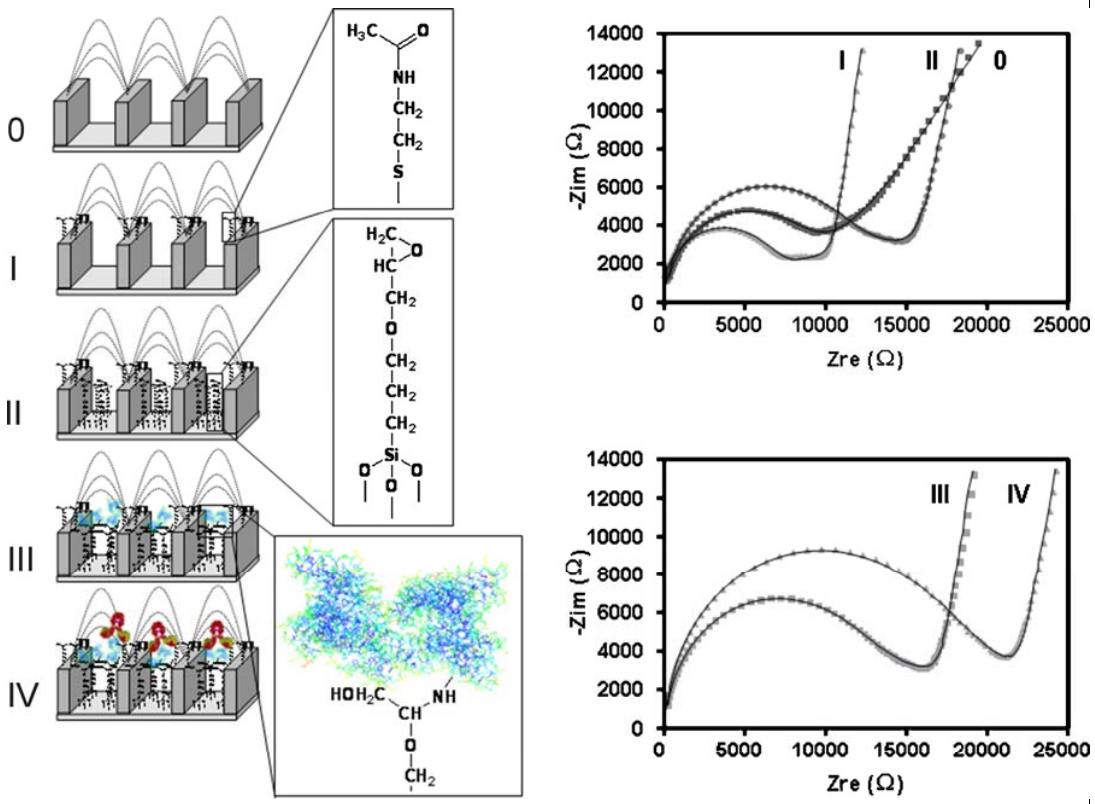
Detection procedures

Label free

Scheme showing steps used to prepare the immunosensor surfaces and antibody binding. *Right: Nyquist plots of the impedance spectra recorded and* corresponding to (a) IDE, (b) step I: *N-acetylcysteamine, gold protection, (c) step II: functionalization of Pyrex substrate with (3-glycidoxy propyl)trimethoxysilane,* (d) step III: coating antigen 2d-BSA, covalent immobilization (1 gmL^{-1}) and (e) step IV: antibody Ab11 (1 gmL^{-1}).



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4.4 Sensors

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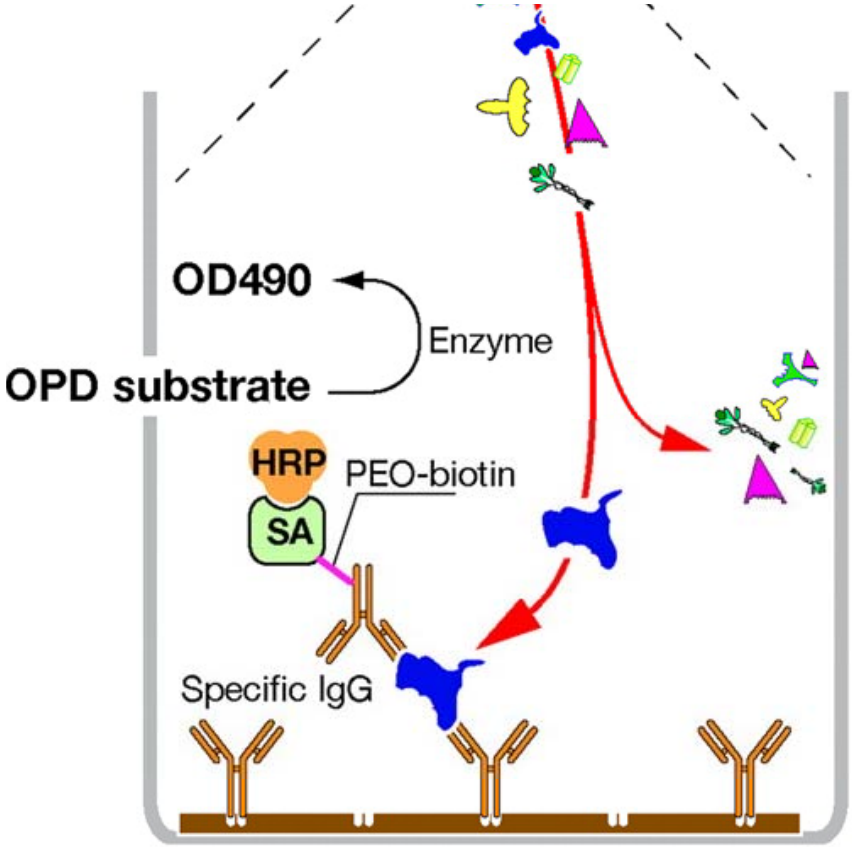
Elisa method



http://www.pnas.org/content/107/45/19490/F1.expansion.html
http://www.elisa-antibody.com/ELISA-Introduction/ELISA-Principle

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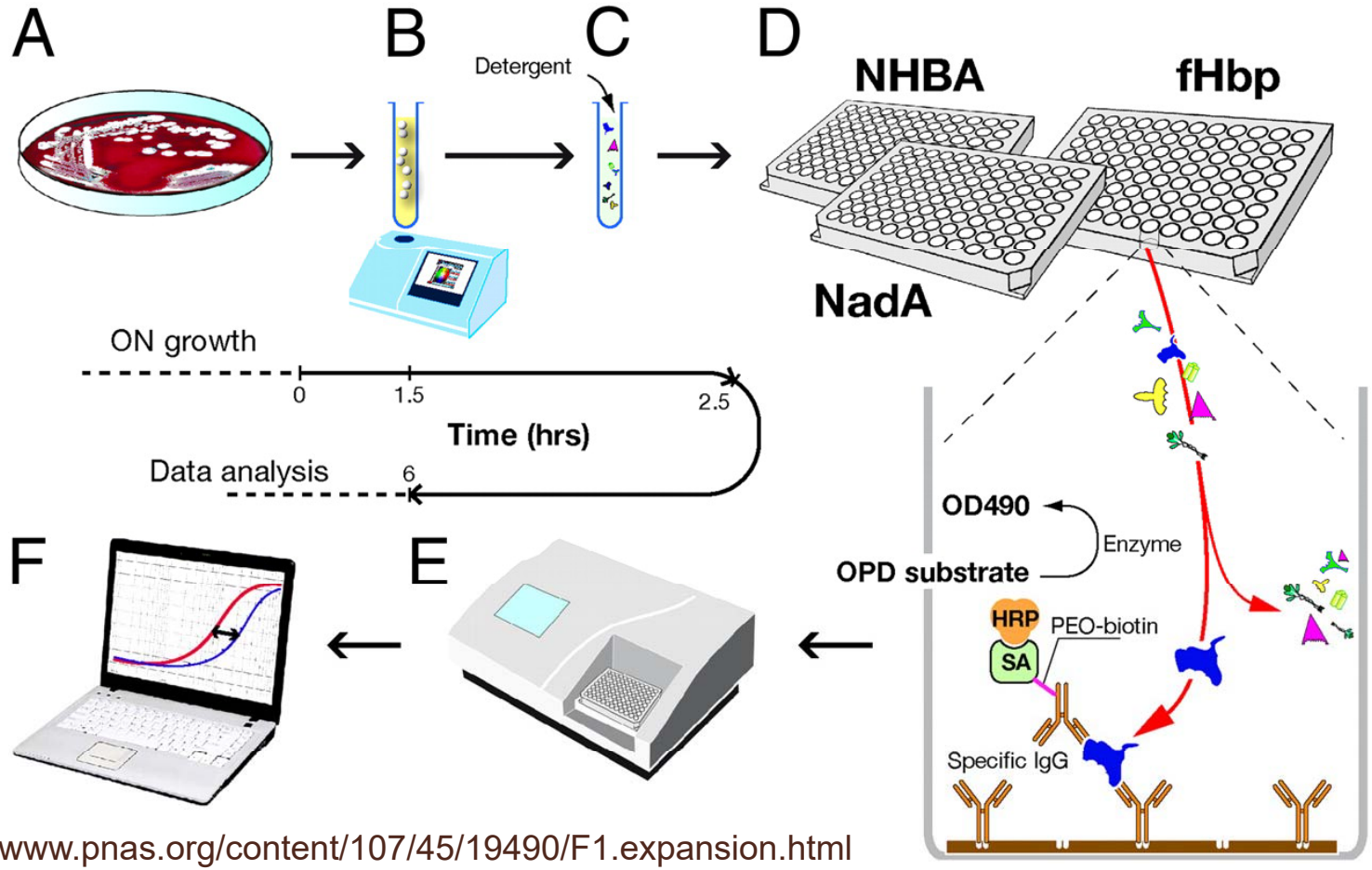
Elisa method



http://www.pnas.org/content/107/45/19490/F1.expansion.html
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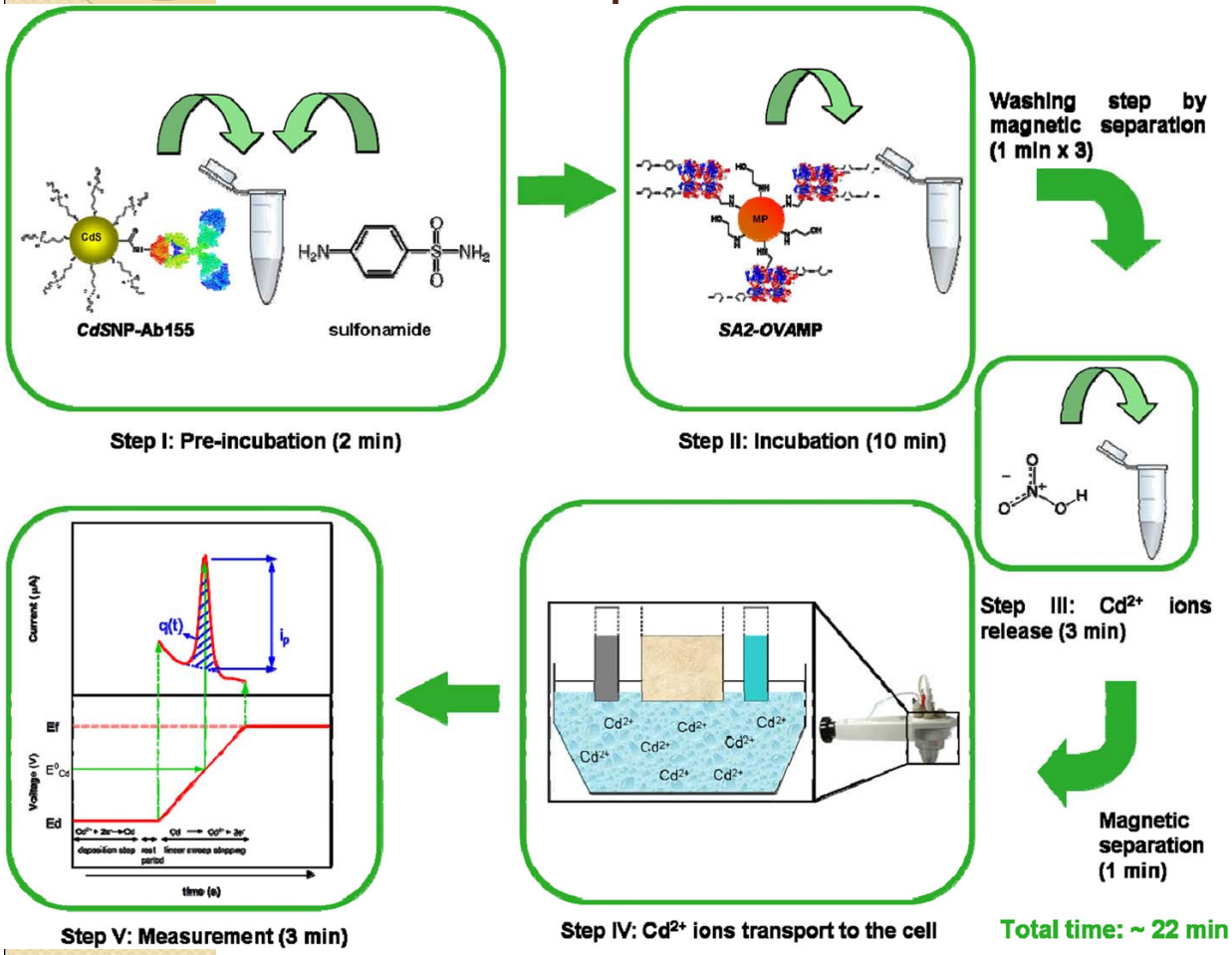

New approaches

Schematic diagram of the complete immunosensor measurement procedure. Firstly,the CdS NP–Ab155 and the analyte are pre-incubated and then,the SA2-OVAMP suspension is added and the mixture incubated during 10min. After three washing steps, performed with the aid of a magnetic rack, the CdS NP in the tube are dissolved and the Cd^{2+} ions released are measured in the electrochemical cell by SWV

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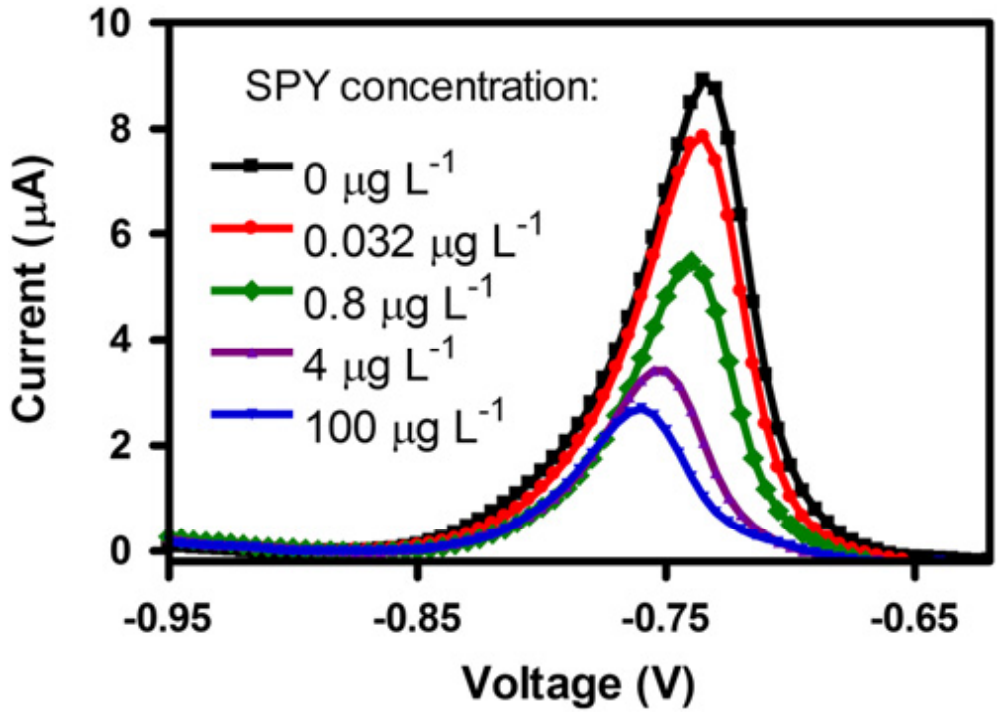

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