The World of Coating: from Monolayers to Thick Films and from Sensors to Medical Implants

THE HEBREW UNIVERSITY OF JERUSALEM

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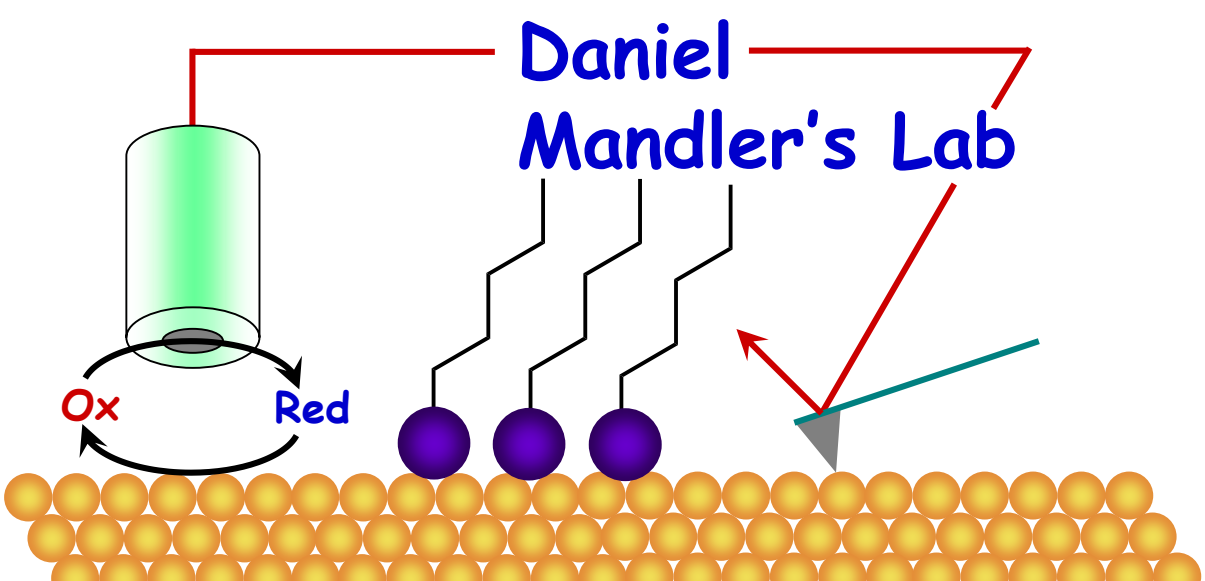
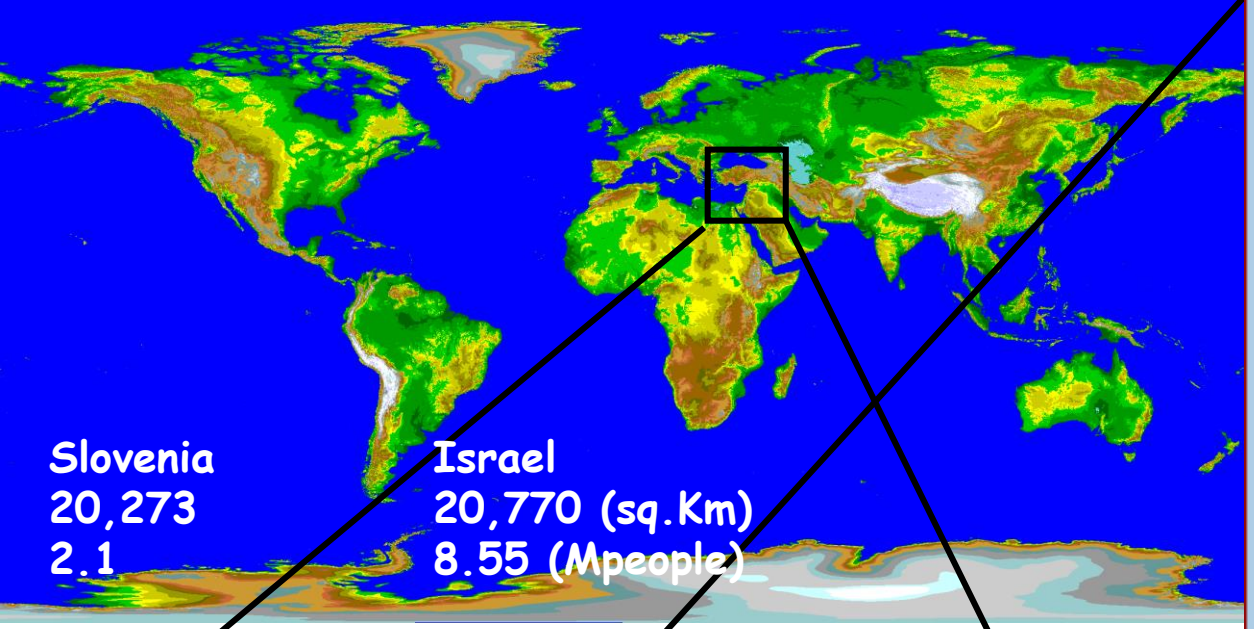
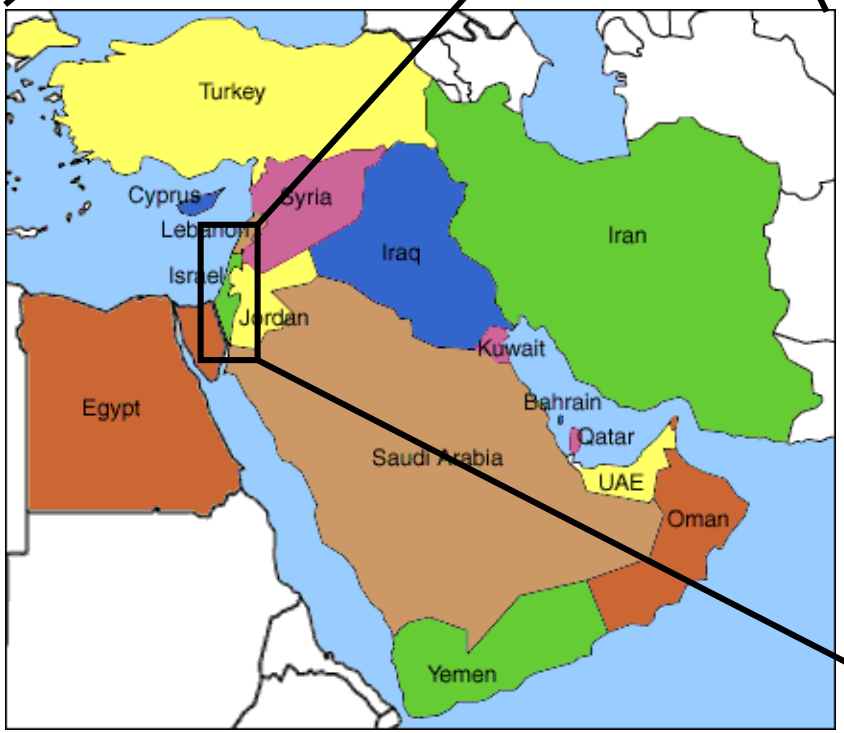
The Pregl Colloquium, November 23, 2017



Fritz Pregl


Slovenia
20,273
2.1
Israel
20,770 (sq.Km)
8.55 (Mpeople)


Turkey
Cyprus
Syria
Lebanon
Israel
Jordan
Iraq
Iran
Kuwait
Bahrain
Qatar
UAE
Saudi Arabia
Egypt
Oman
Yemen


Israel
Israel
The territories
Lebanon
Syria
METULLA
KIRYAT SHMONA
NAHARIYA
KATZRIN
ACRE
HAIFA
TIBERIAS
SEA OF GALILEE
MEDITERRANEAN SEA
NAZARETH
AFULA
HADERA
JENIN
NABLUS
NETANYA
KALKILYA
KFAR SABA
HERZLIYA
ARIEL
TEL AVIV
RAMALLAH
MODI'IN
JERICHO
Jerusalem
ASHDOD
ASHKELON
BETHLEHEM
EREZ
GAZA
HEBRON
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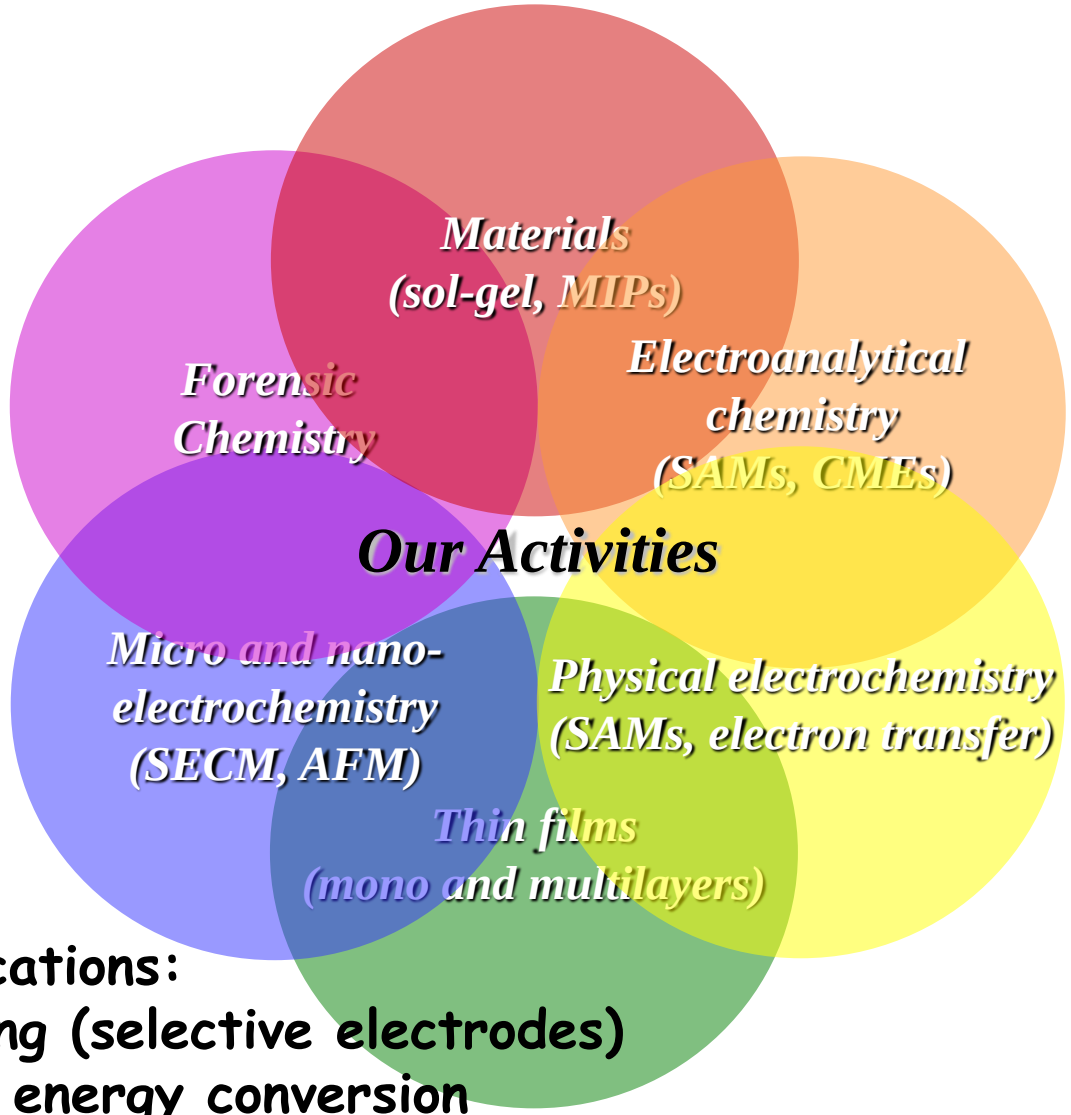
Jerusalem and the Hebrew University

The Hebrew University of Jerusalem is Israel's oldest (1925) university. The First Board of Governors included Albert Einstein, Sigmund Freud, Martin Buber, and Chaim Weizmann.
Four of Israel's prime ministers are alumni of the Hebrew University. In the last decade, six graduates of the University received the Nobel Prize.
In the Academic Ranking of World Universities index, Hebrew University is the top university in Israel and among the world's 100 top universities.

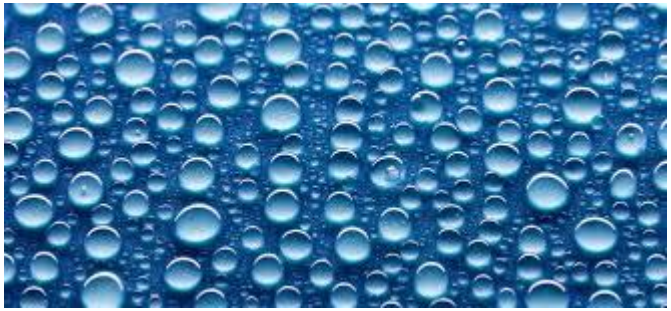
Our Research Activities



Applications:
Sensing (selective electrodes)
Solar energy conversion
Coating medical implants
Fingerprint visualization
And more…

What's the common base between medical implants, selective electrodes and solar energy conversion?

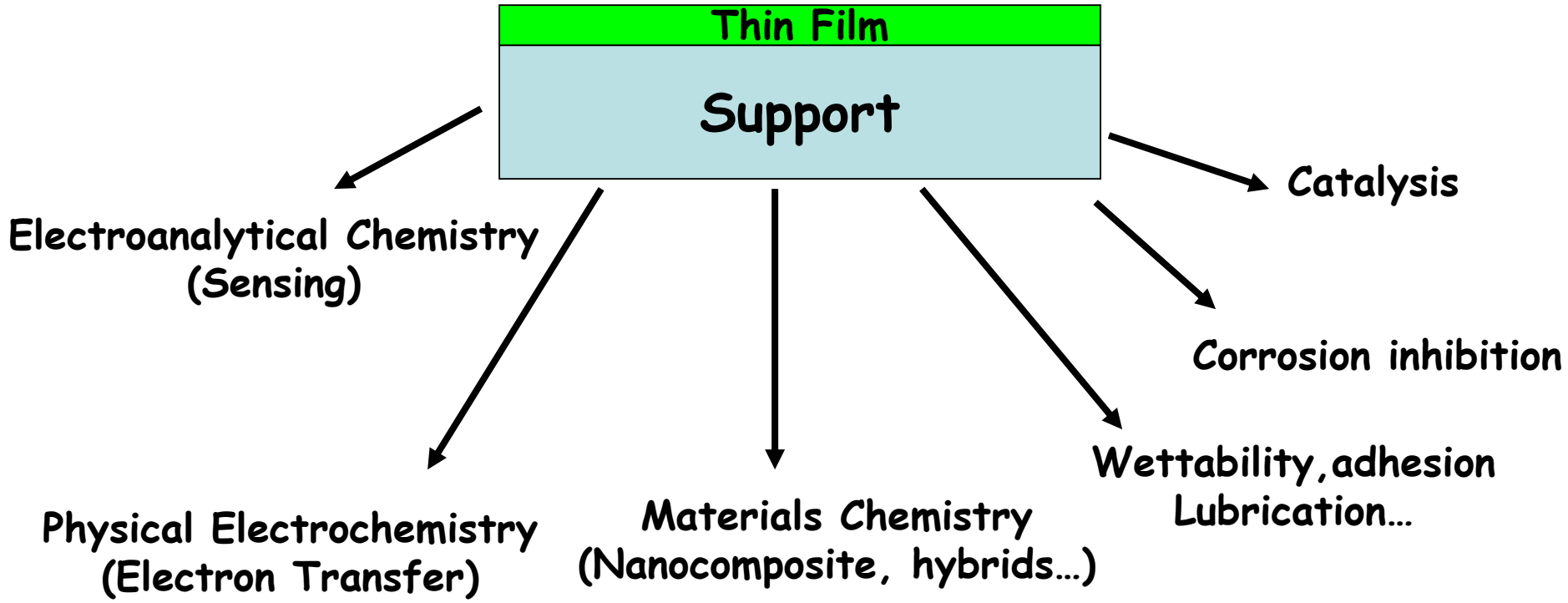
We Live in a World of Coatings



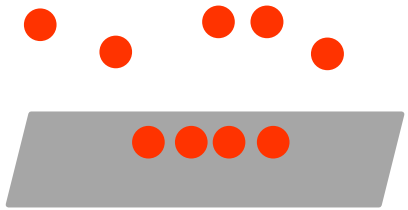
Functional coatings
Smart coatings

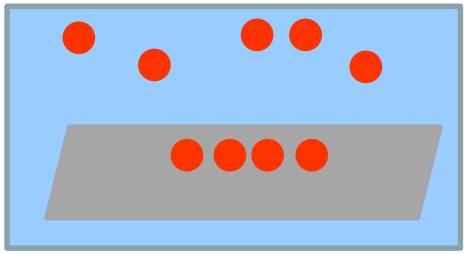
Modifying and Controlling the Interface: Coatings, Films, Layers…

A monolayer or thicker film will affect and control the physical and chemical properties of the interface without (almost) affecting the bulk



Methods of Film Formation





From the gasous phase

Chemical Vapor Deposition
Plasma methods
Atomic layer CVD
Combusting CVD
Photo-initiated CVD

Physical Vapor Deposition
Cathodic arc deposition
Electron beam deposition
Evaporative deposition
Pulsed laser deposition
Sputtering

From the liquid phase

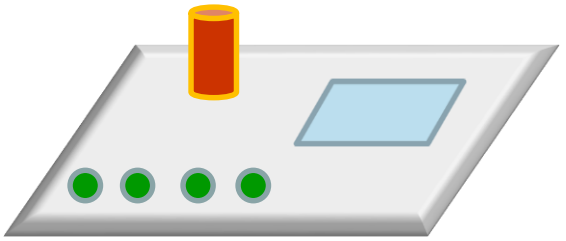
Printing

Wet-coating
Spin-coating
Dip-coating (LbL, LB)
Roll-coating

Electrochemistry

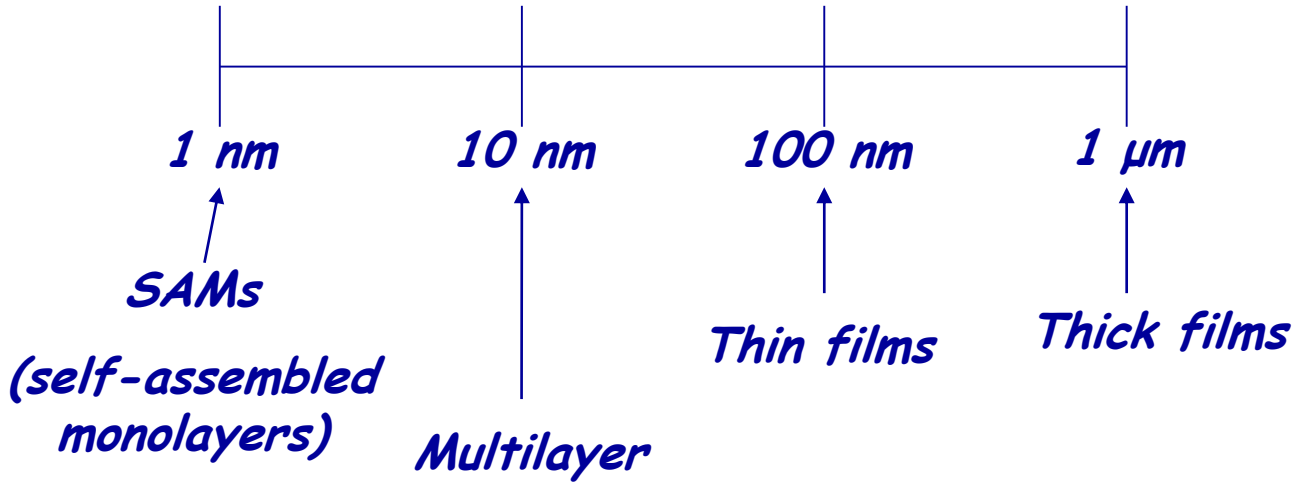
Considerations in Coatings

- ✓ The application
- ✓ The material (metallic, inorganic, organic, biological)
- ✓ The thickness (monolayer (nm) to thick layer (micron))
- ✓ The structure (continuous film, clusters, nano-objects, molecular species)
- ✓ Patterning
- ✓ Control (location, width, thickness…)
- ✓ Cost
- ✓ Equipment
- ✓ Complexity of the structure



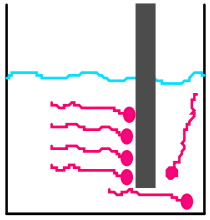
Coatings

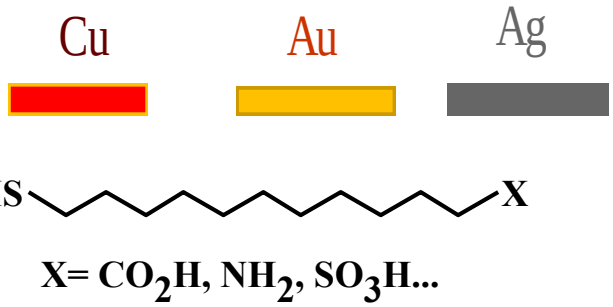

Solid
Thick Films (polymer)

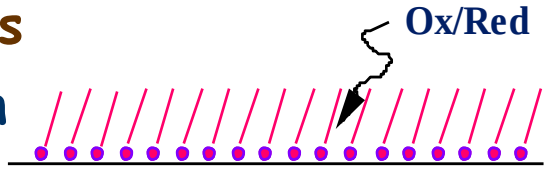

1 nm
10 nm
100 nm
1 μm
SAMs
(self-assembled monolayers)
Multilayer
Thin films
Thick films

Thin Films-Self-Assembled Monolayers

- Simple to form
- Different substrates (e.g., metals, metal oxides)
- Can be functionalized
- Fast Diffusion
- No accumulation of Undesired products
- Easy to study in detail

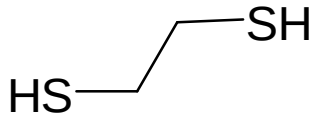


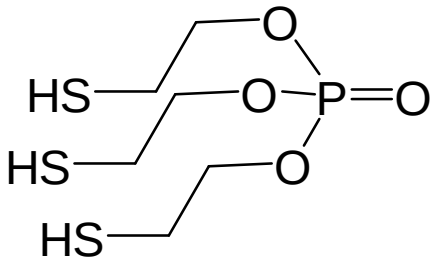




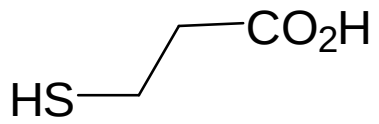
- Require difficult synthesis
- Inert substrates, e.g., Pt, are hardly modified
- Bulky groups introduce disorder
- Not always stable
- Depletion of desired analytes
- We tend to believe that we understand what's going on

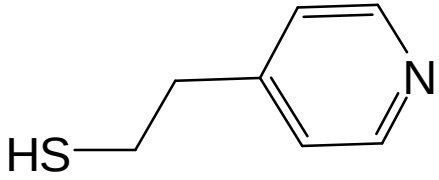
Electrochemical Sensors for Heavy Metals Based on Self-Assembled Monolayers

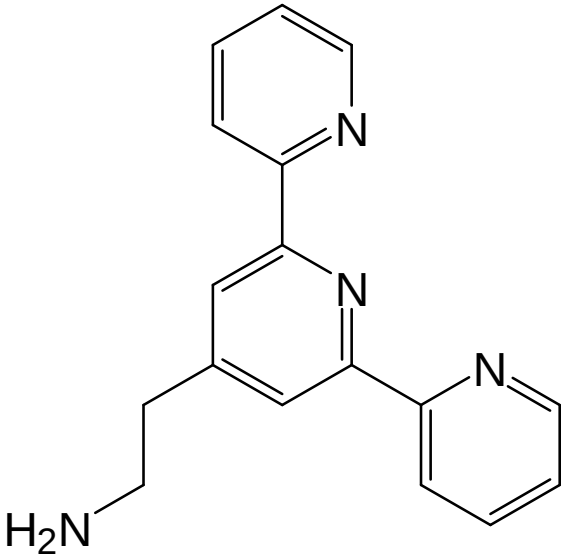




Hg(II)
Cd(II)
Cr(VI)
U(VI)
Fe(II)







Livorno

The Hydronet Project

http://www.hydronet-project.eu/

Developing and testing a new technological platform for improving the monitoring of water bodies based on a network of sensors, sensorized buoys, and autonomous, floating and sensorized robots.

Our part: Design and development of a series of micro-fabricated stable chemo-, bio-, and optical-sensors for the determination of heavy metals and oil in water.

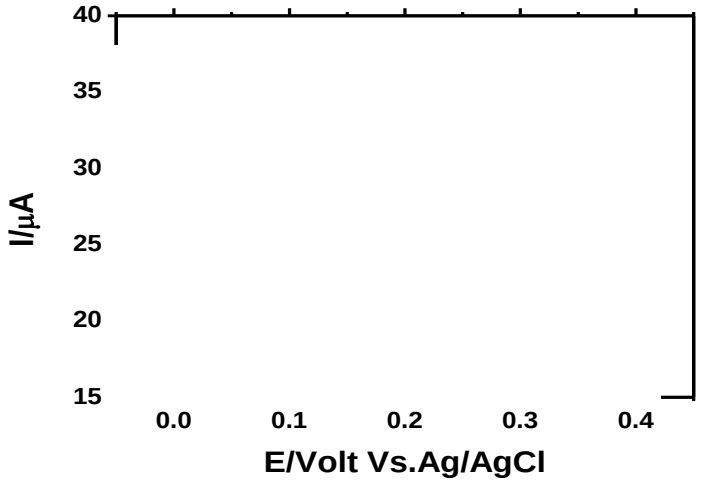
Sensors Specifications

	Cr(VI)	Cd(II)	Hg(II)
Power Consumption (W)	5	5	5
Power Supply (V)	12	12	12
Weight (Kg)	3	3	3
Sampling Water (l)	10 mL	10 mL	10 mL
Measurement time	30 min	30 min	30 min
Sensor maintenance	1 week	1 week	1 week
Detection limit	< 1μg/L=$2 \cdot 10^{-8}$ M	50 ng/L=$4.5 \cdot 10^{-10}$ M	<10ng/L=$5 \cdot 10^{-11}$ M
Accuracy	± 20 %	± 20 %	± 20 %
Range	1-100μg/L	0.05-10μg/L	0.01-1μg/L
Volume	50 mL	50 mL	50 mL
Output Signal	RS232/CAN BUS/Analogic signal		
Oriented (yes/no)	yes	yes	yes
Waste production (for measurement)	10-50 mL	10-50 mL	10-50 mL
Calibration Period (Manual)	every day	every day	every day

From: HydroNet_D2.1_User's needs analysis and HydroNet Platform requirements and specifications_v1.8

Concentrating the Analyte onf the Electrode Surface – Stripping Voltammetry

Anodic Stripping Analysis

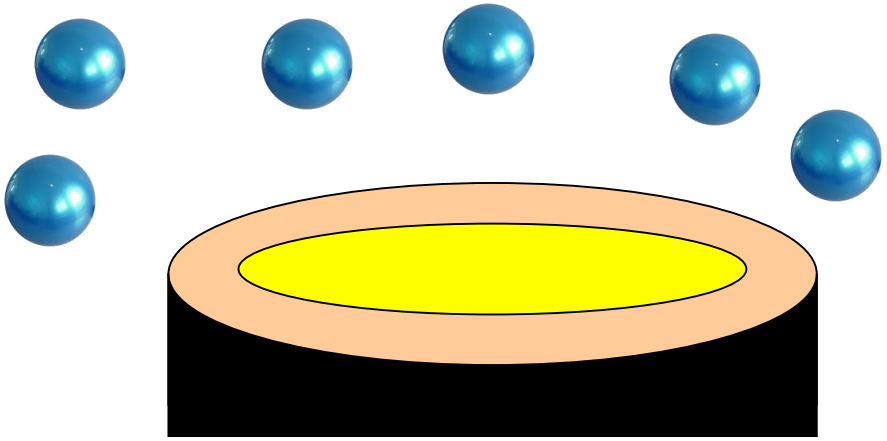


1. Metal Deposition (Reduction)

$$Hg^{2+} + 2e^{-} \longrightarrow Hg^{0}$$

2. LSV - Stripping (Oxidation)

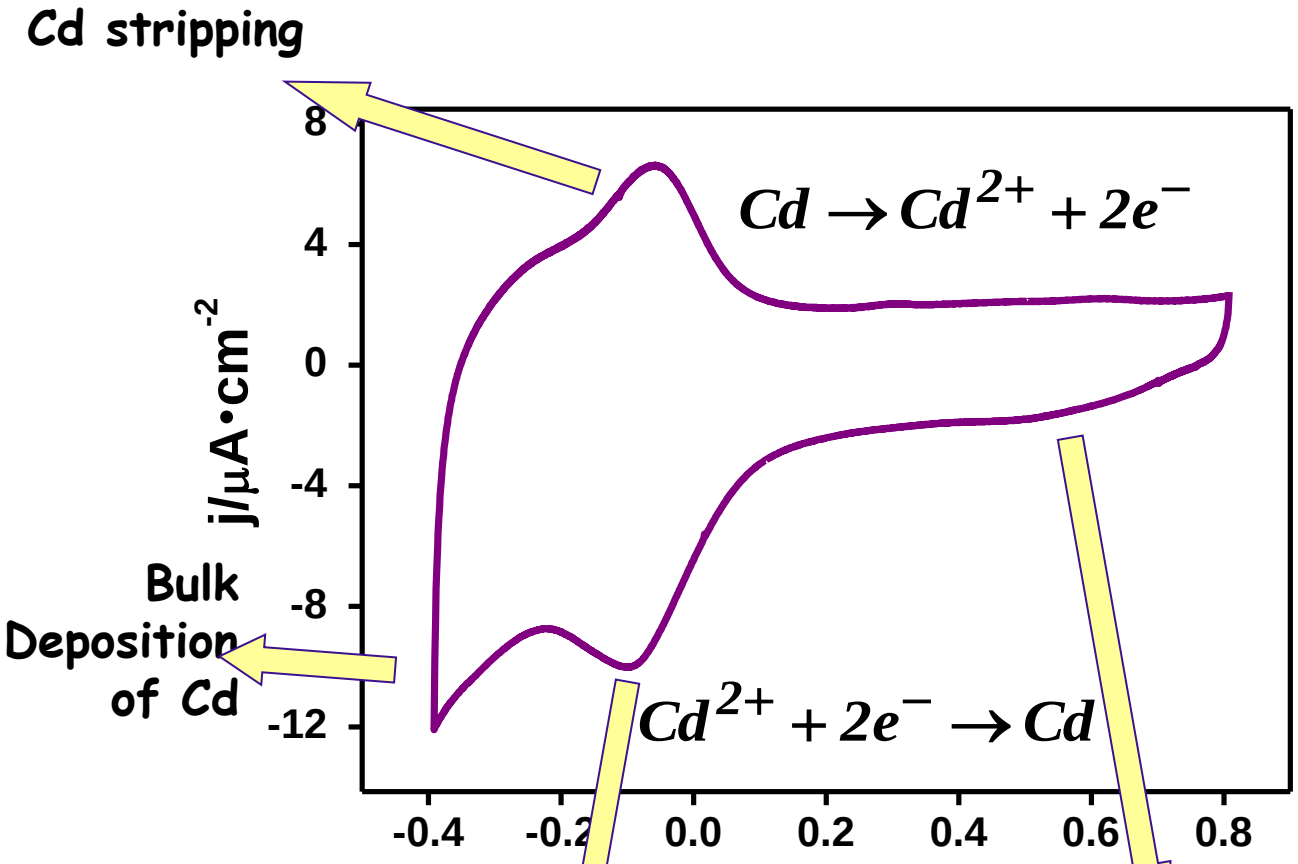
$$Hg^{0} \longrightarrow Hg^{2+} + 2e^{-}$$



$$Ox + ne^{-} \rightarrow Red$$

$$Q = nFA\Gamma$$

1. Sensor for Cd(II): The Under Potential Deposition Effect



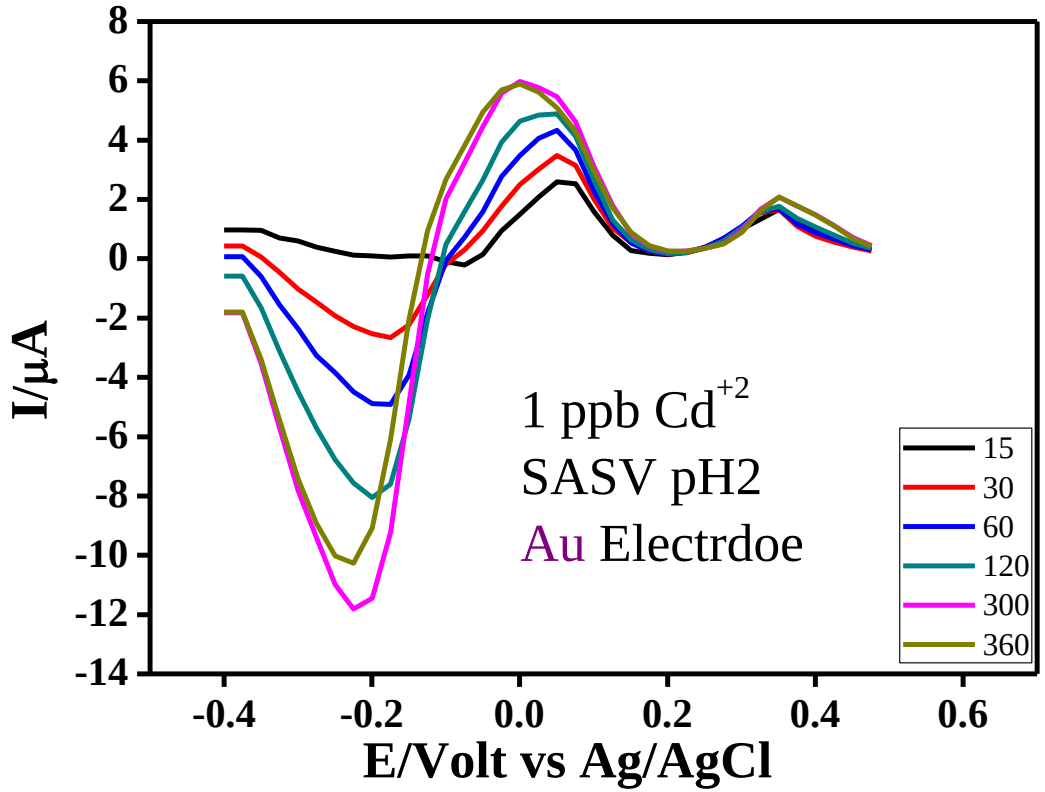
CV of 1mM Cd^{2+} in 0.1 M of H_2SO_4, Au electrode, scan rate 0.1 Vs^{-1}

UPD2

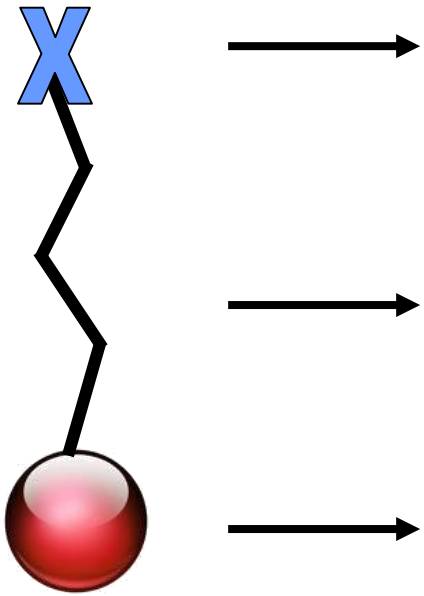
UPD1 (small)

T. Noyhouzer and D. Mandler, Anal. Chim. Acta 2010, 684, 1

The Effect of Time on Cd UPD on a Bare Au Electrode



Self Assembled Monolayers (SAM's)

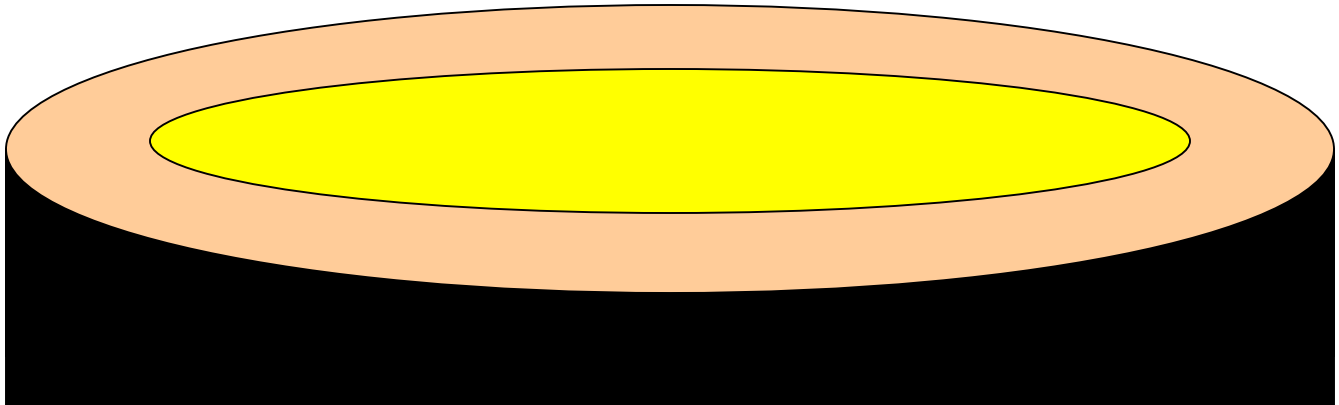


Functional Group :

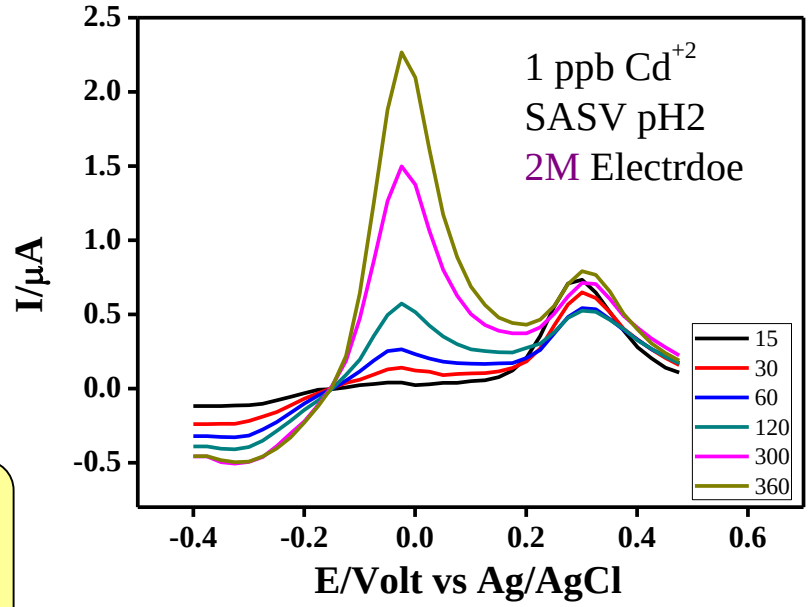
$-COOH$, $-SO_3$, $-NH_2$

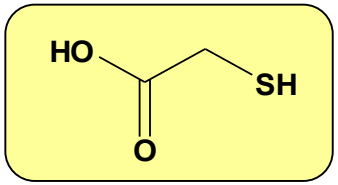
Tail : Alkyl Chain

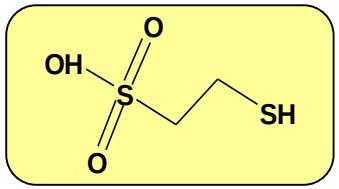
Head Group : SH

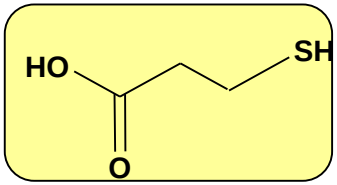


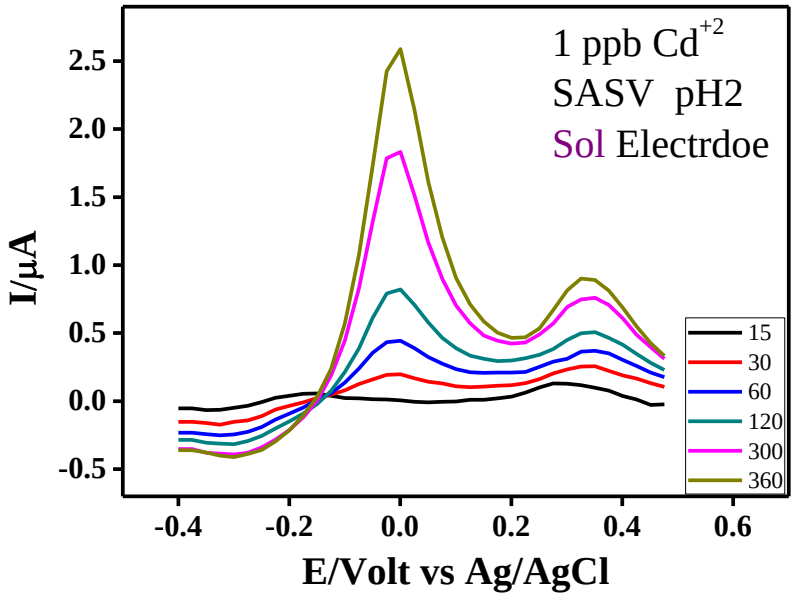
The Effect of a Self-Assembled Monolayer (SAM) on the UPD

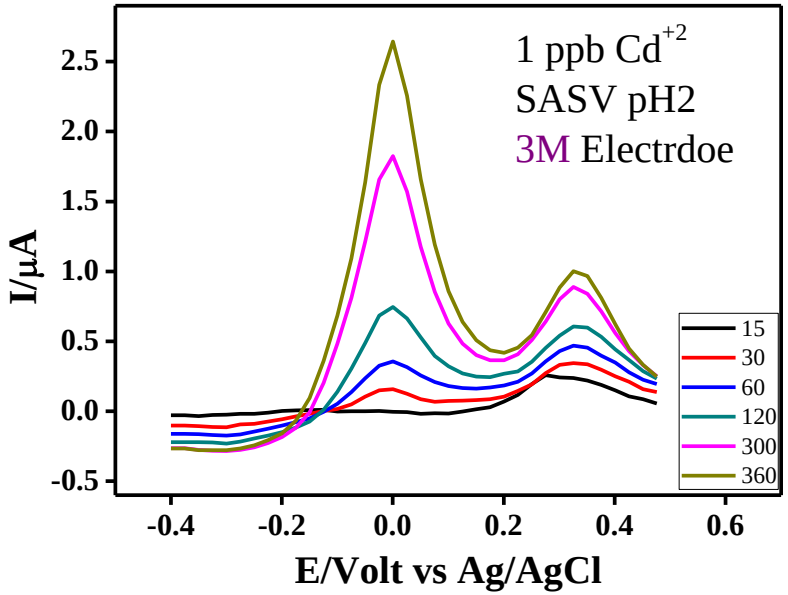






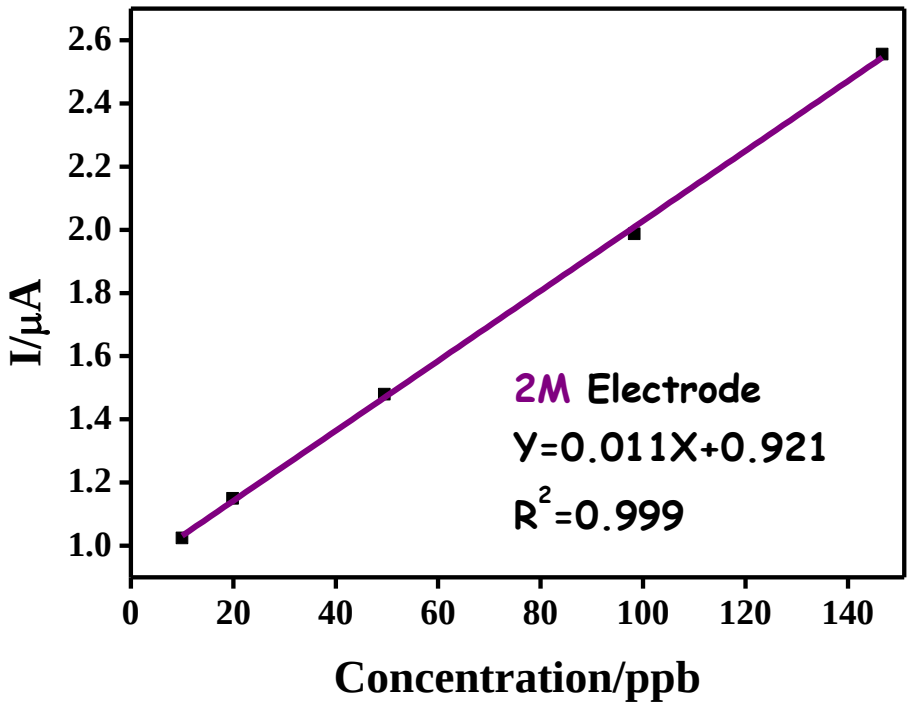


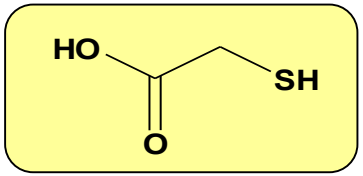




Calibration Curve

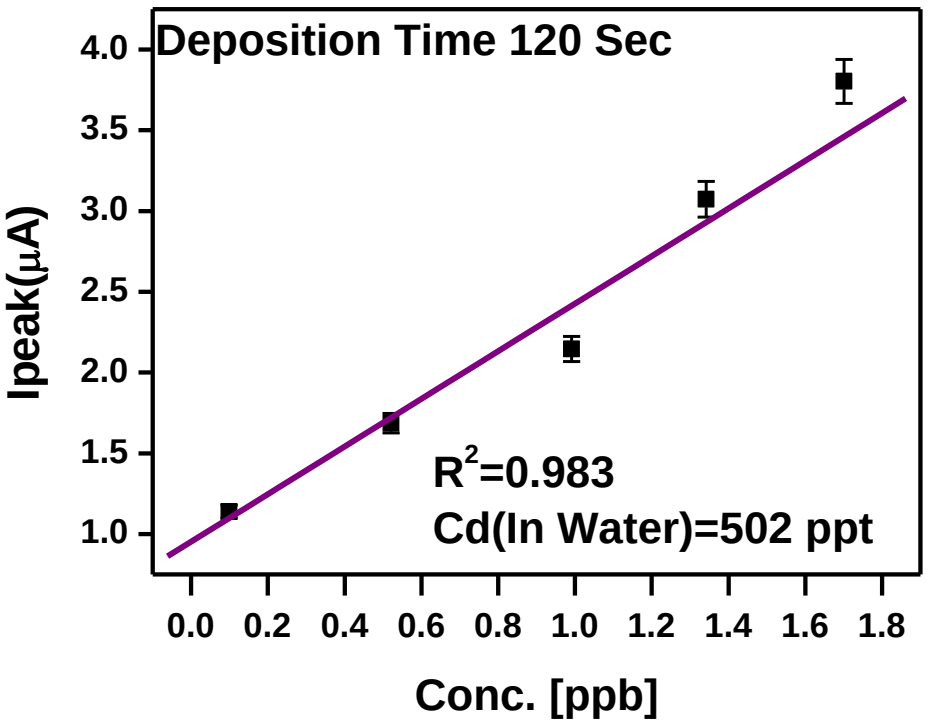
10 ppb to 150 ppb

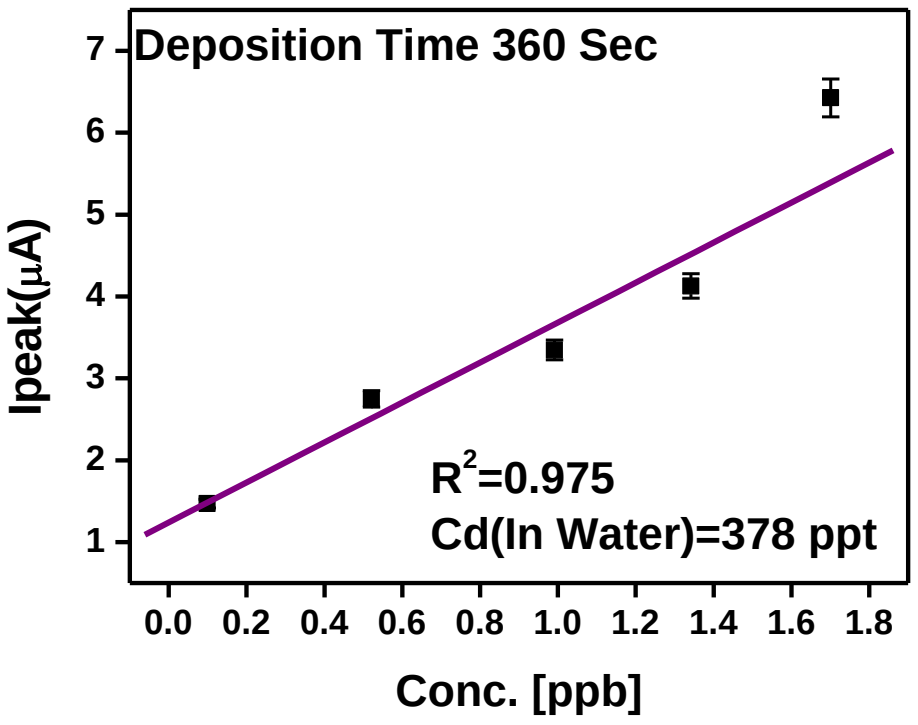




The height of the peak obtained from subtractive square wave anodic stripping voltammetry (SASV) of Cd^{2+} in buffer pH 2, E_{dep}=-0.4 V T_{dep} =360 sec

Measuring Cd in Tap Water

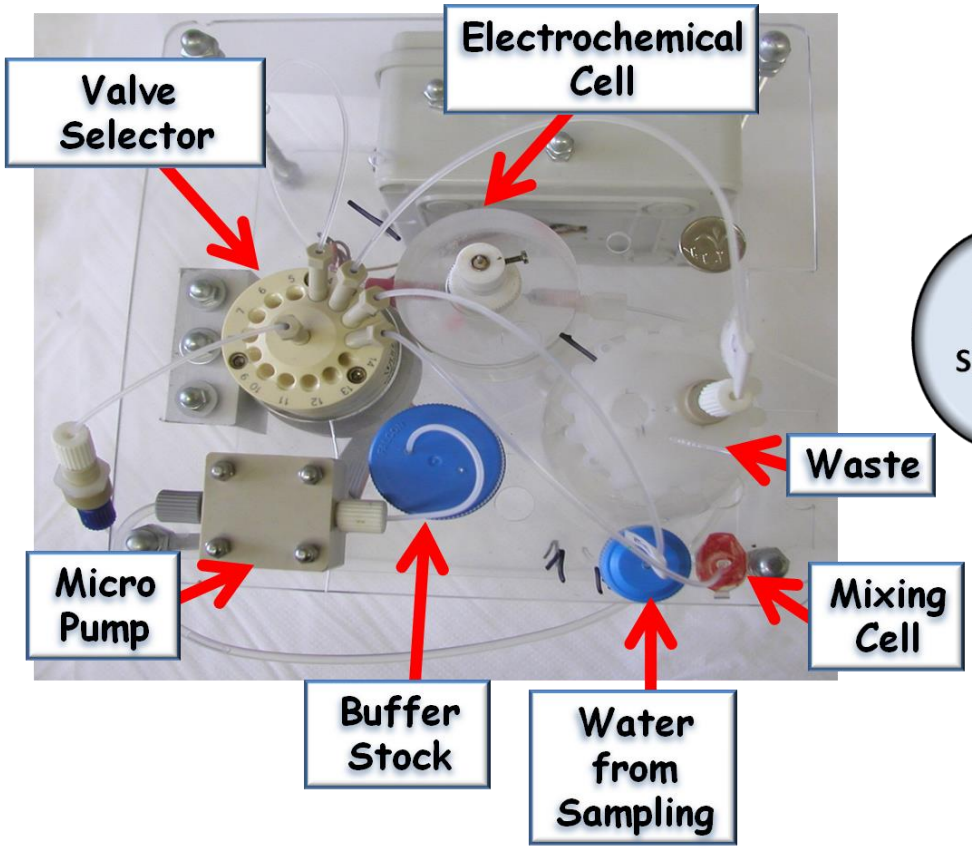


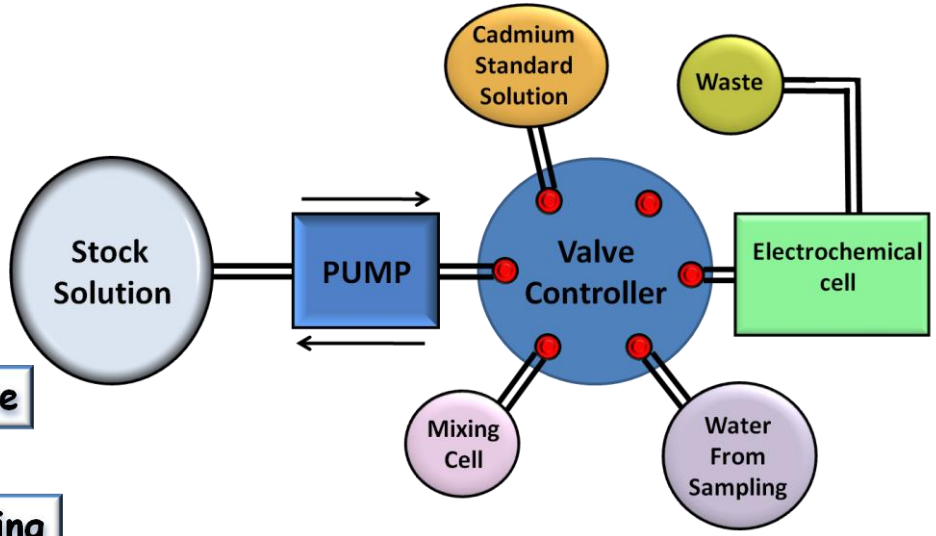


ICP-MS result was 320±8

The height of the peak obtained from a standard addition experiment using subtractive square wave anodic stripping voltammetry (SASV) of Tap Water acidified to pH 3, E_{dep}=-0.5 V

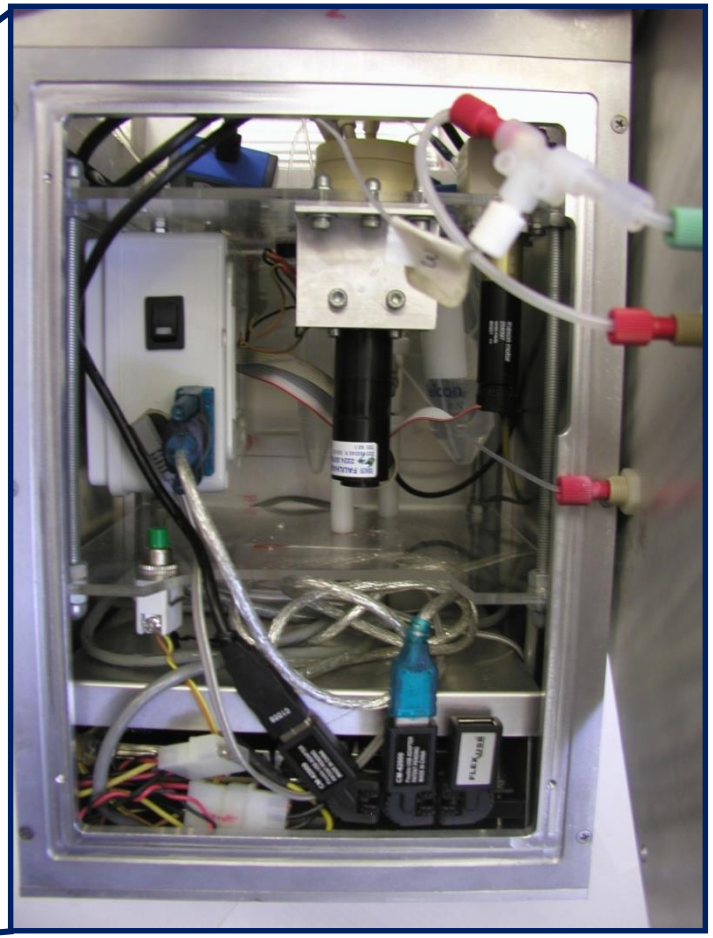
Designing a Flow System



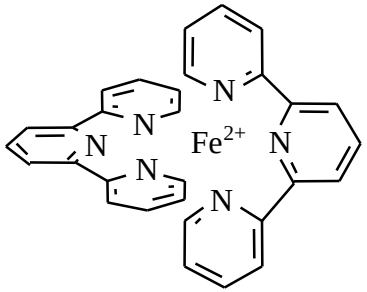


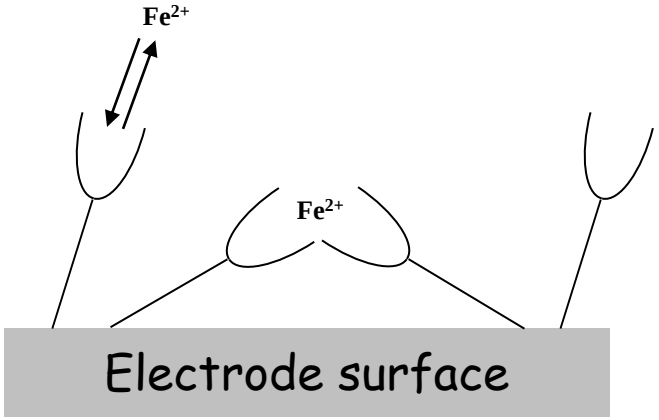
Development of an Automated Flow System

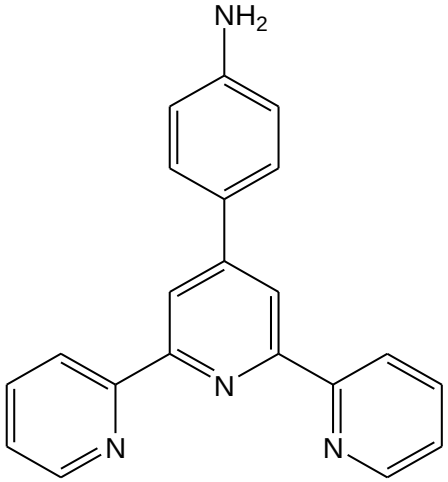
Complete System



2. Electrochemical Determination of Fe(II) by a Terpyridine-Based Self-Assembled Monolayer



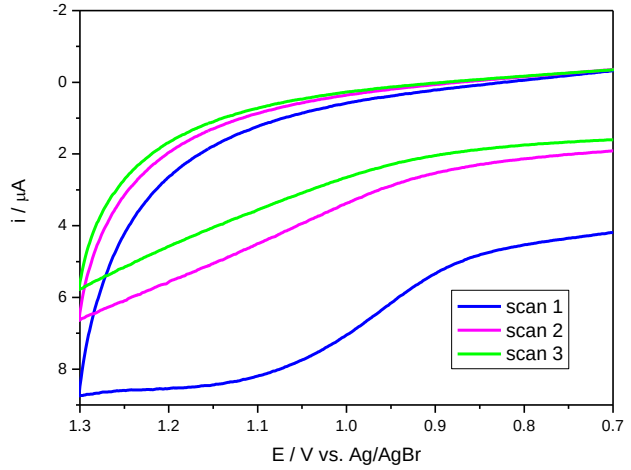


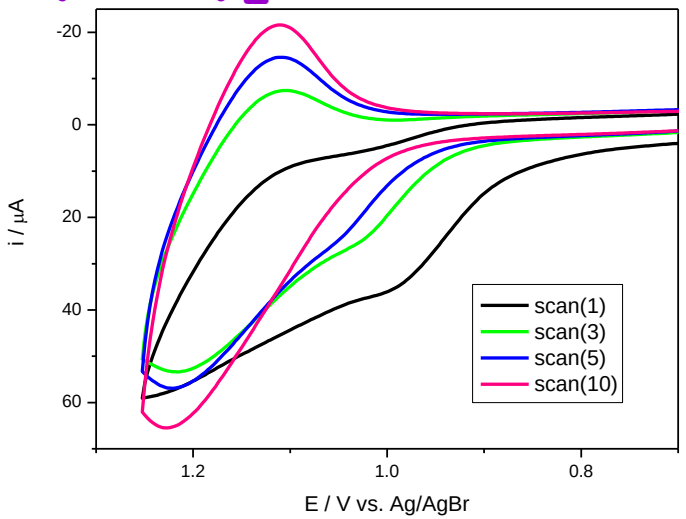


APT = p-anilino-2,2':6',2''-terpyridine

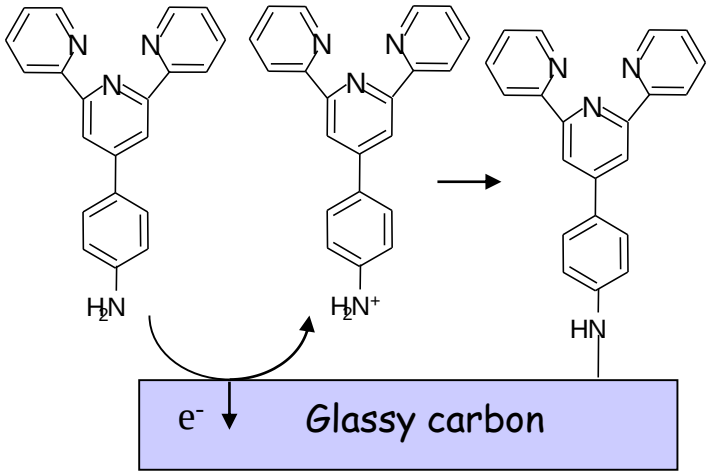
- Positive redox potential ~1.0 V vs. Ag/AgCl
- Formation of an octahedral complex
- Very large complexation constant
- Colorful

Attachment of APT and $Fe(APT)_2^{2+}$ onto ITO

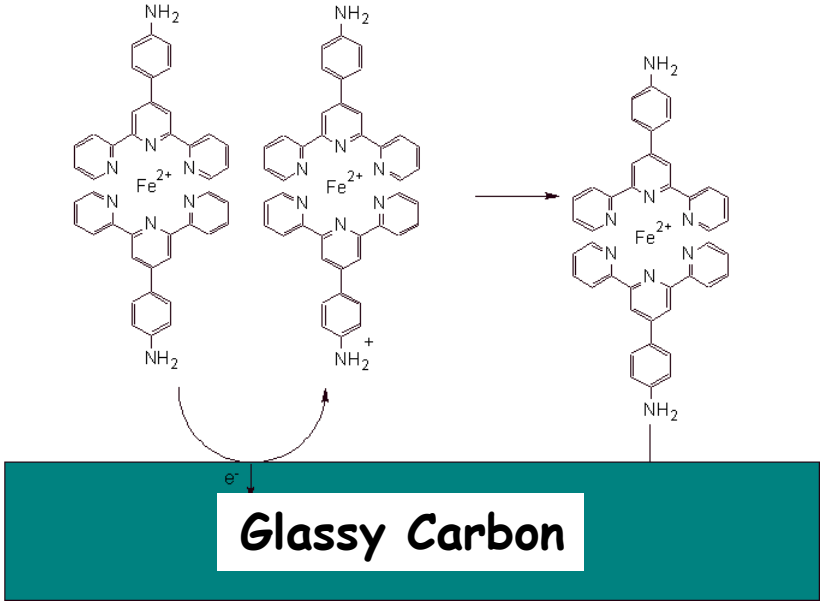




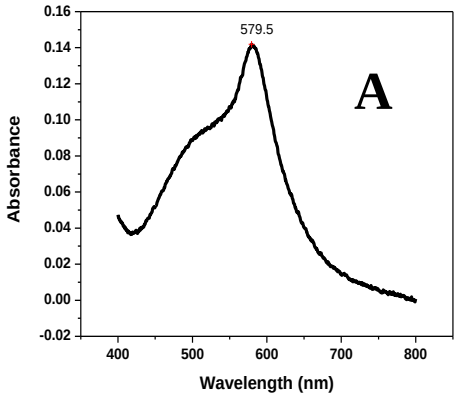
Oxidation of APT (1 mM) on GC in ACN, 0.1M TBATFB



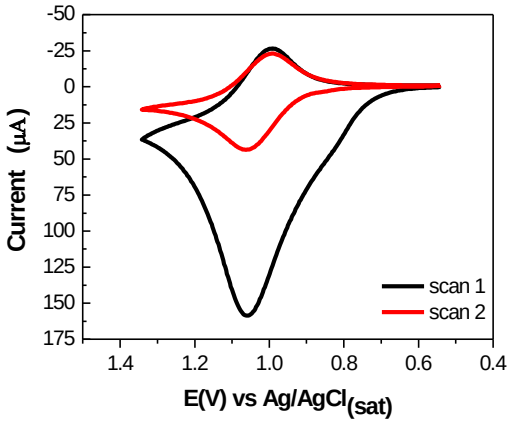
Oxidation of $Fe(APT)_2^{2+}$ (0.5 mM) on GC in ACN, 0.1M TBATFB



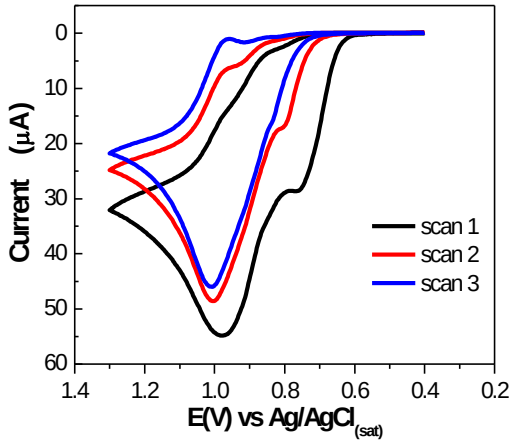
Attachment of $Fe(APT)_2^{2+}$ onto ITO



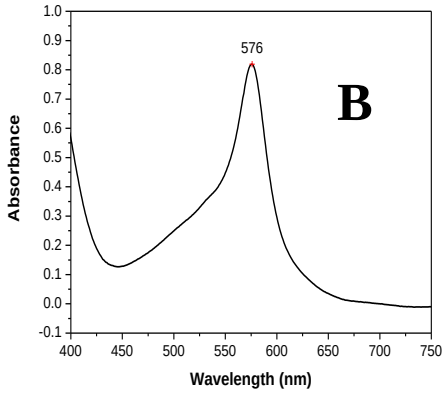
$\Gamma = 4.6.10^{-9}$ mol·cm^{-2}



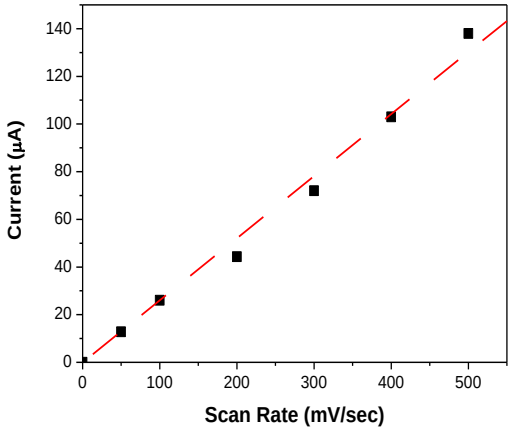
CV (50 mV·s^{-1}) of the modified ITO in 0.1 M K_2SO_4 (pH4.0)

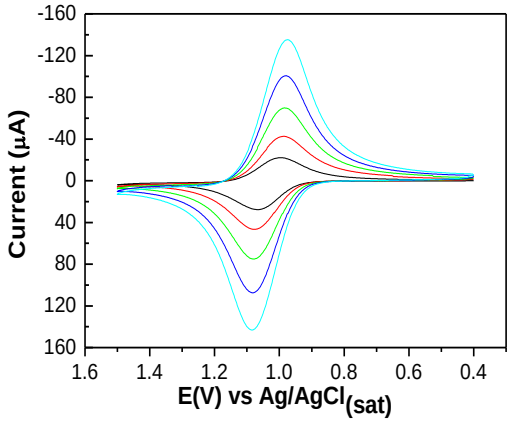


CV (50 mV·s^{-1}) of 1 mM $Fe(APT)_2^{2+}$ in 0.1 M K_2SO_4 (pH4.0)



Absorption spectrum of: A- ITO/$Fe(APT)_2^{2+}$ and B- $Fe(APT)_2^{2+}$ in ethanol





$\Gamma = 3 \cdot 10^{-9}$ mol·cm^{-2}

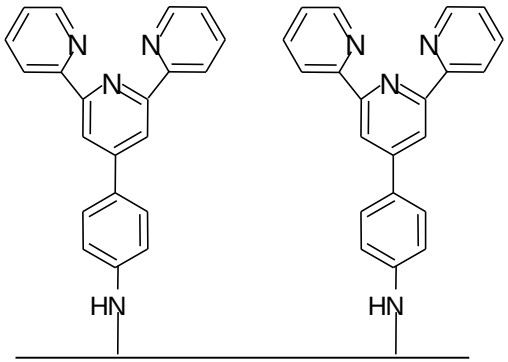
CV of ITO/$Fe(APT)_2^{2+}$ in 0.1 M K_2SO_4 (pH4.0) at different scan rates and the dependence of the peak current on scan rate

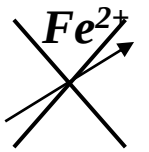
Observations:

- Trying to extract Fe^{2+} by the APT (aniline-tpy) monolayer was not successful
- Extracting Fe^{2+} by the $Fe(APT)_2^{2+}$ was also not successful
- Extracting $Fe(tpy)_2^{2+}$ was questionable
- The monolayers were studied by XPS, capacity, contact angle and other surface techniques suggesting that the monolayers are not highly organized

Conclusions:

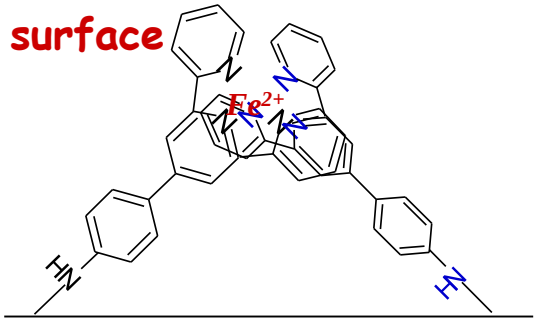
- APT can be covalently attached onto the surface, however, is not sufficient flexible to allow complexation by two adjacent ligands
- Probably a ligand substitution reaction can take place on the surface

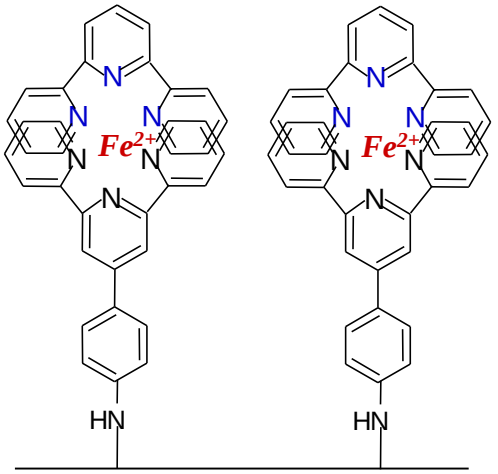




$Fe(tpy)_2^{2+}$

?



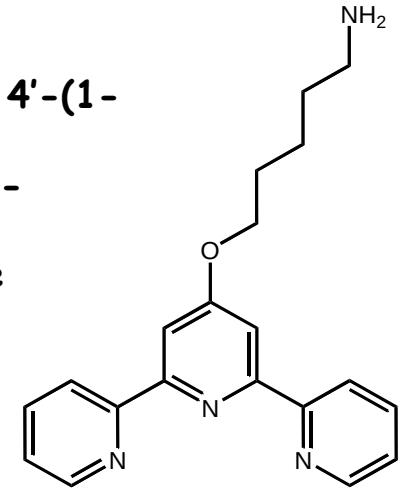


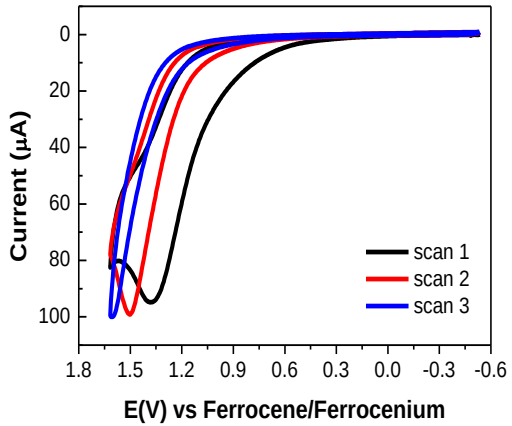
Solution:

- Synthesize a more flexible arm

Attachment of APOTPY onto ITO

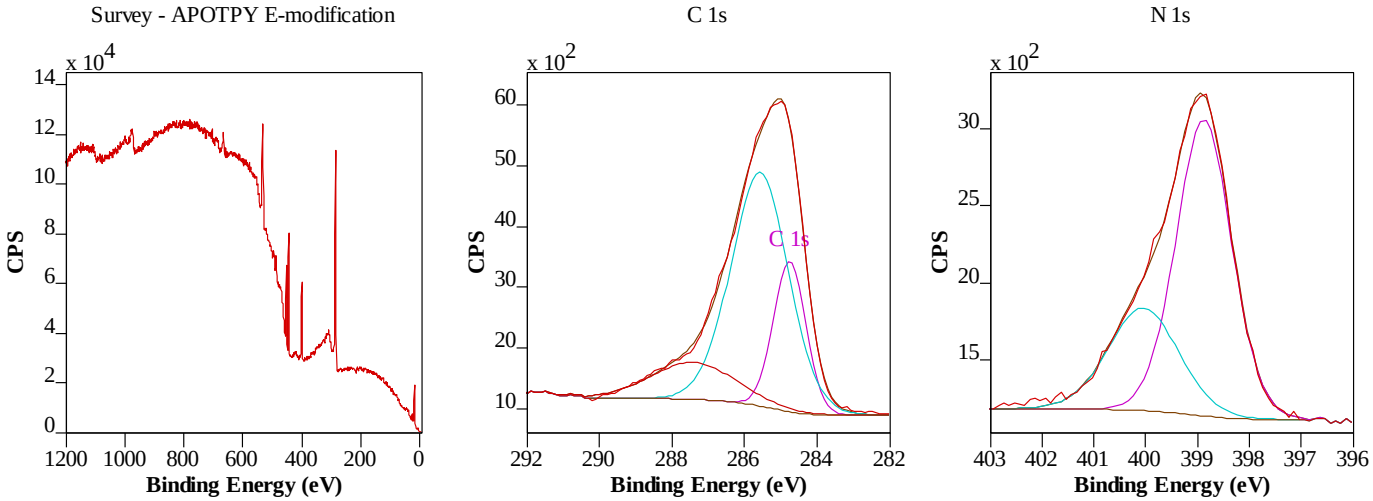
APOTPY = 4'-(1-amino-5-pentanoxy)-2,2':6',2''-terpyridine





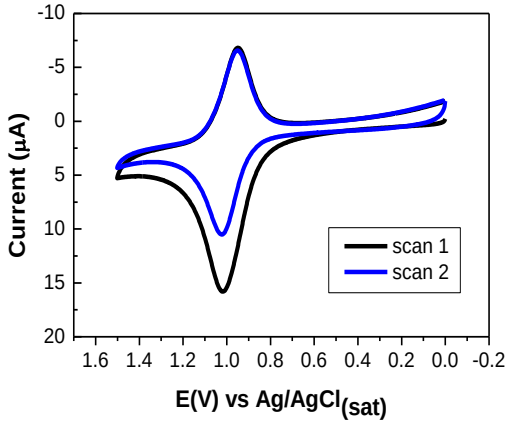
CV (50 $mV \cdot s^{-1}$)of ITO APOTPY 1 mM and 0.1 M TBATFB in ACN

XPS of APOTPY

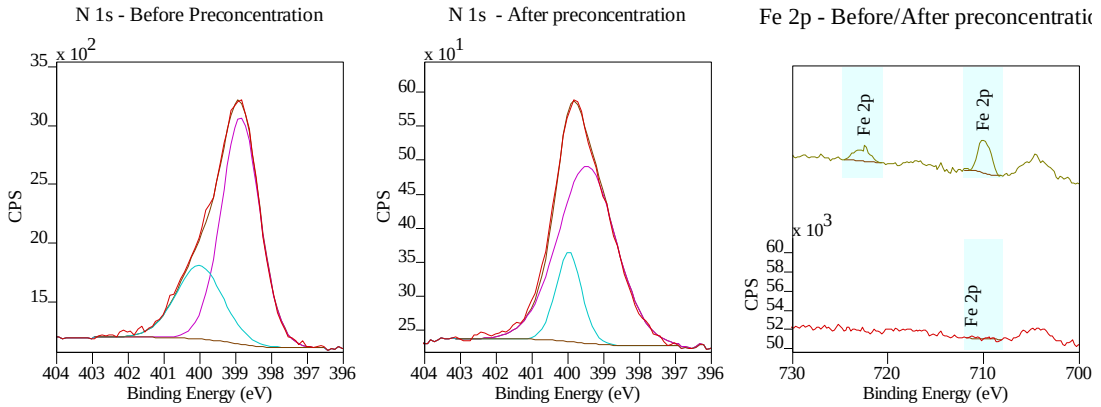


APOTPY/ITO

Extraction of Fe^{2+} by an ITO/APOTPY



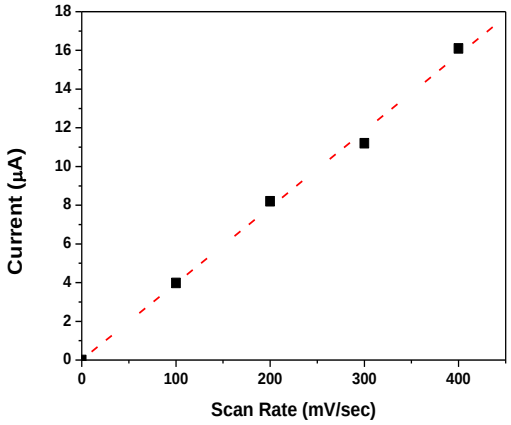
CV (50 $mV \cdot s^{-1}$) of ITO/APOTPY after extraction of Fe^{2+} (1 mM)

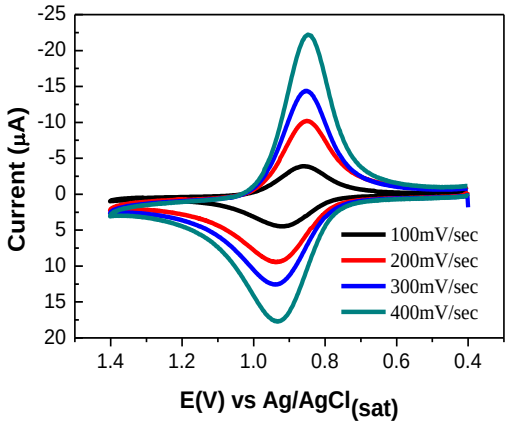


After

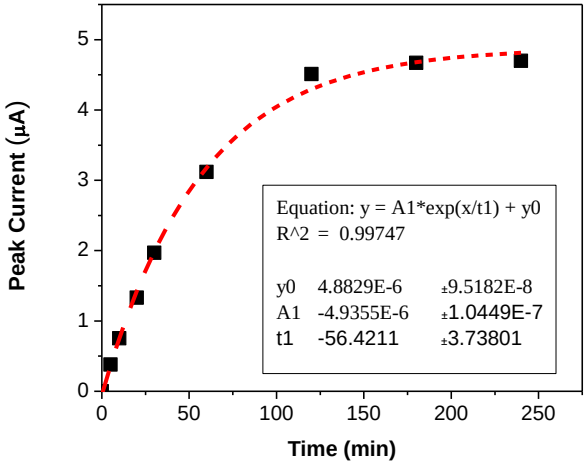
Before

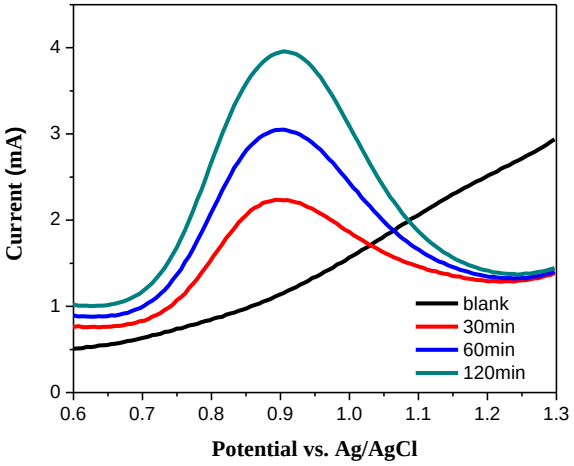
XPS of an ITO/APOTPY electrode after extraction of Fe^{2+}





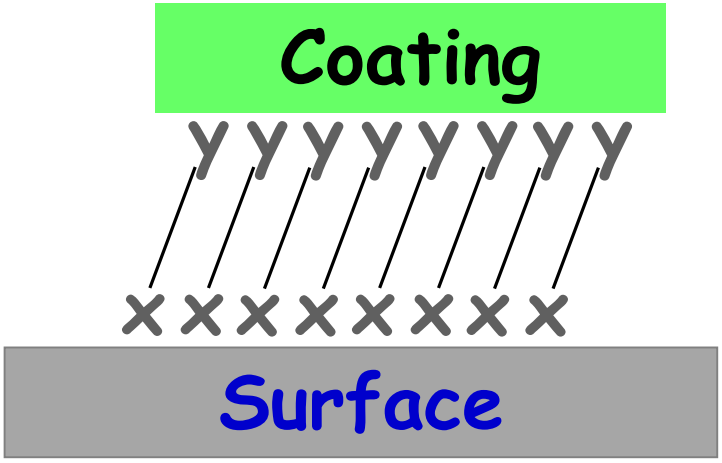
Effect of scan rate $\Gamma = 2.8 \cdot 10^{-10} mol \cdot cm^{-2}$





Effect of time of preconcentration (SWV, 0.1 mM Fe^{2+})

3. SAM for Increasing the Adhesion



Coating medical implants

Metoki et al, Langmuir, 2014, *30*, 6791

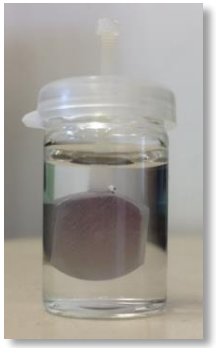
Orthopedic Implants

- Arthroplasty is an operative procedure of orthopedic surgery, in which the hip joint is replaced.[1]

- According to the American Academy of Orthopedic Surgeons (AAOS), in 2008, there were a total of 277,399 total hip replacements performed in the US.[2]

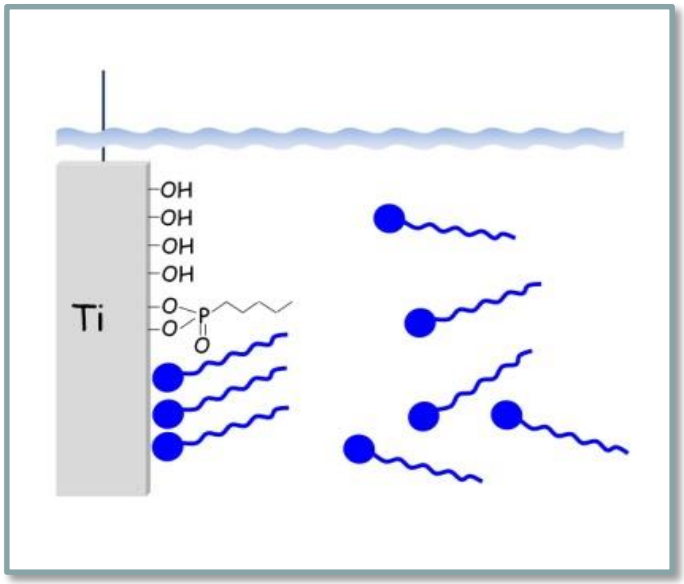
Ti-6Al-4V

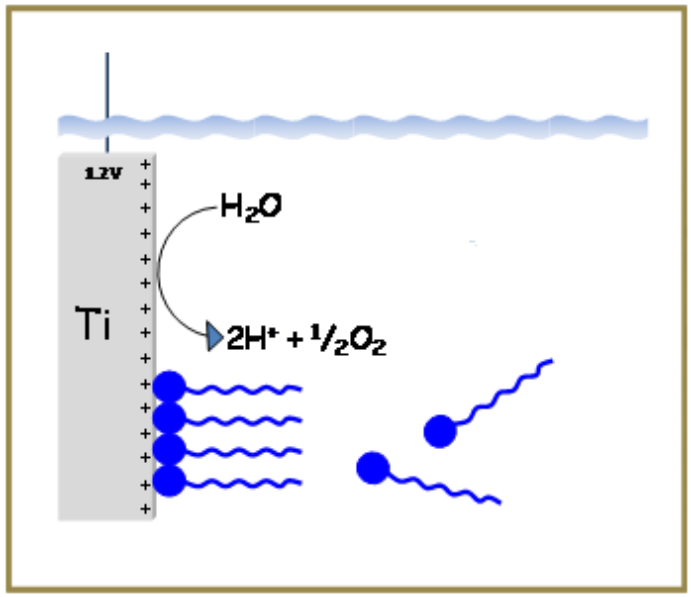
Preparations of Alkyl Phosphonic Acid SAM on Titanium Surface

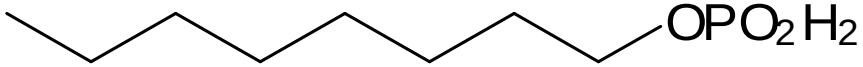


Chemically prepared

Electrochemically prepared

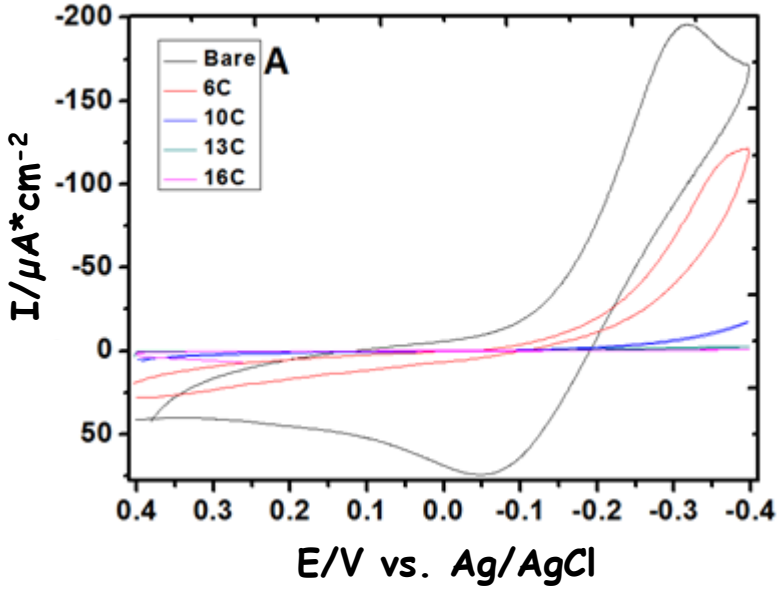






Preparations of Alkyl Phosphonic Acid SAM on Titanium Surface

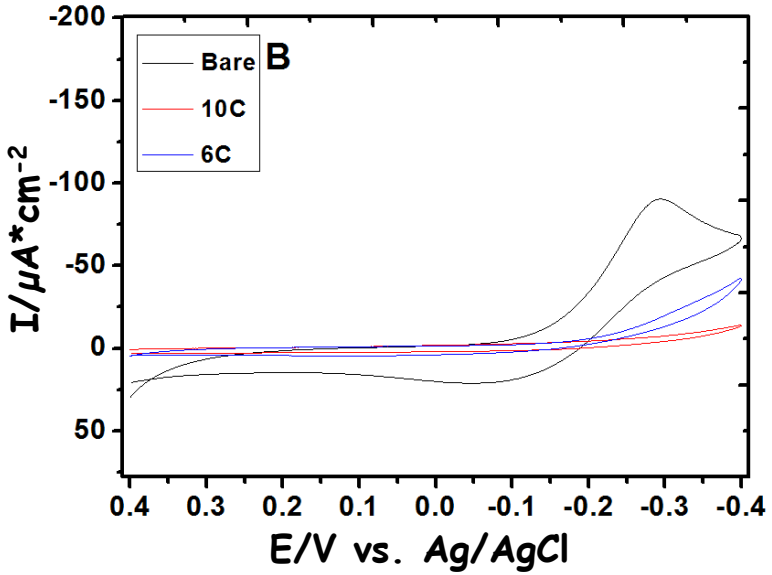
Chemically prepared



$$I \propto e^{-d}$$

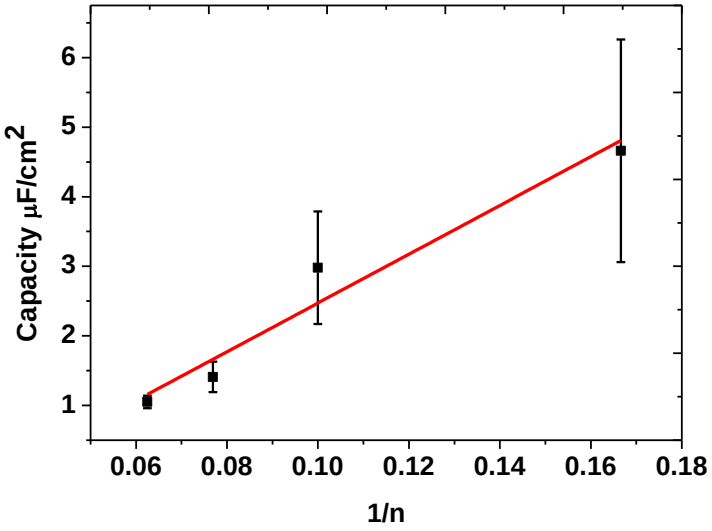
$Ru(NH_3)_6^{3+} + e^- \rightarrow Ru(NH_3)_6^{2+}$

Electrochemically prepared



Preparations of Alkyl Phosphonic Acid SAM on Titanium Surface

Sample	Chemisorbed	Electrochemically prepared
	Mean Capacitance [μF/cm^2]	Mean Capacitance [μF/cm^2]
Control	39.25±8.14	39.89±1.06
6C	4.66±1.60	5.42±1.35
10C	2.98±0.81	2.70±0.27
13C	1.41±0.22	-
16C	1.05±0.09	-



$$C_{dl} = \frac{\varepsilon \varepsilon_0 A}{d}$$

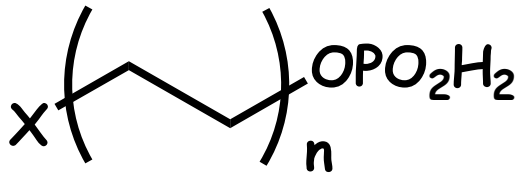
Controlling the Deposition of Hydroxyapatite

$$Ca_{10}(PO_4)_6(OH)_2$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

$$HPO_4^{2-} + OH^- \rightarrow PO_4^{3-}$$

$$10Ca^{2+} + 6PO_4^{3-} + 2OH^- \rightarrow Ca_{10}(PO_4)_6(OH)_2$$



- Length of chain:

  PO_3H_2-$(CH_2)_n$-PO_3H_2, n=3,6,12

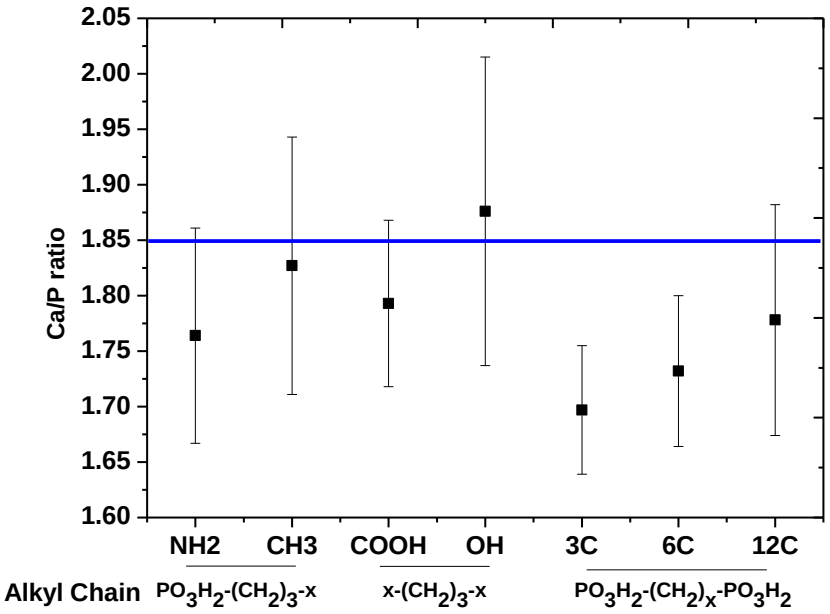
- End group charge:

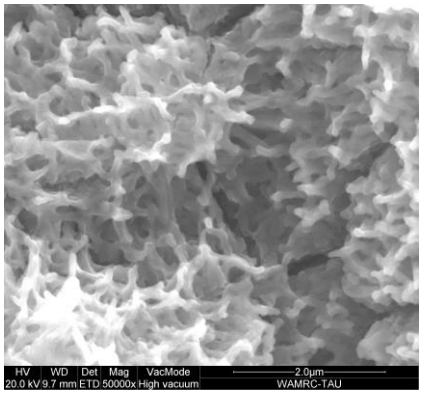
  PO_3H_2-$(CH_2)_3$-x, x= PO_3H_2, NH_2, CH_3

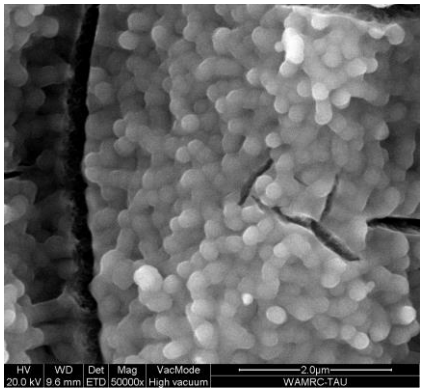
- Anchoring group:

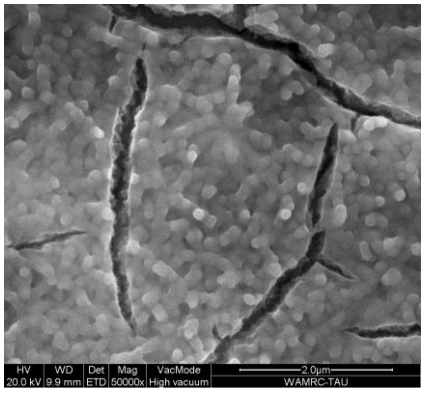
  x-$(CH_2)_3$-x, x= PO_3H_2, COOH, OH

Calcium Phosphate Coatings and SAMs



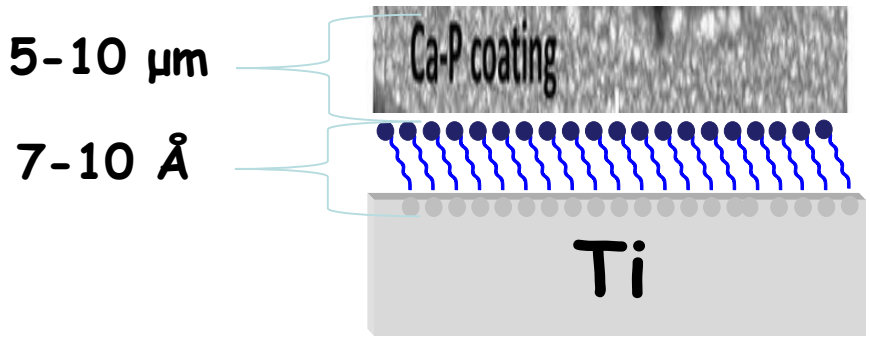




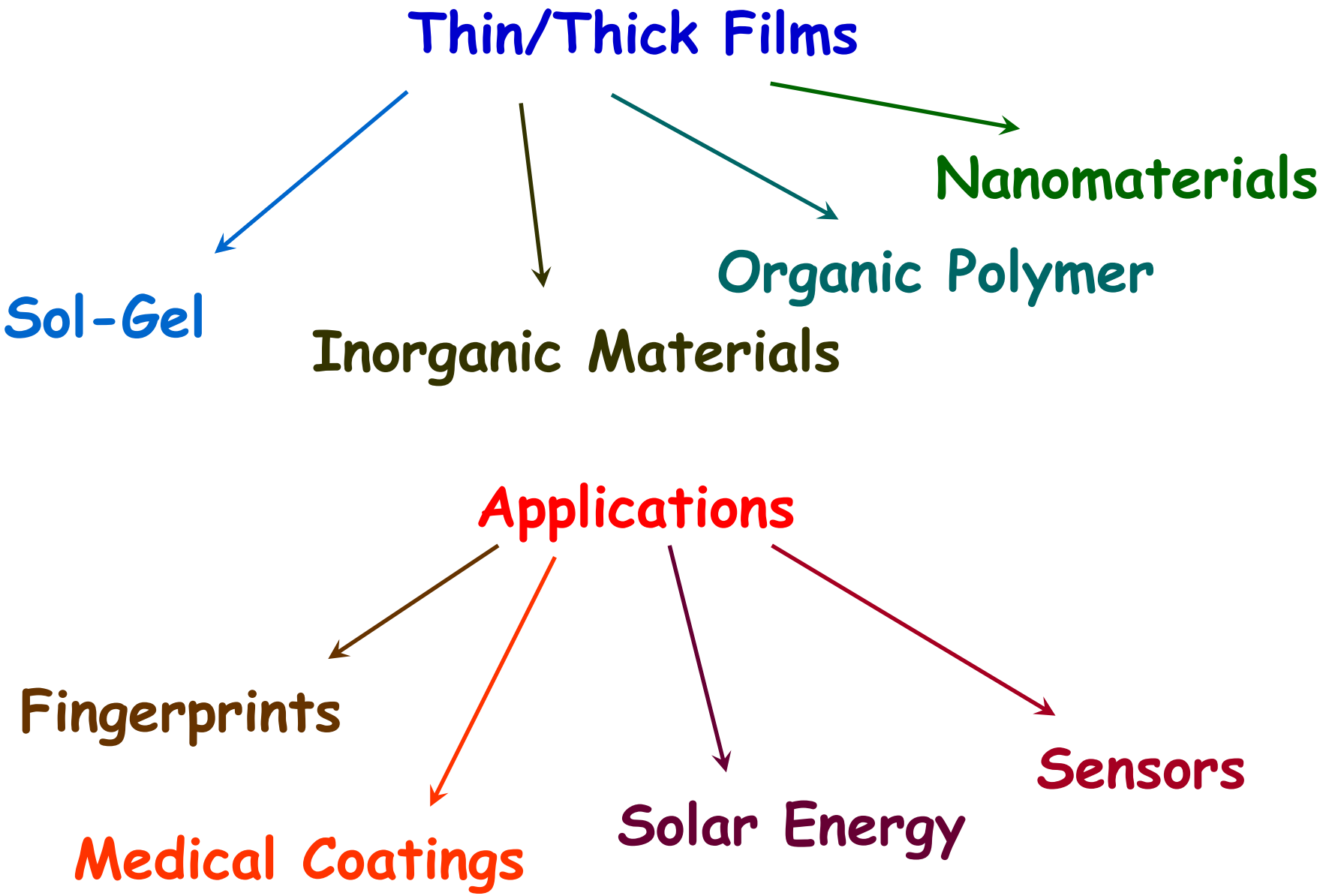


The Effect of the SAM on Stress Failure Test

Sample	Stress to failure [MPa] (GB)	Stress to failure [MPa] (NaOH)
No SAM	8.08±0.52	26.18±6.60
PO_3H_2-$(CH_2)_3$-PO_3H_2	48.45±6.12	22.6±4.48
PO_3H_2-$(CH_2)_6$-PO_3H_2	37.26±6.86	45.52±16.36



It's time to move to thicker films…



The Sol-Gel Process

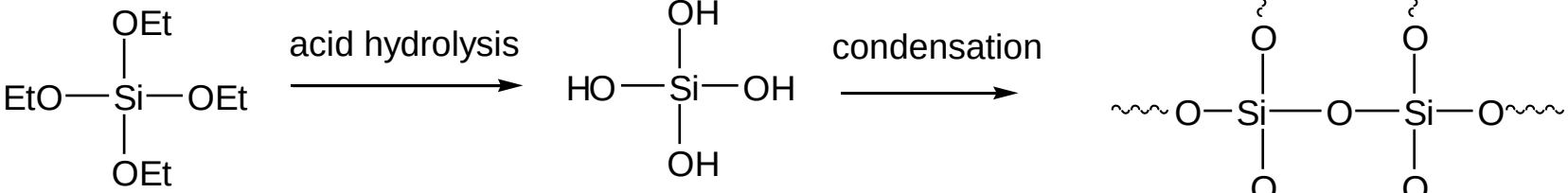
$MX_4 \longrightarrow MO_2$

M= Si, Zr, W, Ti…

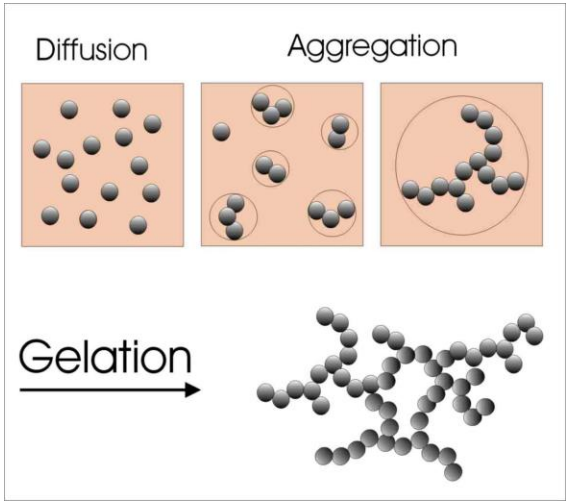
X= RO, RO_2, X (halides)…

Hydrolysis $M(OR)_4 + H_2O \xrightarrow{H^+ \text{ or } OH^-} M(OR)_3(OH) + ROH$

Condensation $M(OR')_4 + M(OR)_4 \longrightarrow (R'O)_3M\text{-}O\text{-}M(OR)_3 + ROR'$



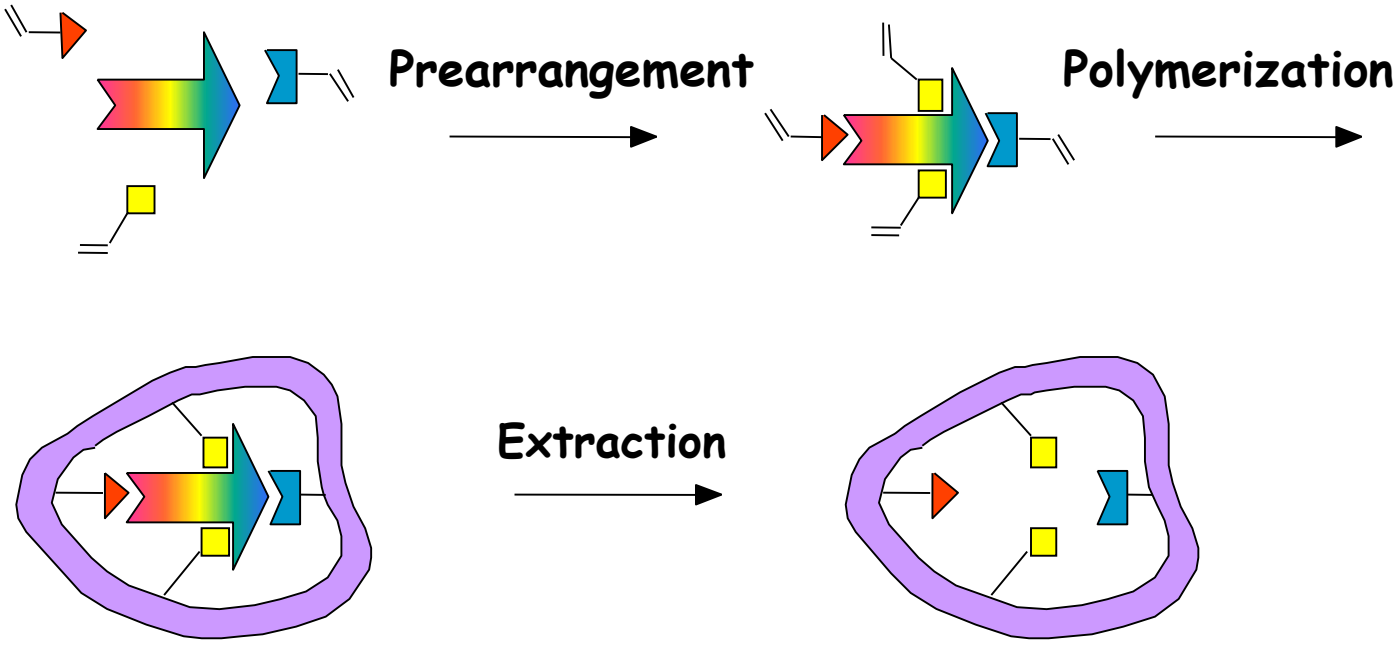
TEOS
(tetraethoxy silane)



The final product is a 3-D network based on M-O-M bonds

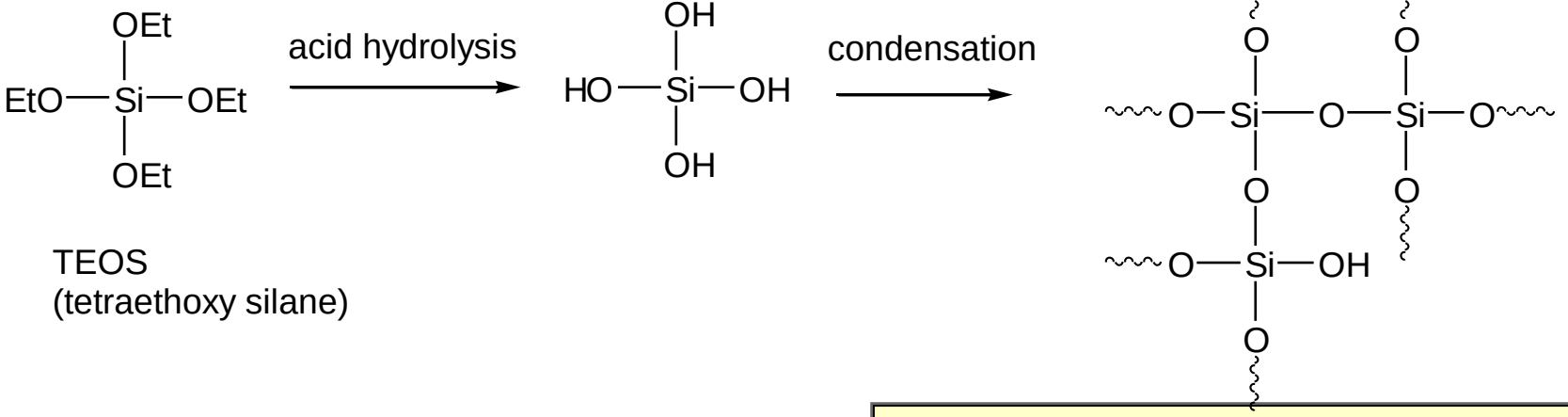
The properties of the network depend on R and M

4. Molecularly Imprinted Polymers (MIP)

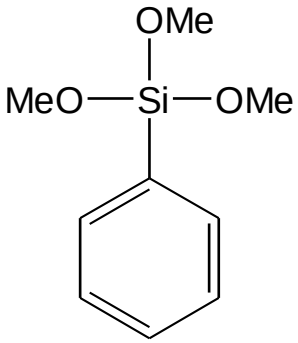


Supramolecular interactions such as hydrogen bonding, p-p interactions, hydrophobic-hydrophilic and electrostatic interactions are used

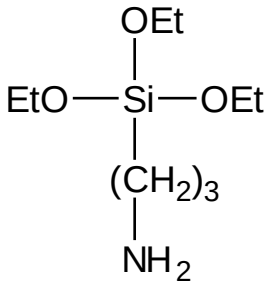
Determination of Parathion
Formation of a Molecularly Imprinted Polymer



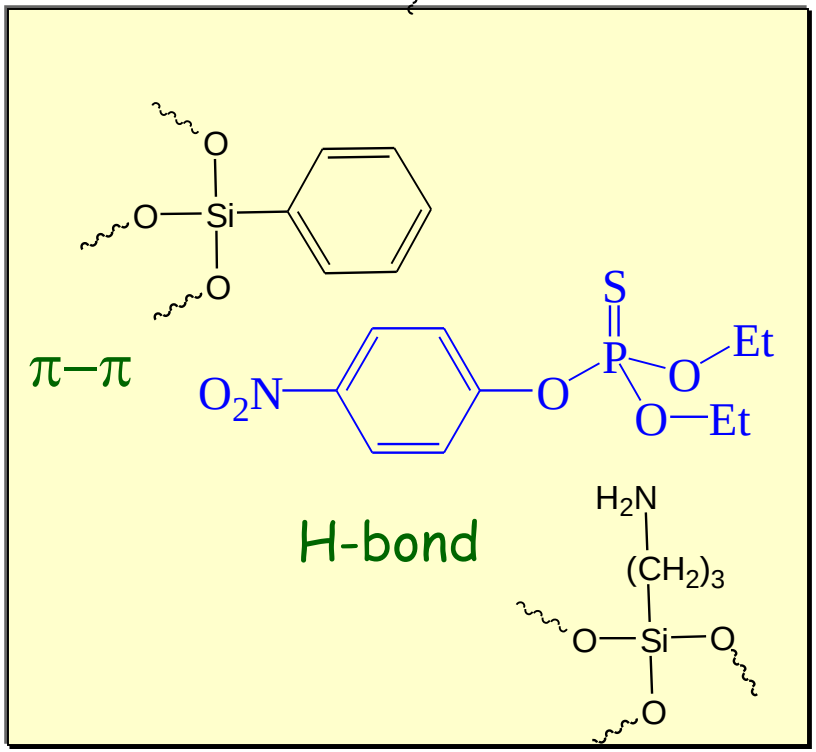
TEOS
(tetraethoxy silane)



PTMOS
Phenyl trimethoxy silane

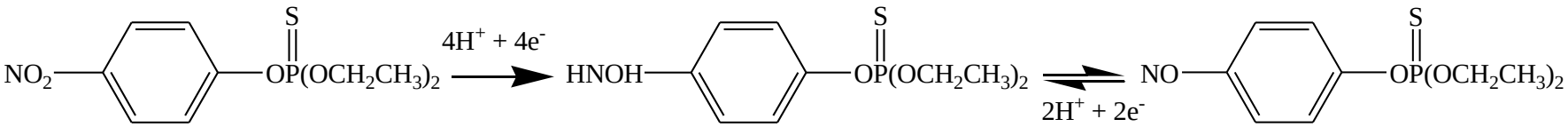


APTES
aminopropyl triethoxy silane

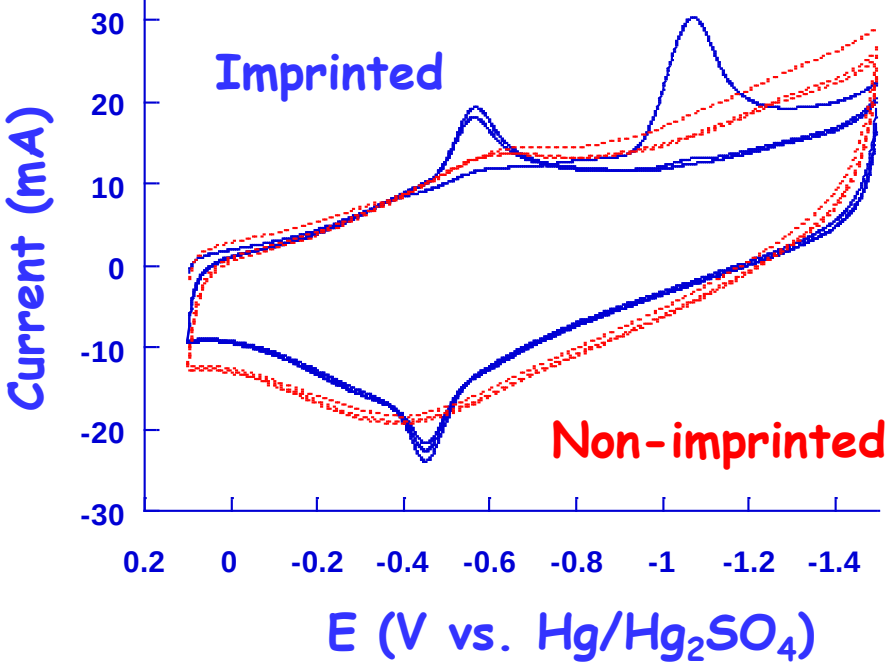


Anal. Chem., 2004, 76, 120-126

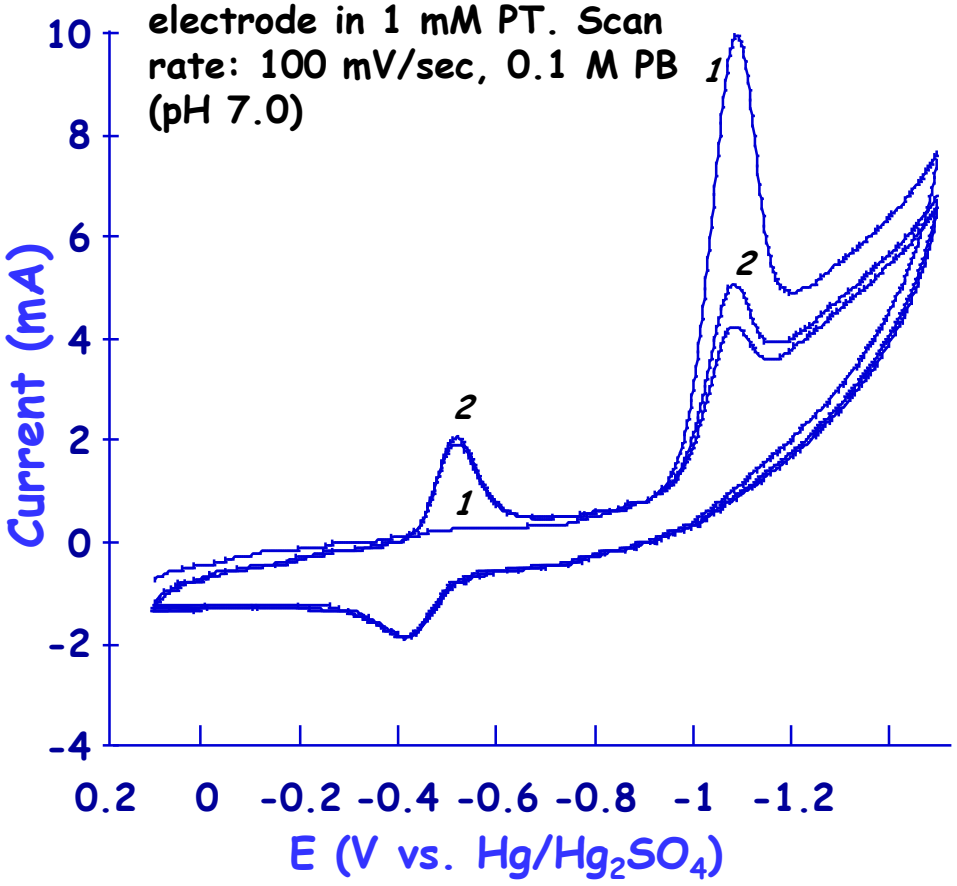
Cyclic Voltammetry of Parathion



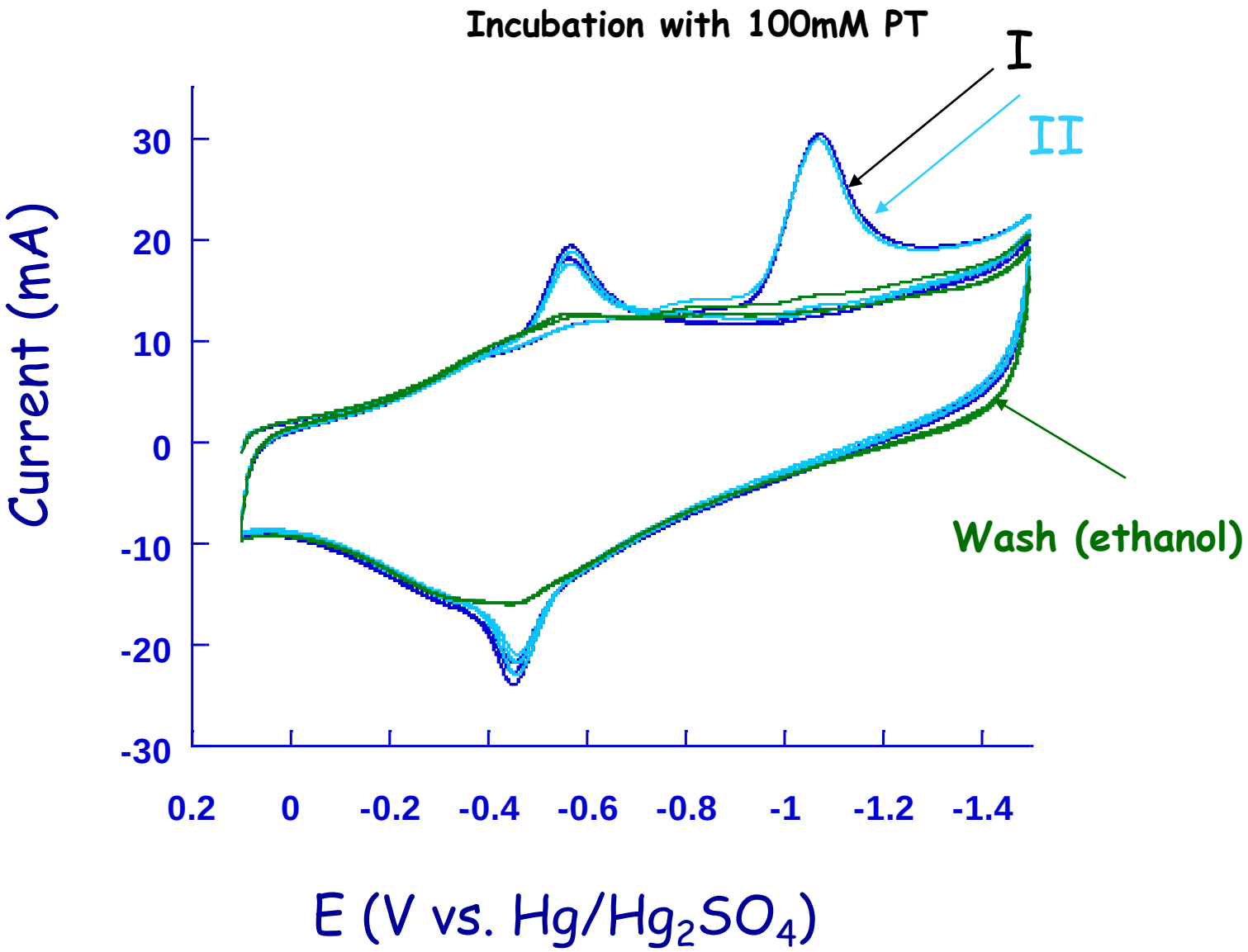
Cyclic voltammetry of a GC electrode coated with a PT imprinted film (blue) and non-imprinted film (red) after incubation in 0.1 mM solution of PT in 0.1M PB (pH 7.0) for 10 min. Scan rate: 100 mV/sec, 0.1 M PB (pH 7.0)



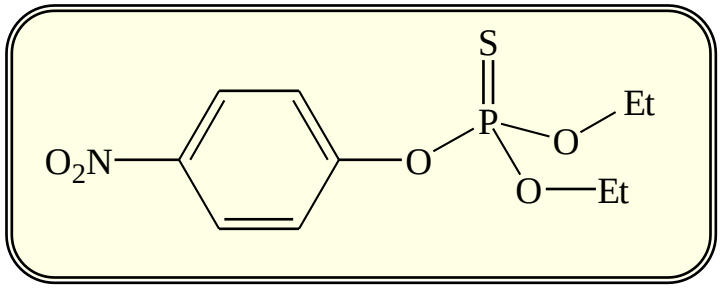
Cyclic voltammetry of a GC electrode in 1 mM PT. Scan rate: 100 mV/sec, 0.1 M PB (pH 7.0)



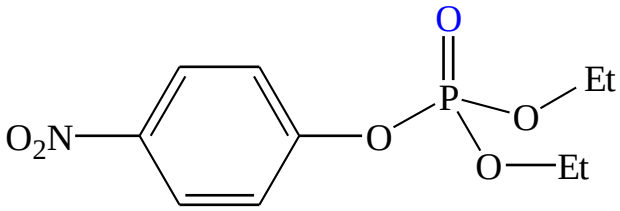
Recycling of the electrode



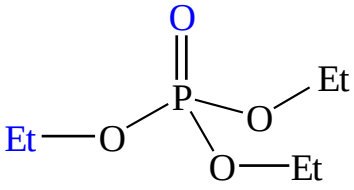
Selectivity in Binding Parathion vs. Derivatives



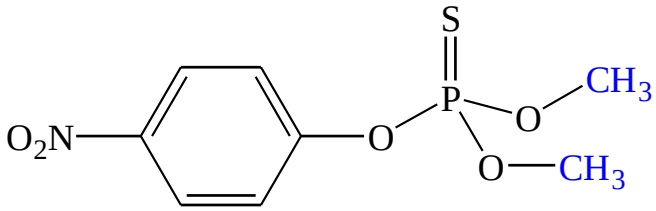
parathion



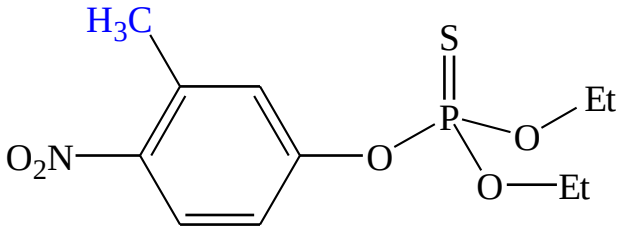
paraoxon



TEP

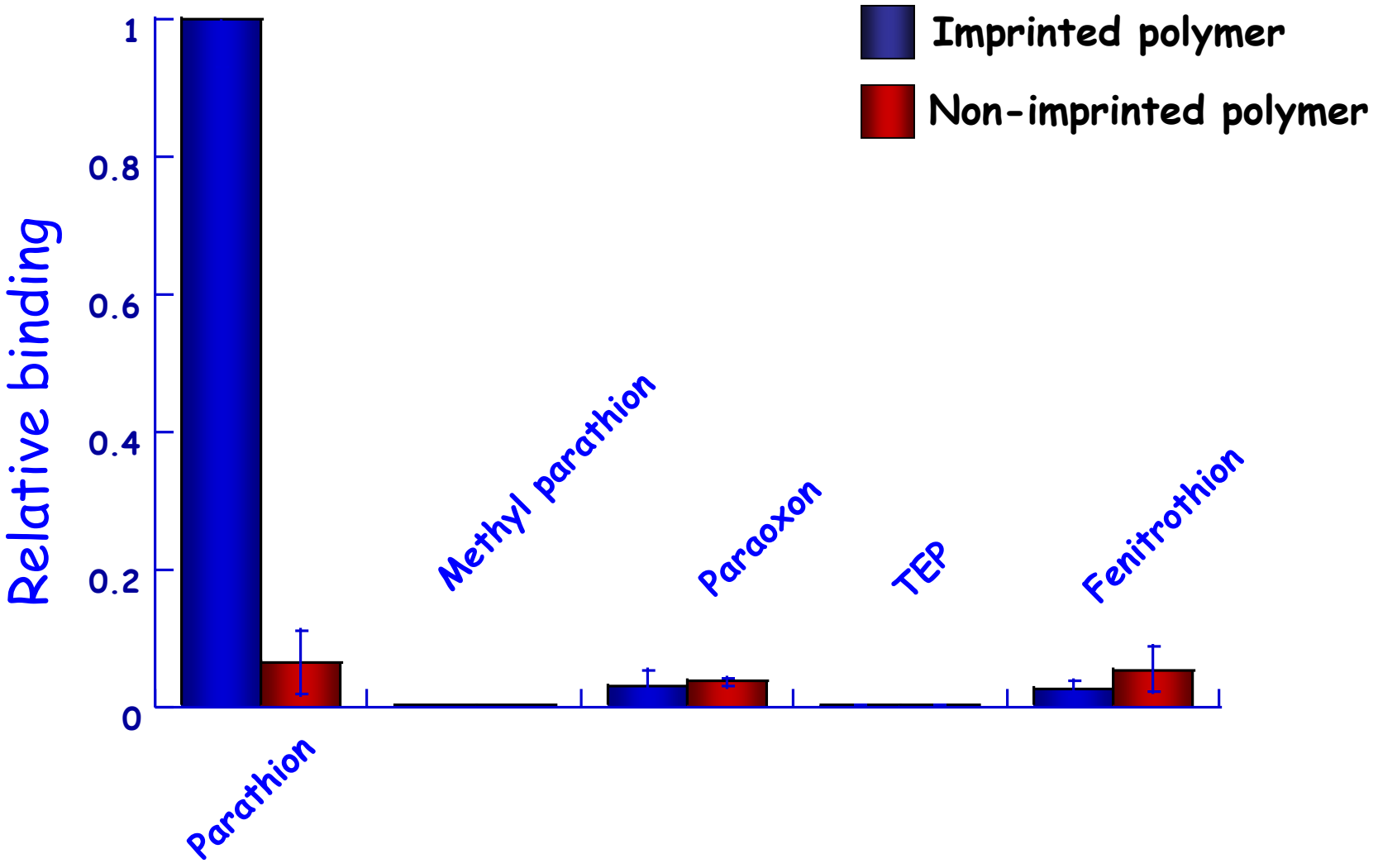


parathion-Me



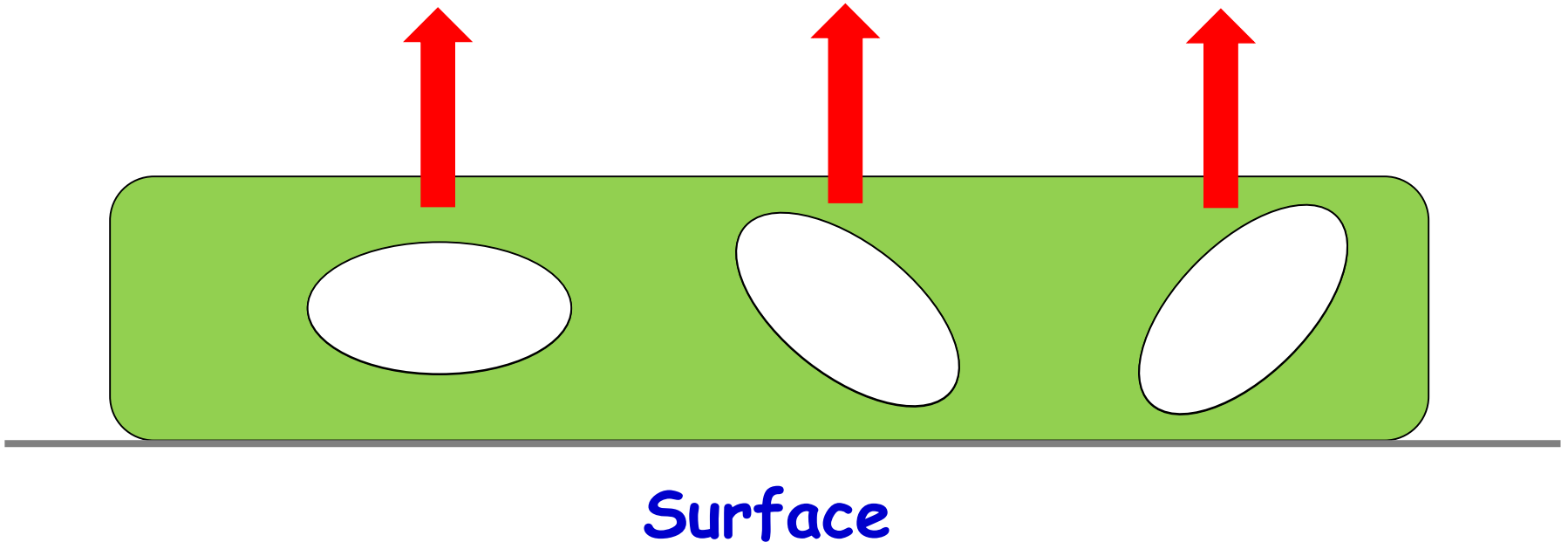
fenitrothion

Selectivity for Parathion



5. Nanoparticles Imprinted Polymers (NIP): Can We Recognized Nanoparticles Based on their Shape?

The Concept: imprinting a nanoparticles followed by its removal to form a hole that will selectively recognize the same nanoparticles

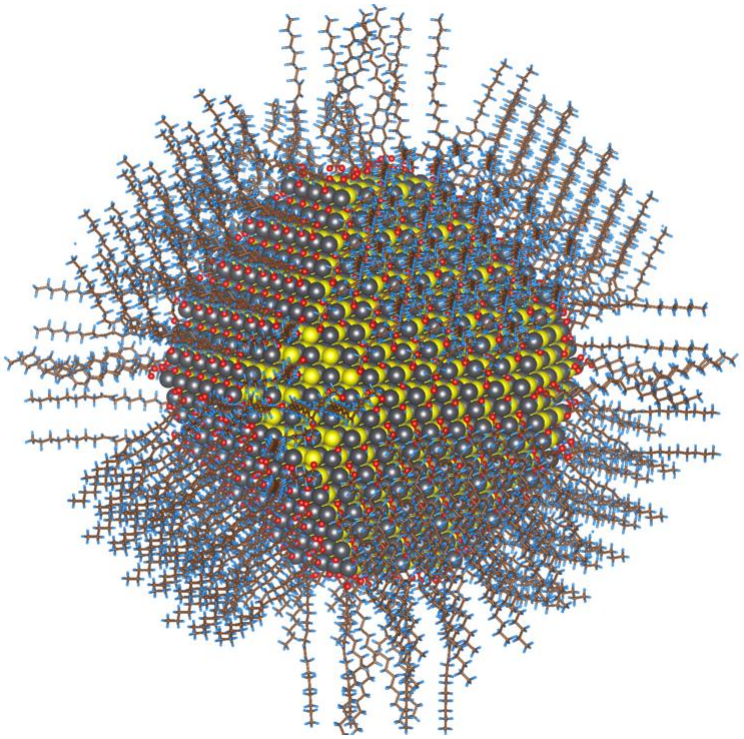


S. Kraus-Ophir, Angew. Chem. 2014, 53, 294-298

Why NIPs?

Nanotoxicology:

Due to their nm size NPs can exhibit high toxicity independent of the material they are made of. Their toxicity depends on size, structure and shell.

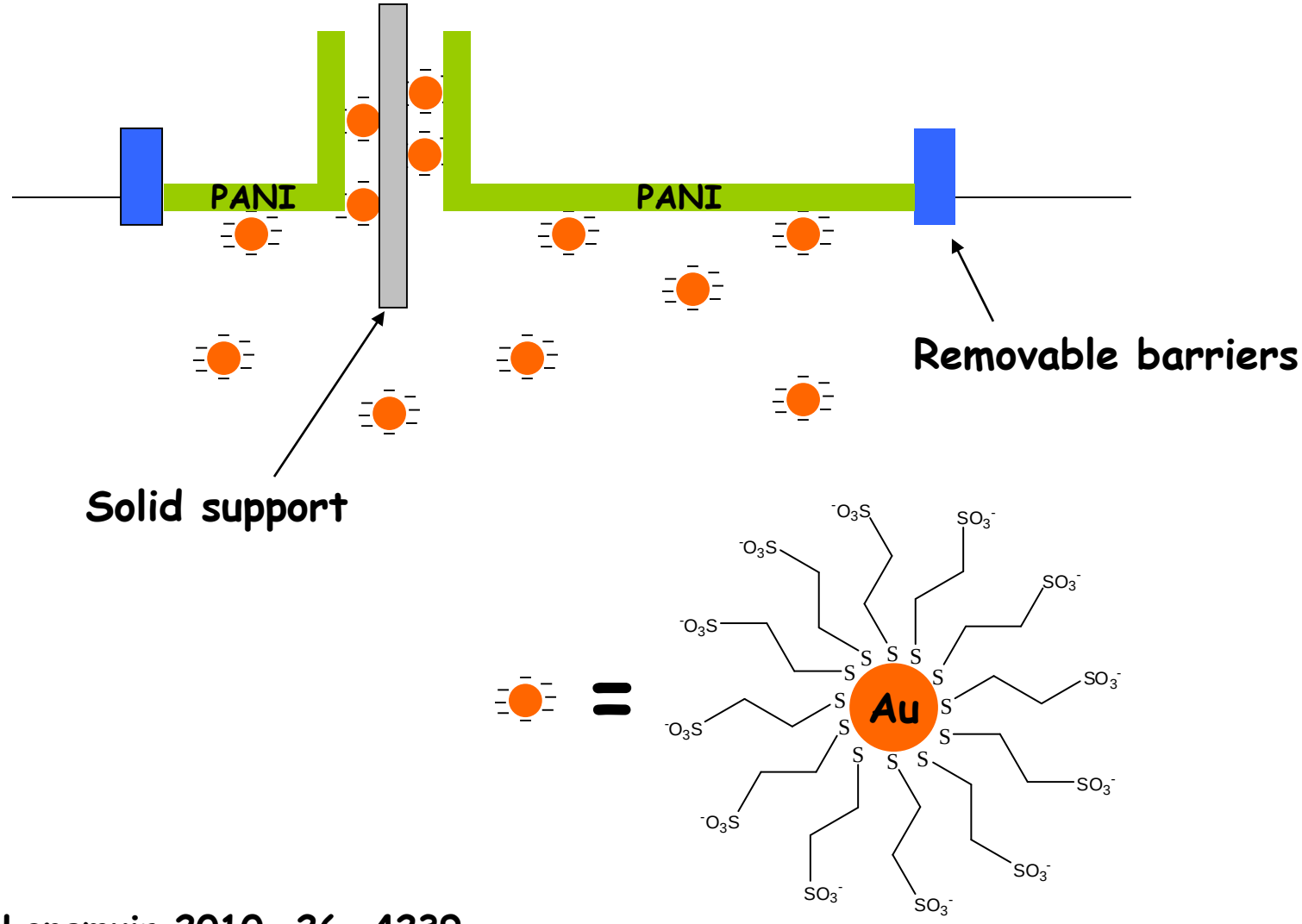


Semiconductor nanoparticle of PbS coated by oleic acid, oleyl and hydroxyl (size ~5nm)

There is a need for simple analytical methods for differentiation between nano-objects:

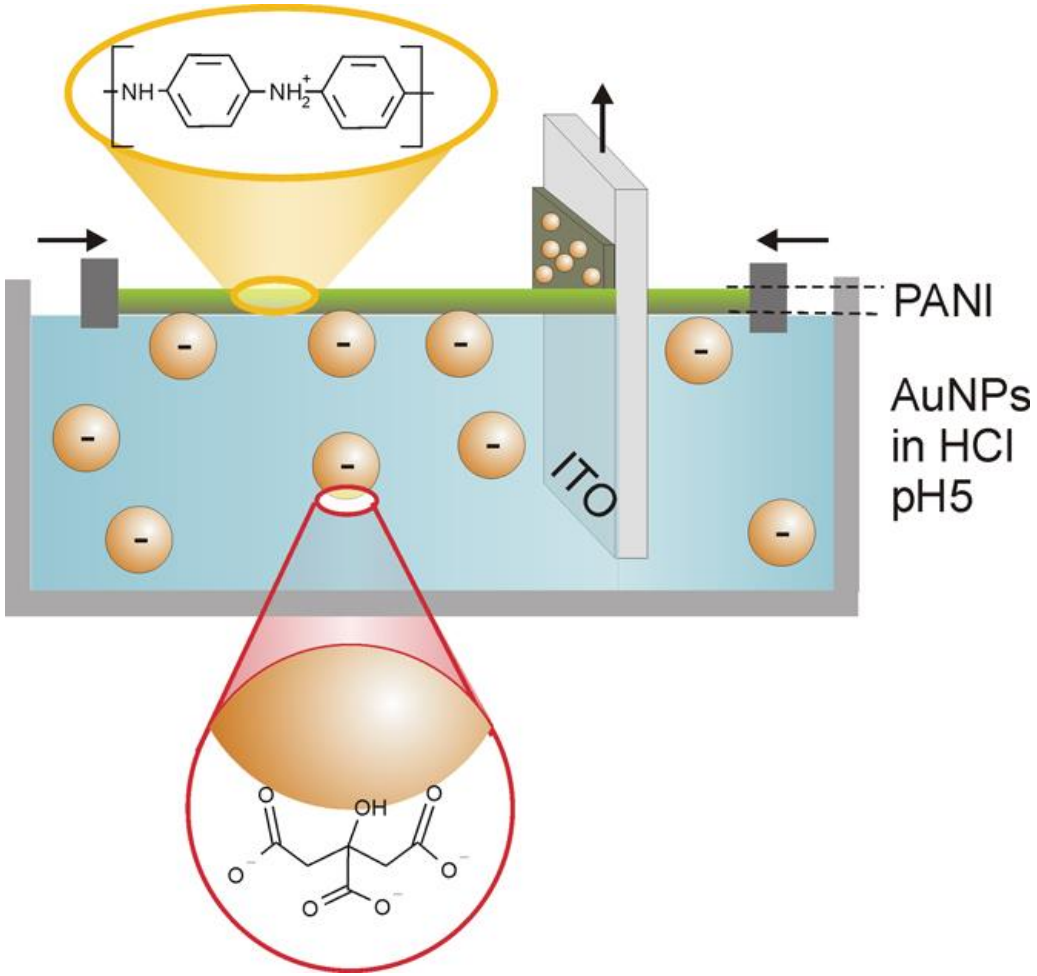
Nanoobject Speciation

Nanocomposites - LB films of PANI/Au Nanoparticles



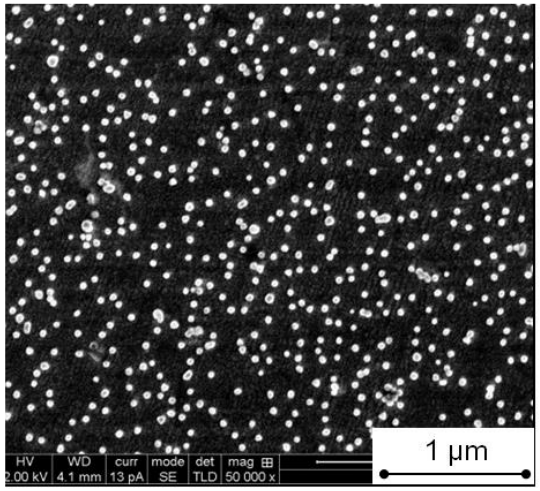
Tanami G. Langmuir 2010, 26, 4239

Nanoparticles Imprinted Polymers: The System



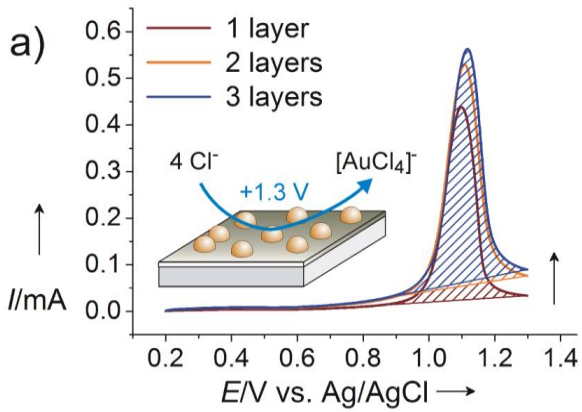
Electrostatic interaction between positively charged PANI and negatively charged AuNPs to form nanocomposite at the water-air interface enabling its transfer onto ITO

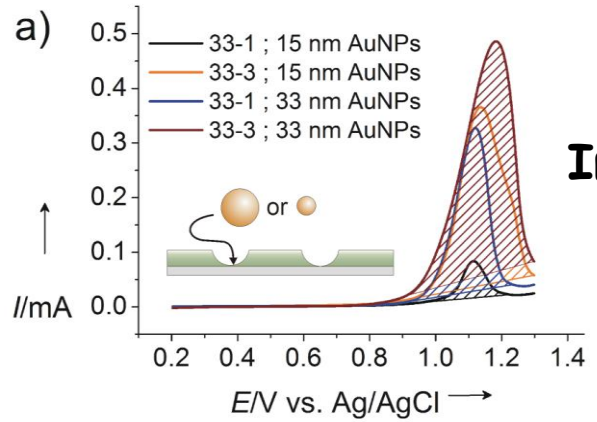
SEM images before and after removal



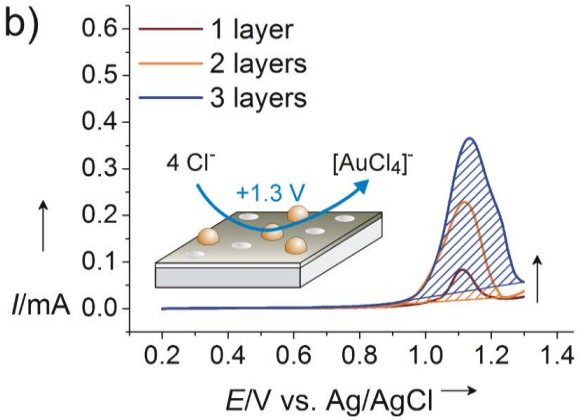
SEM images of two LB layers of 33 nm diameter AuNPs@PANI nanocomposite deposited at 28 $mN \cdot m^{-1}$ before (a) and after (b-d) electrochemical dissolution of gold

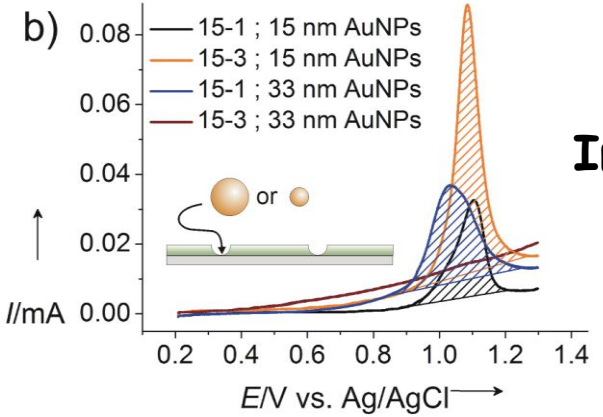
LSV of oxidation the Au NPs





Imprinted by 33 nm



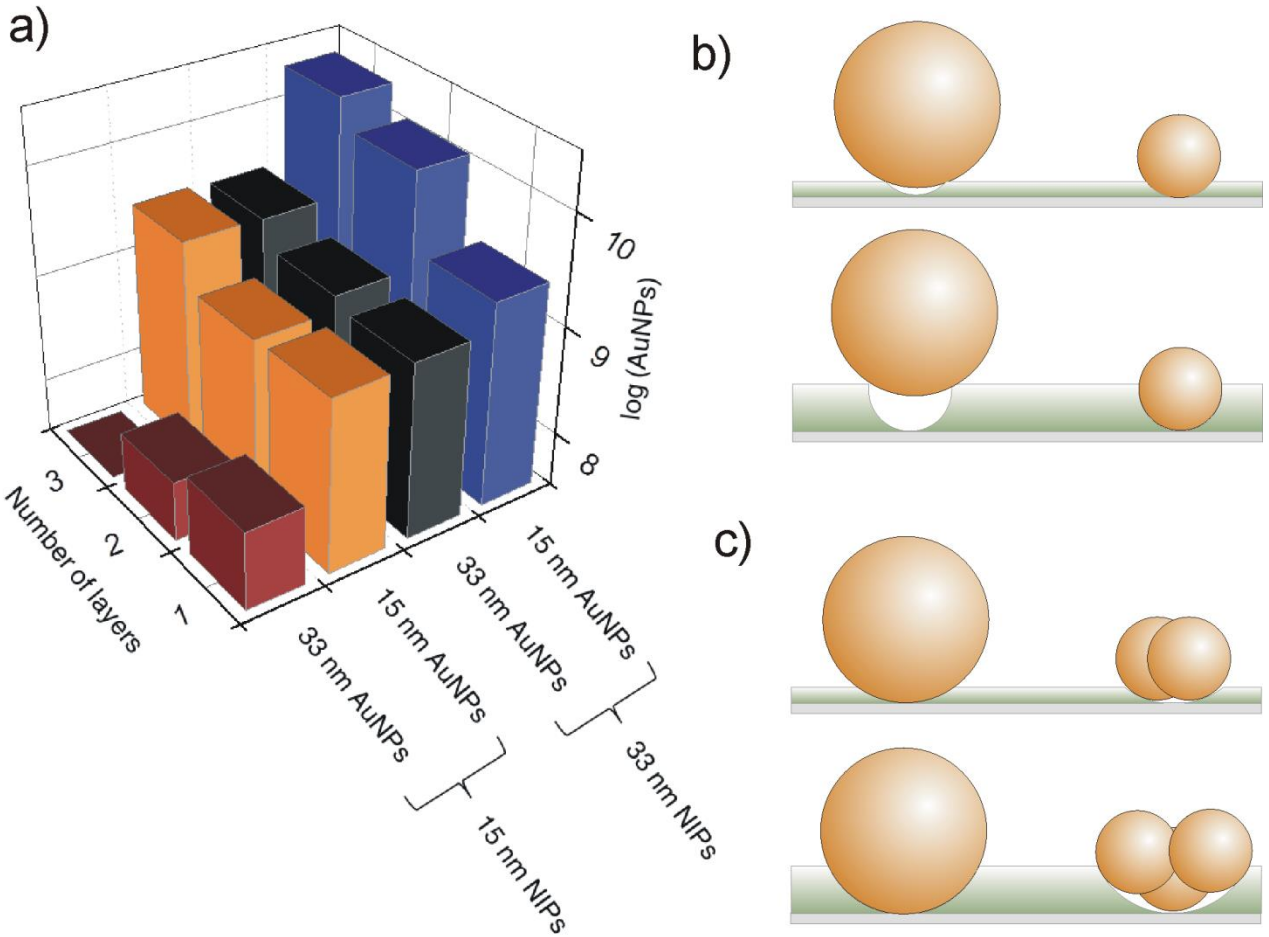


Imprinted by 15 nm

LSV of 1-3 deposited NIP (33 nm AuNPs) layers recorded in 0.1 M KCl with a scan rate of 50 $mV \cdot s^{-1}$: (a) removal of the initially imprinted AuNPs; (b) removal of the reuptaken AuNPs

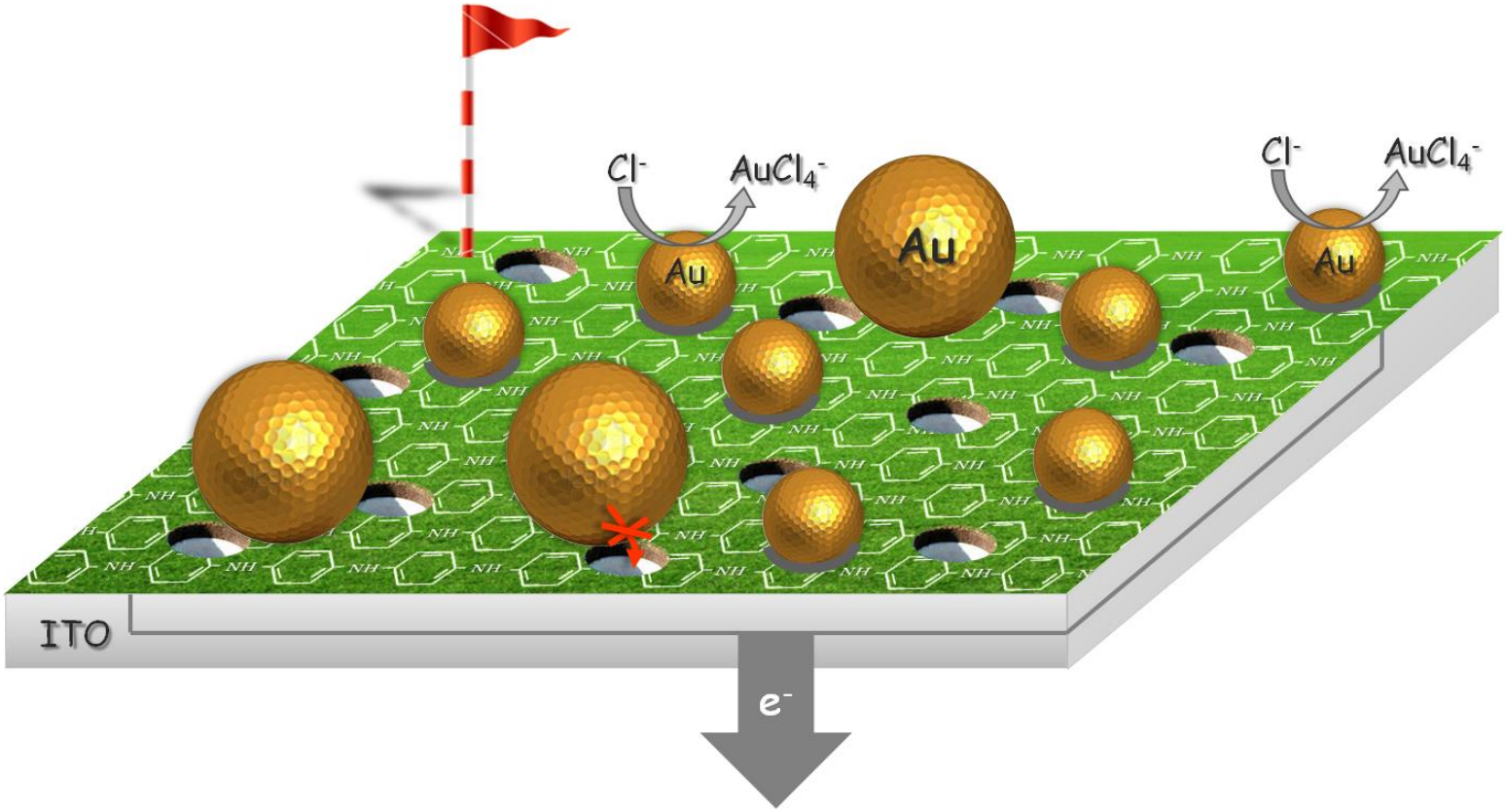
LSV after reuptake of 33 and 15 nm AuNPs by 1 and 3 layers of NIPs imprinted by 33 (33-1 and 33-3) (a) and 15 nm (15-1 and 15-3) (b) NPs

Summary of the reuptake experiments

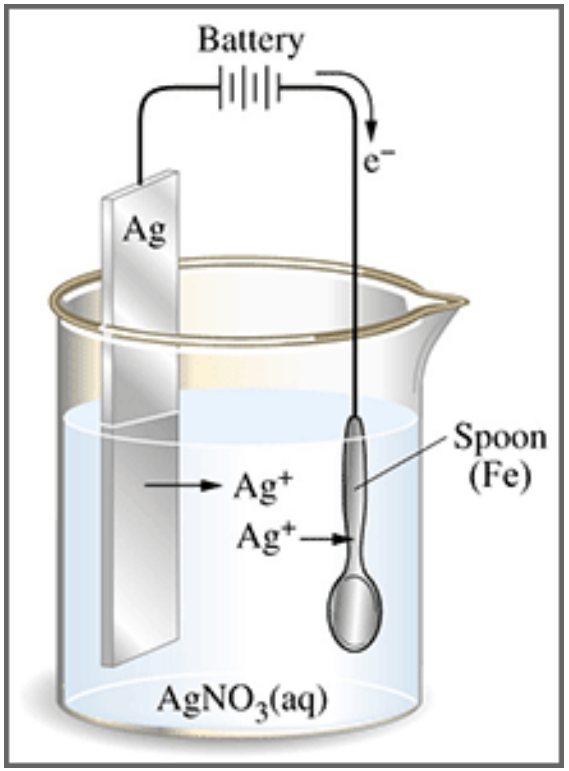


(a) Log of 15 and 33 nm AuNPs reuptaken by 1-3 LB layers of NIPs imprinted by either 15 or 33 nm AuNPs. (b)-(c) Schematics of the reuptake process by the various NIPs as a function of number of layers and imprinted AuNPs

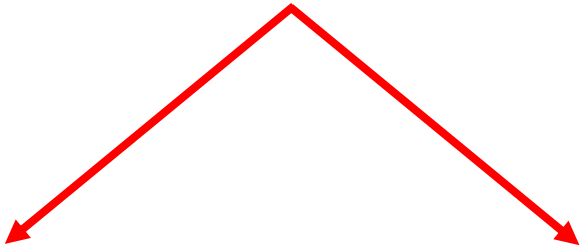
Golf with Au NPs…



A Few Words About Electroplating…



So, What's New?



Indirect Deposition

Nano Deposition

Electrochemical Deposition

Direct electrochemical deposition:

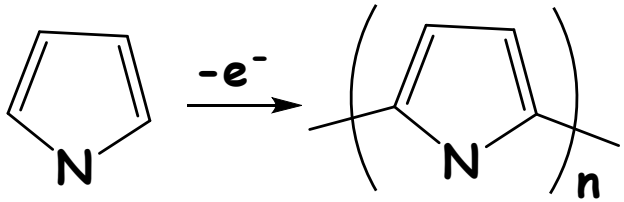
$$Ox_{(aq)} + ne^- \rightarrow Red_{(s)}$$

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$$

$$Fe^{2+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + e^-$$

$$Fe^{3+}_{(aq)} \xrightarrow{OH^-} Fe(OH)_{3(s)}$$

Electrochemical polymerization:



Indirect electrochemical deposition:

$$Ox_{(aq)} + ne^- \rightarrow Red_{(aq)}$$

$$Red_{(aq)} + A_{(aq)} \rightarrow P_{(s)}$$

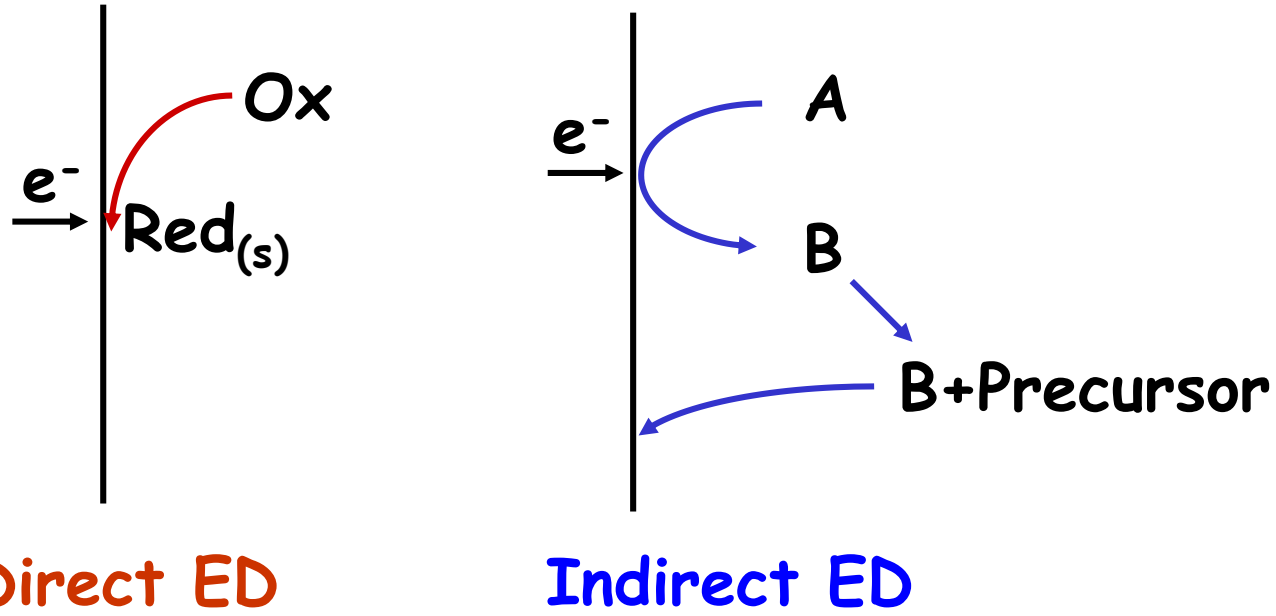
$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

$$Fe^{3+}_{(aq)} + 3OH^- \rightarrow Fe(OH)_{3(s)}$$

$$A \xrightarrow{OH^-} P$$

Advantages of Indirect Electrochemical Deposition

- Deposition of electrochemically inactive materials
- Codeposition of more than one substance
- Deposition is not limited to electron transfer region
- …



Electrochemical Deposition of Polymer Films: Sol-Gel Deposition

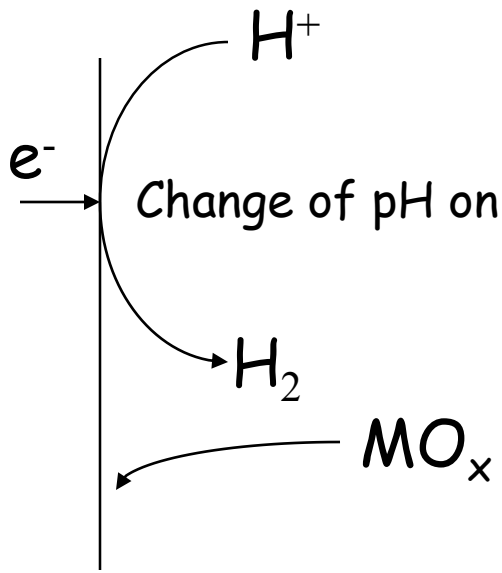
Due to the fact that almost every functional group can be introduced into the sol-gel matrix, it is possible to tune the properties of the coating

Hydrolysis

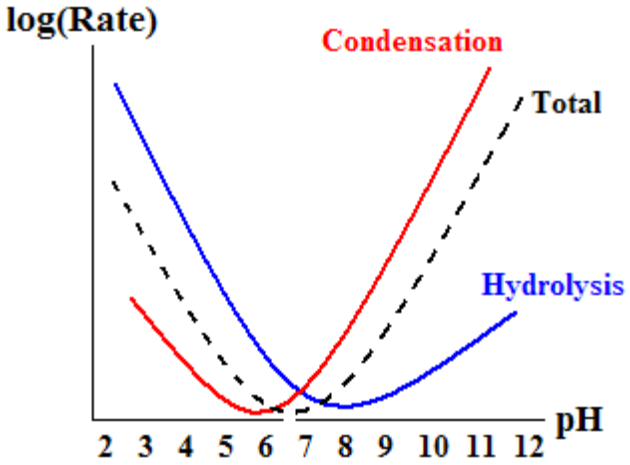
$$MX_4 + H_2O \longrightarrow MX_3OH + HX$$

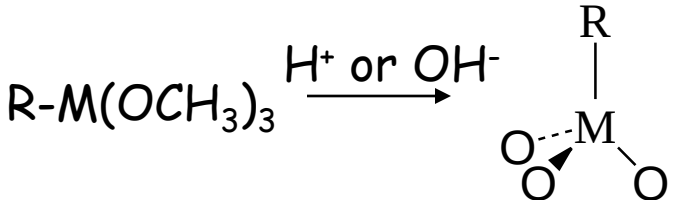
Condensation

$$MX_3OH + M(OH)_4 \longrightarrow X_3M\text{-}O\text{-}M(OH)_3 + H_2O$$



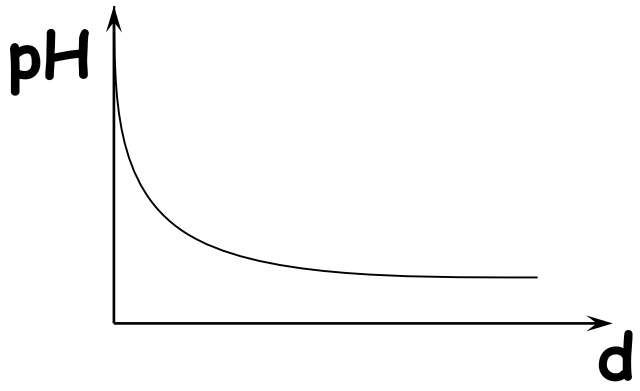
It is possible to deposit oxide layers by altering the pH on the electrode surface as a result of applying a potential





Altering the surface pH by electrochemistry

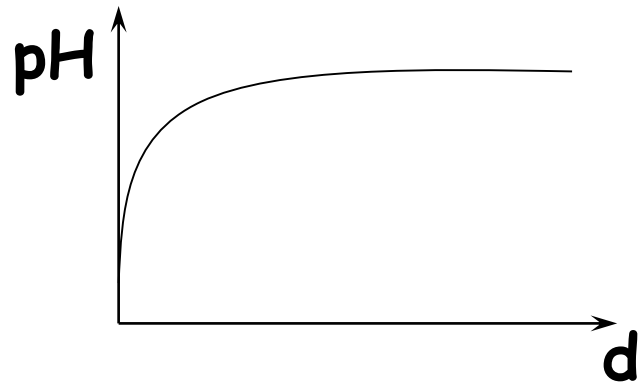
Reduction



$$H_2O_{(l)} + e^- \rightarrow \frac{1}{2}H_{2(g)} + OH^-_{(aq)}$$

$$ROH_{(l)} + e^- \rightarrow \frac{1}{2}H_{2(g)} + RO^-_{(l)}$$

Oxidation

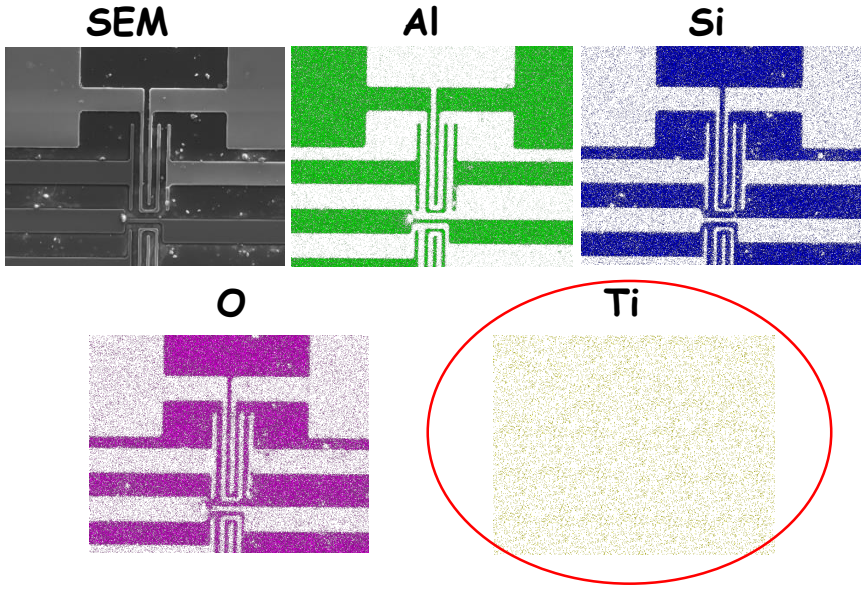


$$H_2O_{(l)} \rightarrow \frac{1}{2}O_{2(g)} + 2H^+_{(aq)} + 2e^-$$

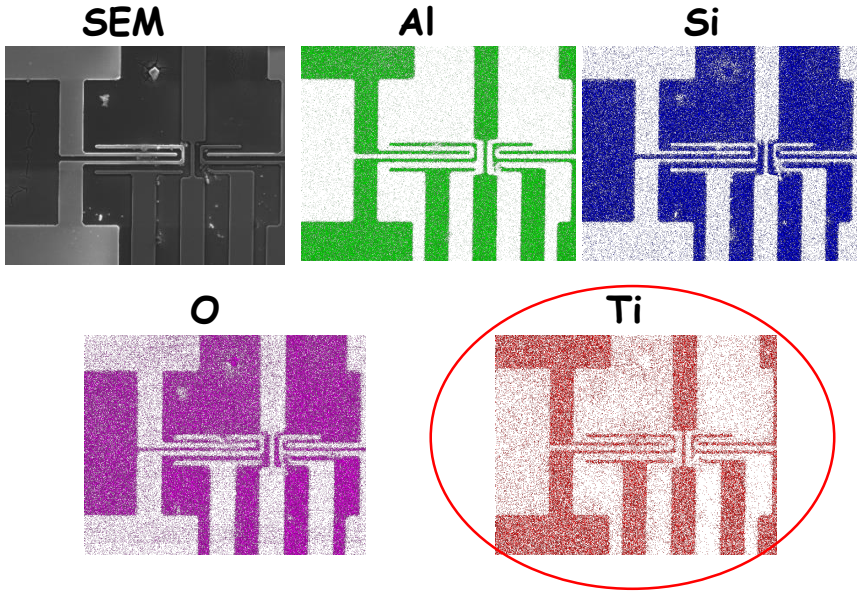
$$RCH_2OH_{(l)} \rightarrow RCHO_{(l)} + 2H^+_{(aq)} + 2e^-$$

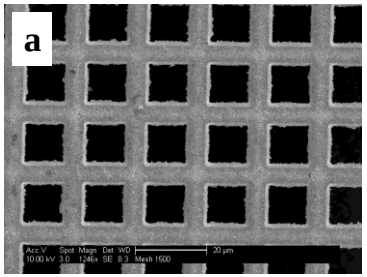
Coating complex geometries

Conventional dip coating of TiO_2

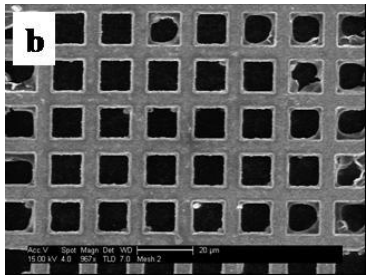


Electrochemical deposition of TiO_2

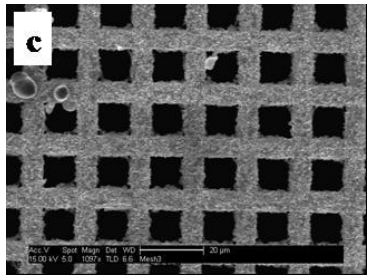




Bare Au grid



Ti dip-coated Au grid

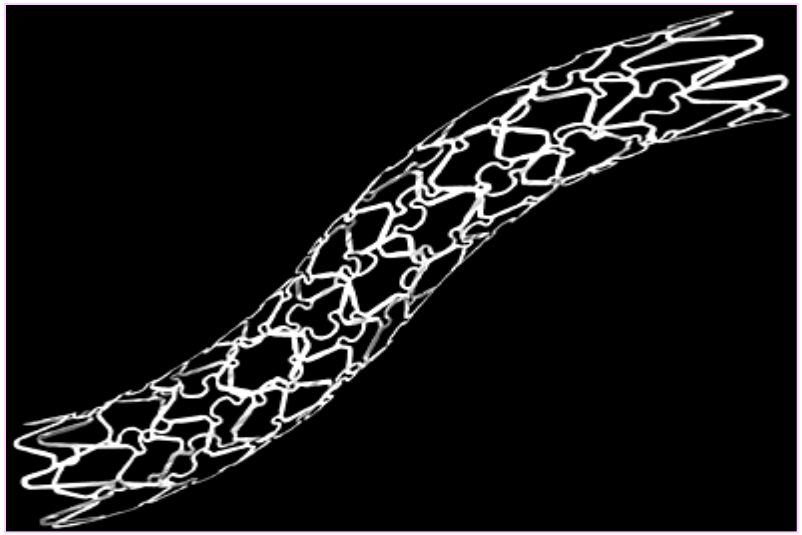


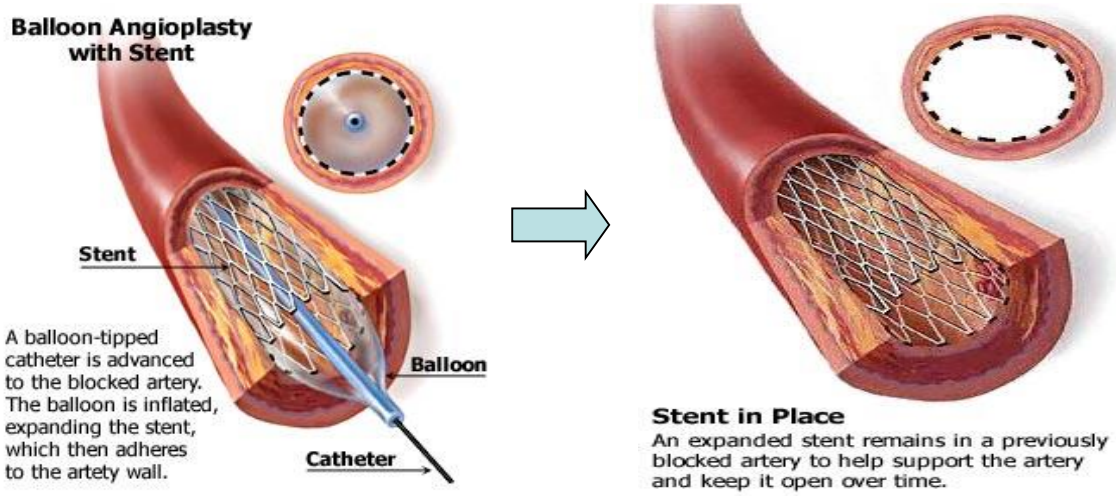
Ti electrodeposited Au grid

6. Biomedical Engineering
Coating of Medical Implants–Stents

Problems

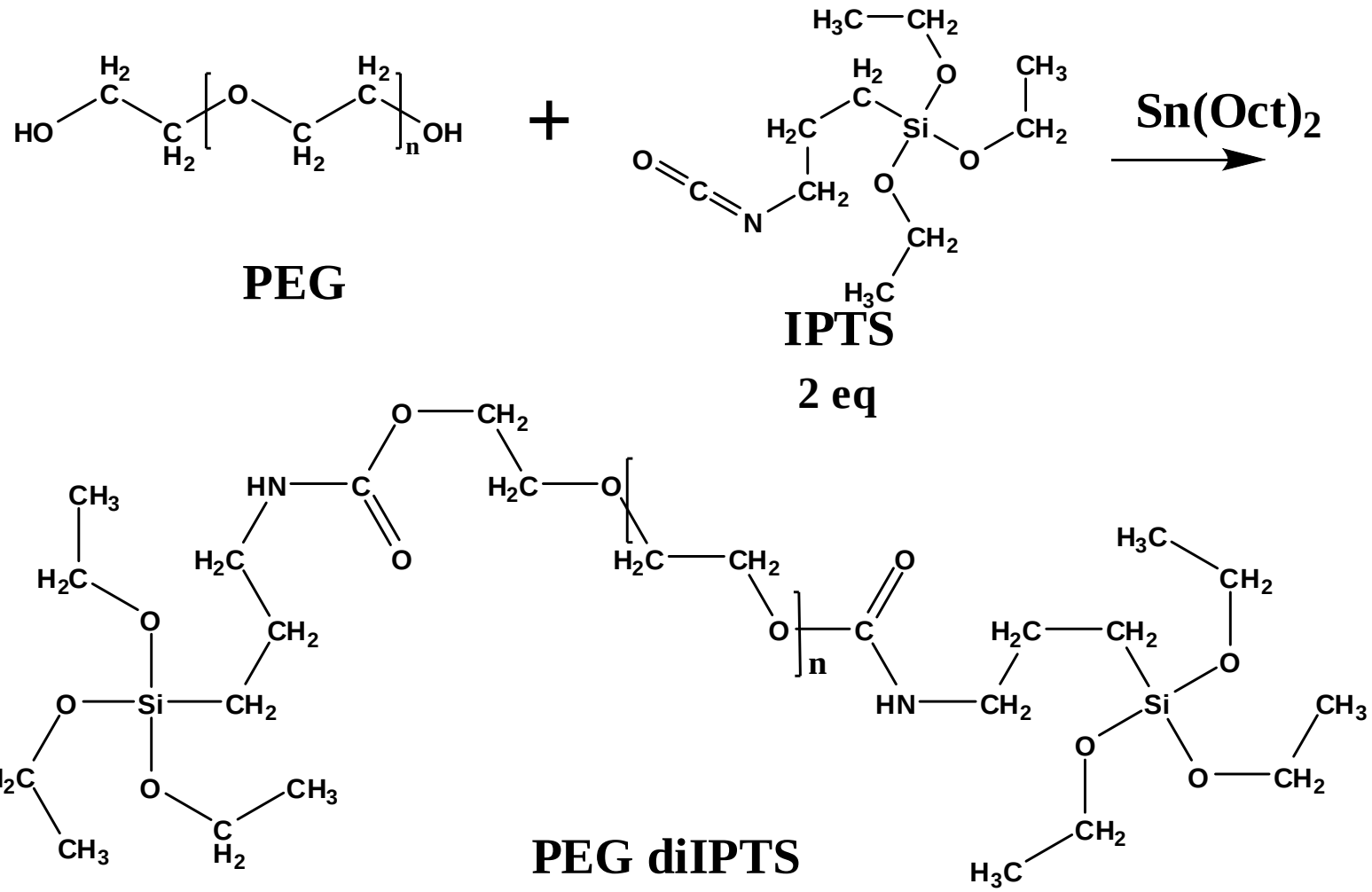
- Short term:
  - *Hemorrhagic complications*
  - *Thrombus formation*
- Long term:
  - *Restenosis*
  - *SMC proliferation*





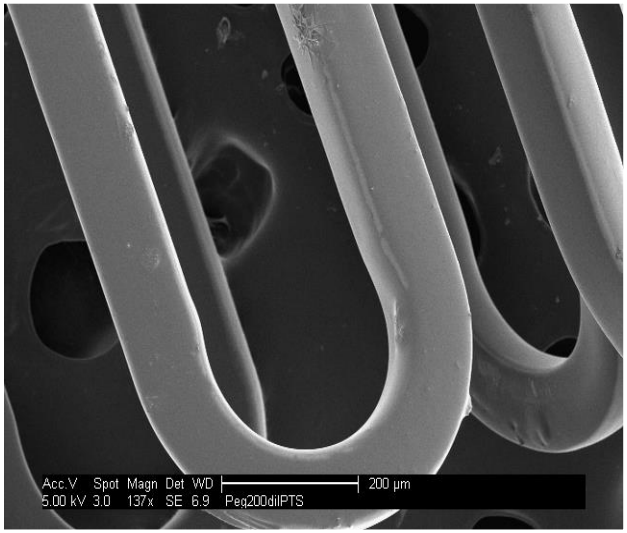
Possible solution: coating by electrodeposition of polymers

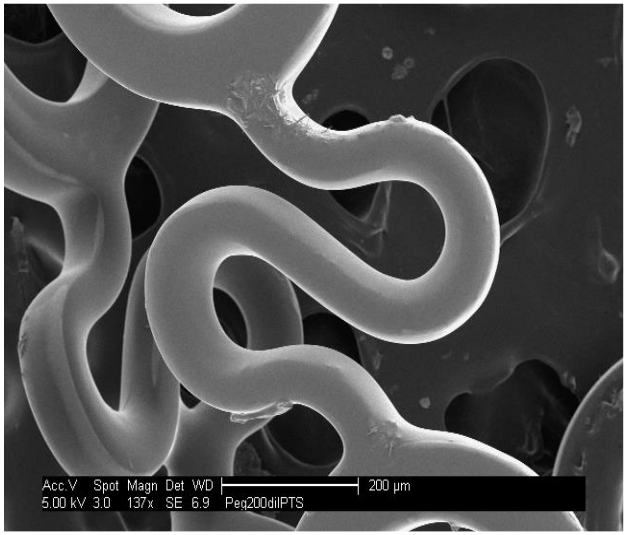
Synthesis of PEG-Sol-Gel Precursor

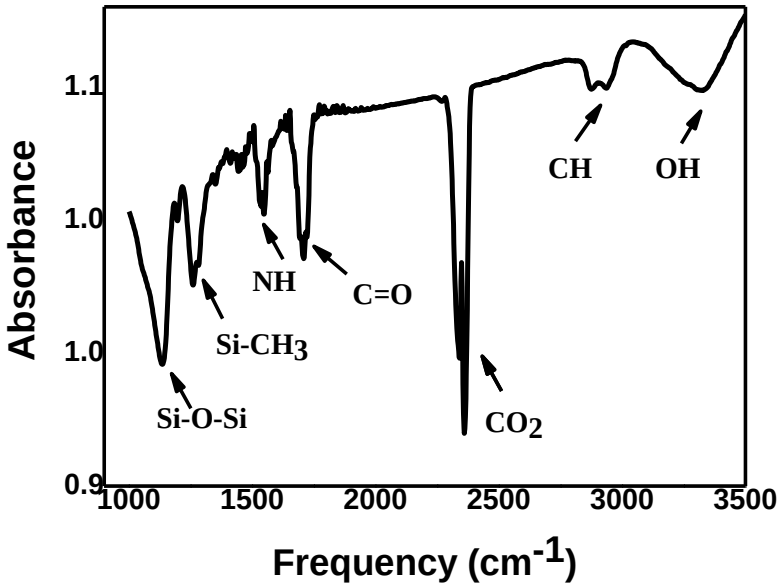


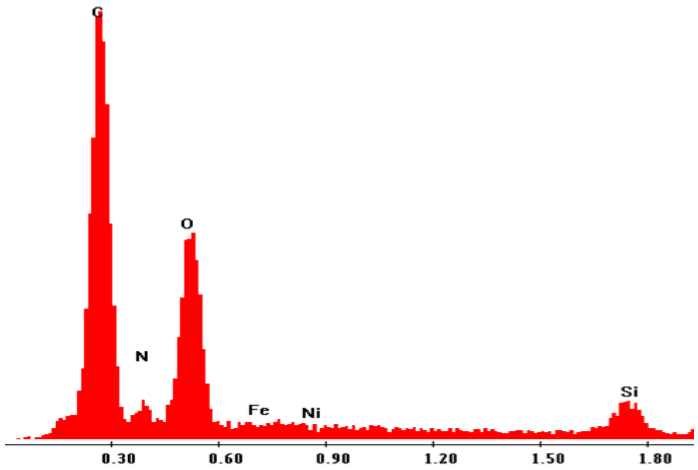
Okner et al. New J. Chem., 2009, 33, 1596–1604

Stent Coated with PEG-Sol-Gel





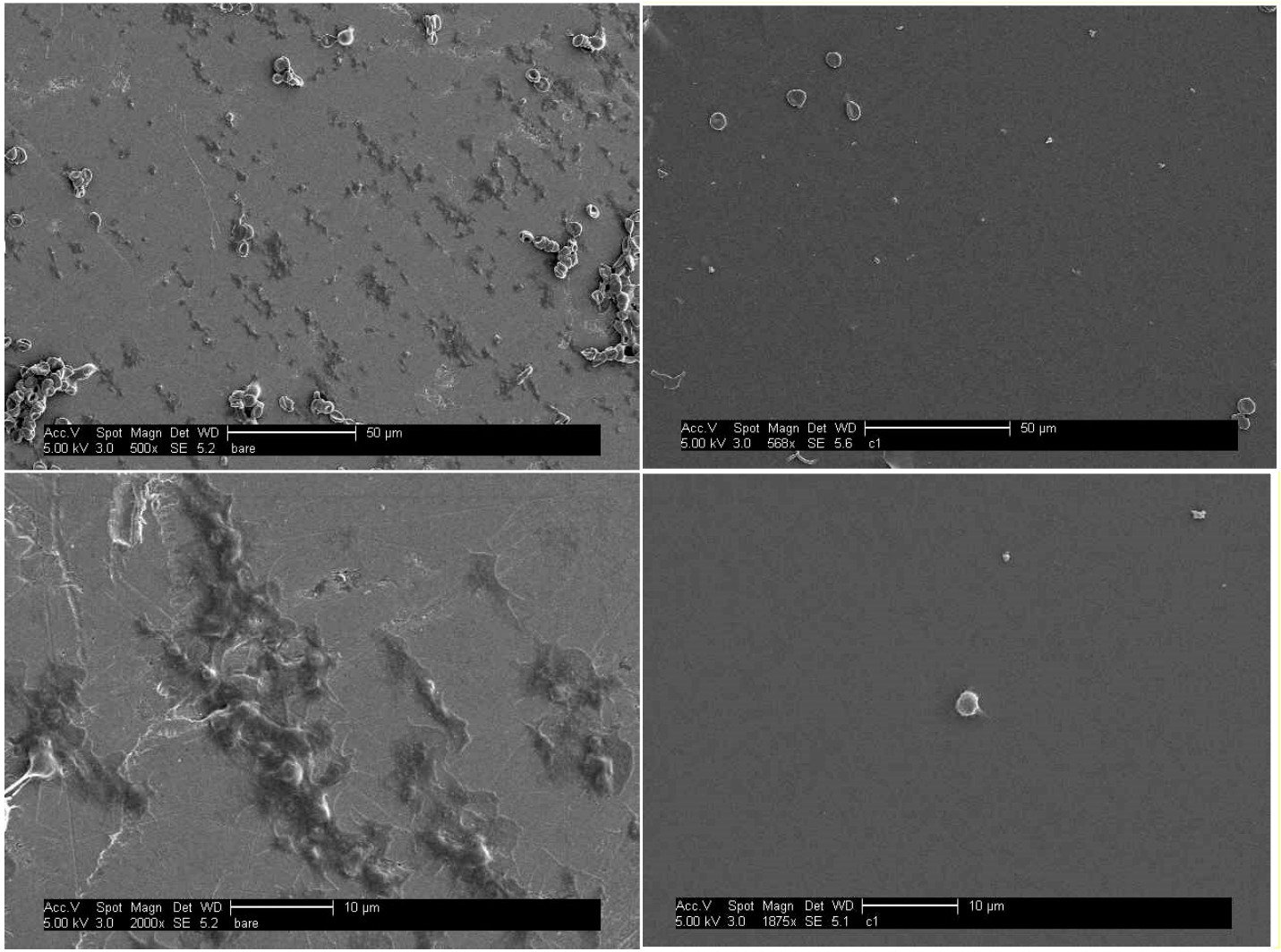




Platelet Adhesion to Coated and Uncoated Stainless Steel Substrates

X500

X2000



Uncoated surface

Coated surface

Applications of Electroassisted Deposition of Sol-Gel Films

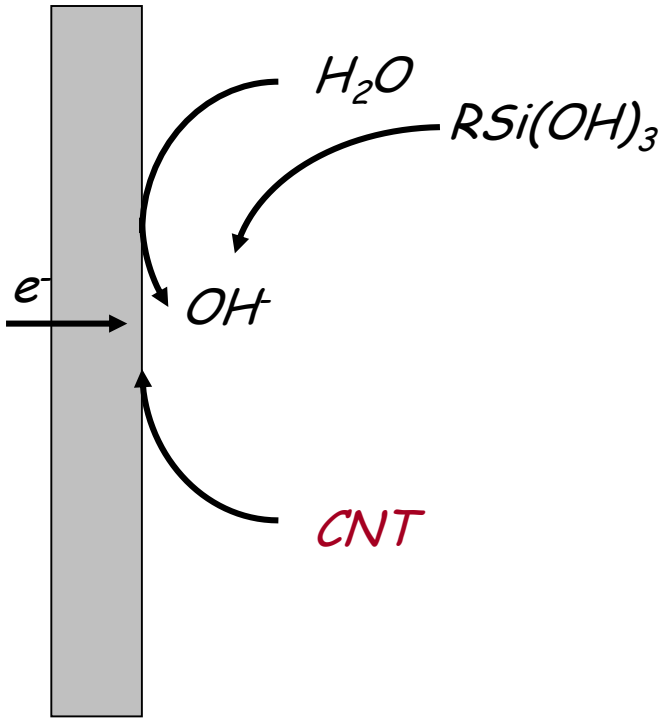
Deposition

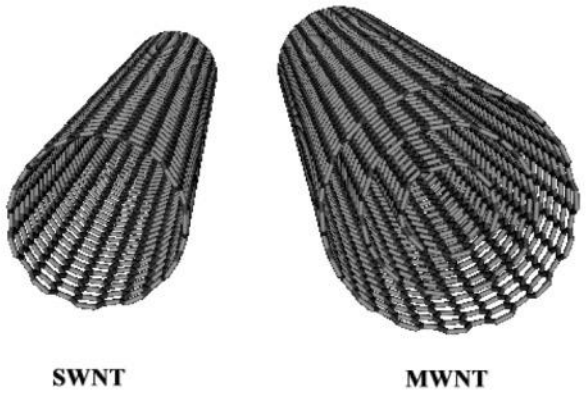
- *Formation of controllable thin films of silica, zirconia and titania*
- *Coating complex geometries*
- *Corrosion inhibition*

Codeposition

- *Encapsulation of dyes in the course of the deposition process*
- *Codeposition of metals*
- *Codeposition of nanoparticles*
- *Codeposition of conducting and non-conducting polymers*
- *Deposition of hybrid materials, e.g., silica and zirconia*

7. Sol-Gel/CNT Electrochemical Codeposition



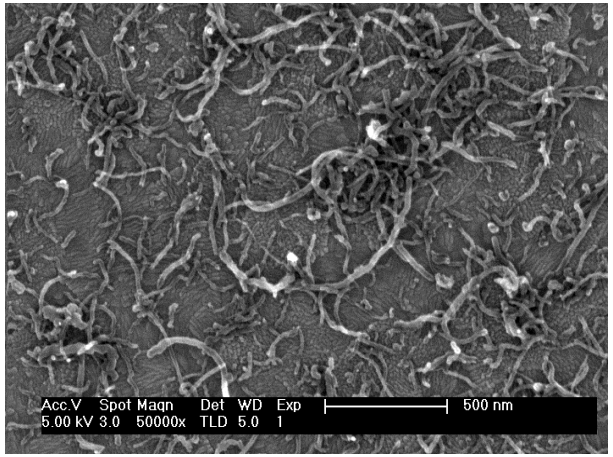


Dispersion of CNT:
0.2 mol/L TMOS
1 wt.% CTAN
0.5 wt.% MWCNT (CheapTubes)
Solvent: 1:1 v/v NMP:H_2O.

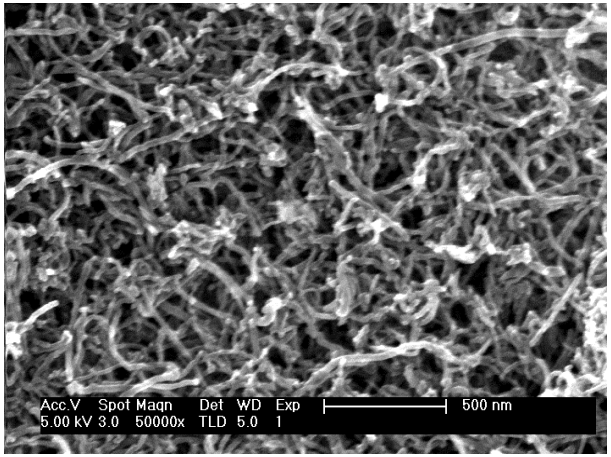
Liu et al., Electrochem. Commun., 2014, 48, 56

Characterization of Sol-Gel/CNT Electrodeposition

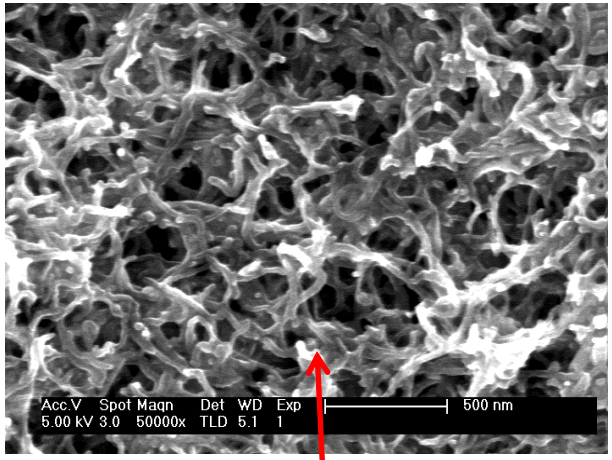
Dip-coating



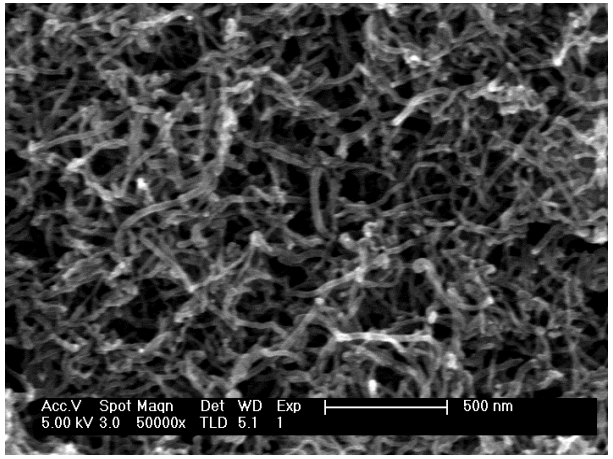
-0.65 V, 5 min



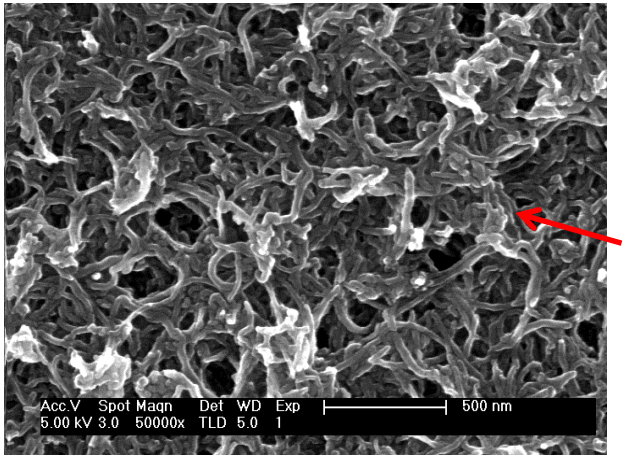
-1.1 V, 5 min



-0.9 V, 5 min

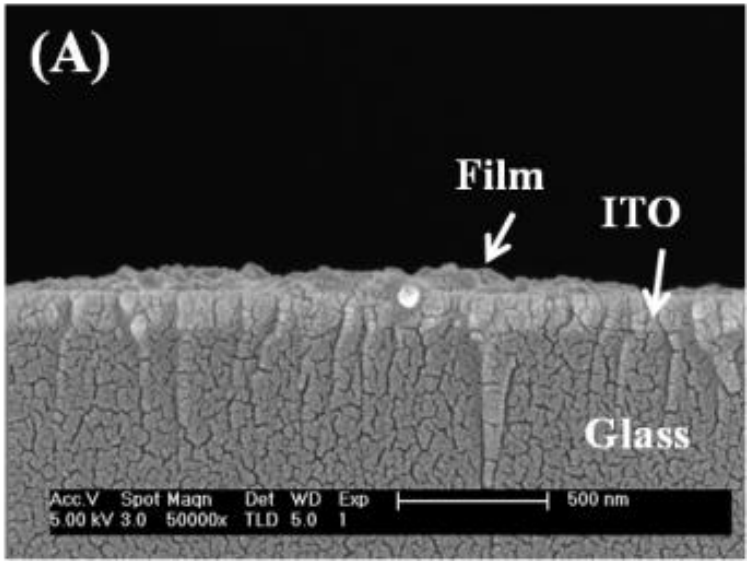


-0.9 V, 10 min

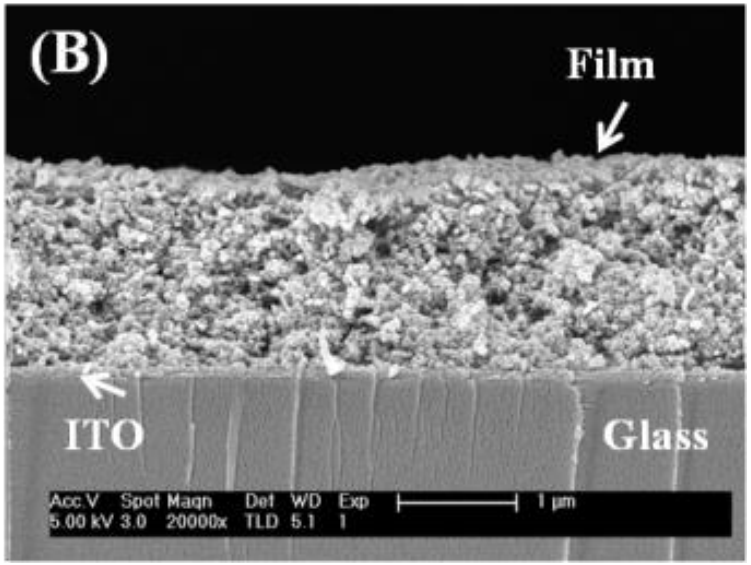


CNTs are embedded with silica

Cross-Section of the Film

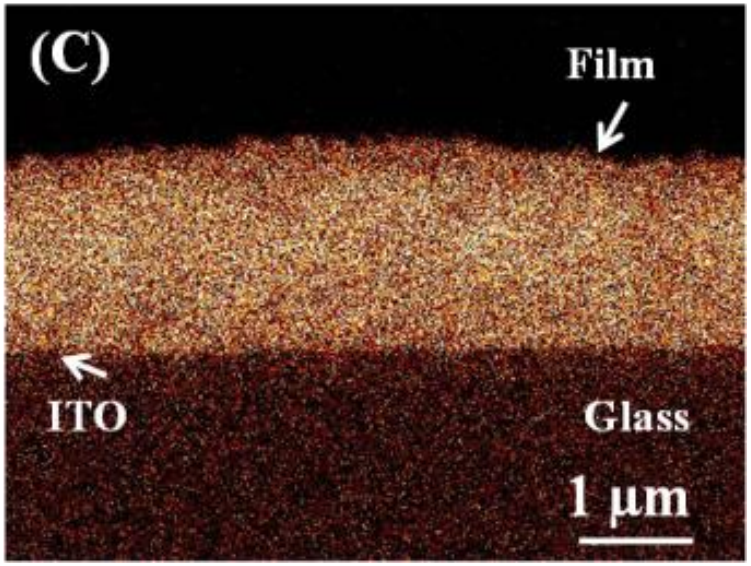


-0.75 V

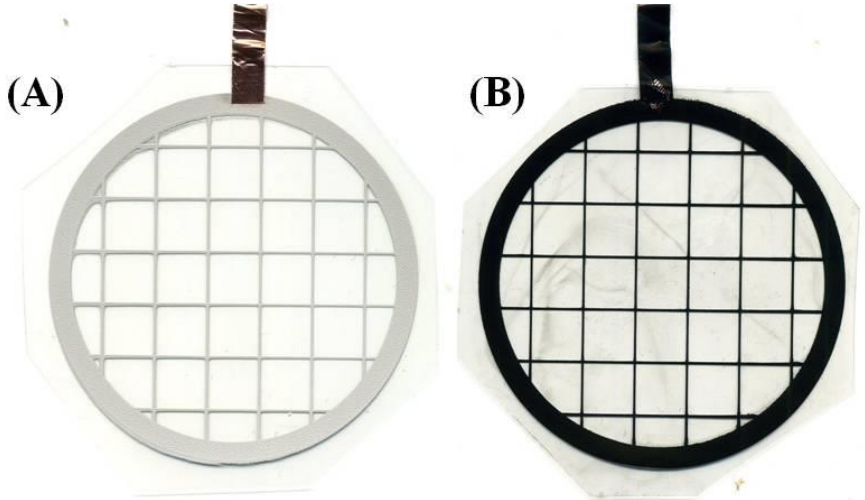


-1.2 V

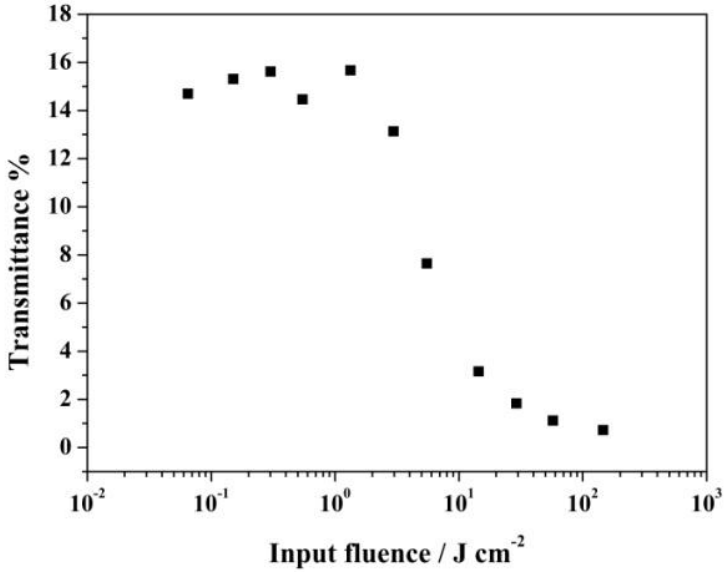
Cross-section SEM images of the sol-gel/CNT composite films electrodeposited at −0.75 V (A) and −1.2 V (B) for 2 min
(C): EDX mapping of carbon for (B).



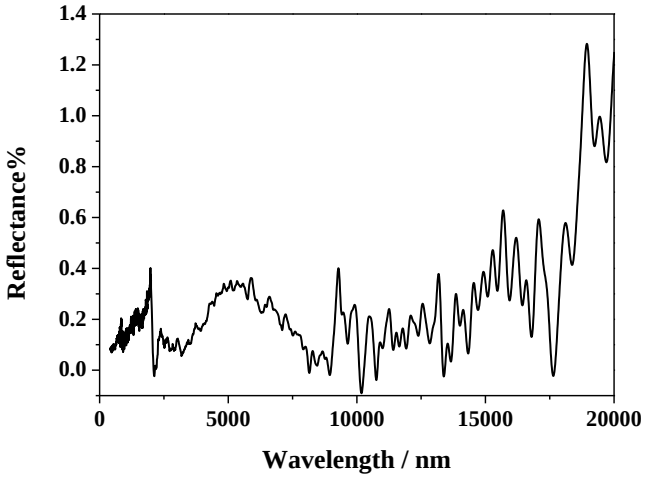
Applications of CNT/Sol-Gel Films



Ag grid printed on PET before (A) and after (B) electrodeposition of sol-gel/CNT composite films at –0.9 V for 2 min

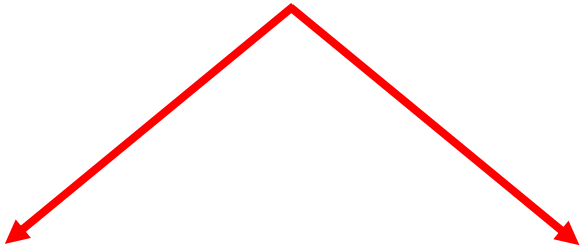


Non-linear optical performance of sol-gel/CNT composite films electrodeposited on ITO at –0.9 V for 2 min.



Specular reflectance of sol-gel/CNT composite films

So, What's New?



Indirect Deposition

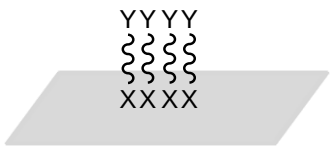
Nano Deposition

Deposition of Nanometric vs. Molecular Species

Molecular deposition:

Pro:
- Monolayer formation
- Complex assemblies (multilayers)

Con:
- Limited to molecular structures or requires further treatment
- Limited mostly to organic and biological species



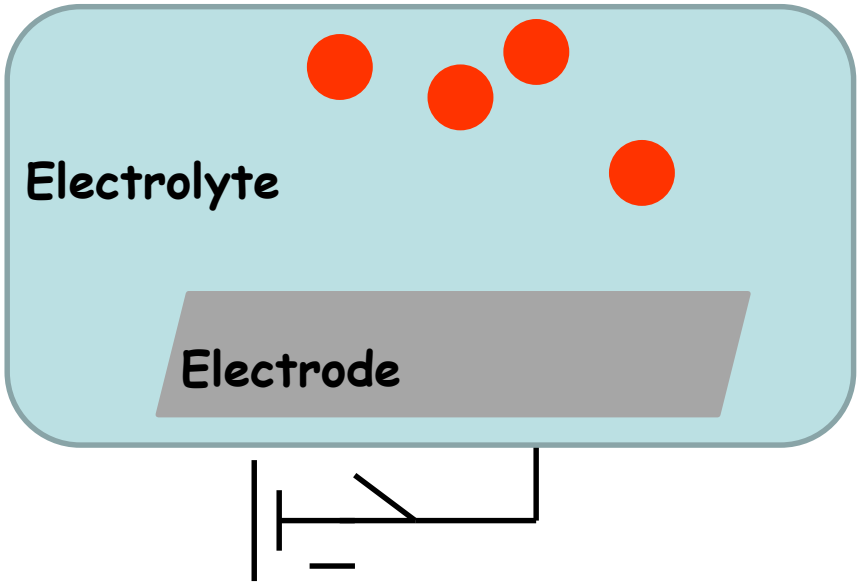
Nano-objects deposition:

Pro:
- Allows manipulation of nanometric structures
- Allows deposition of final structures with well-defined properties

Con:
- Requires dispersions
- Limited mostly to metallic and inorganic structures
- Not simple to construct complex (3D) structures

From Nano (in Solution) to Nano (on Surface)

The challenge:

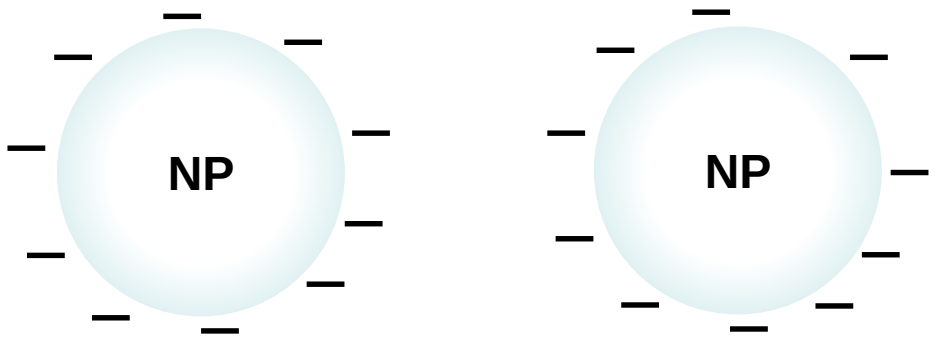


Foreseen problems:

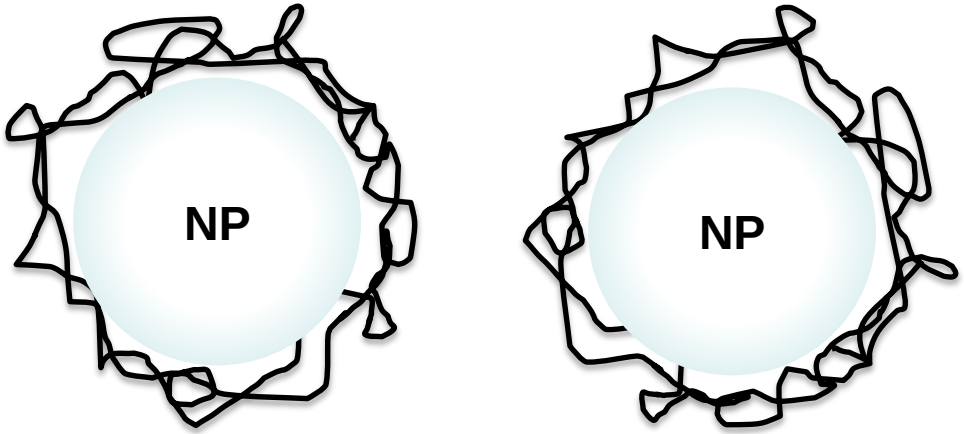
- Deposition is not a redox reaction
- Presence of electrolyte
- Control of the process
- Other parallel reactions

Electrochemical Control of the Interparticle Forces

Electrostatic repulsion

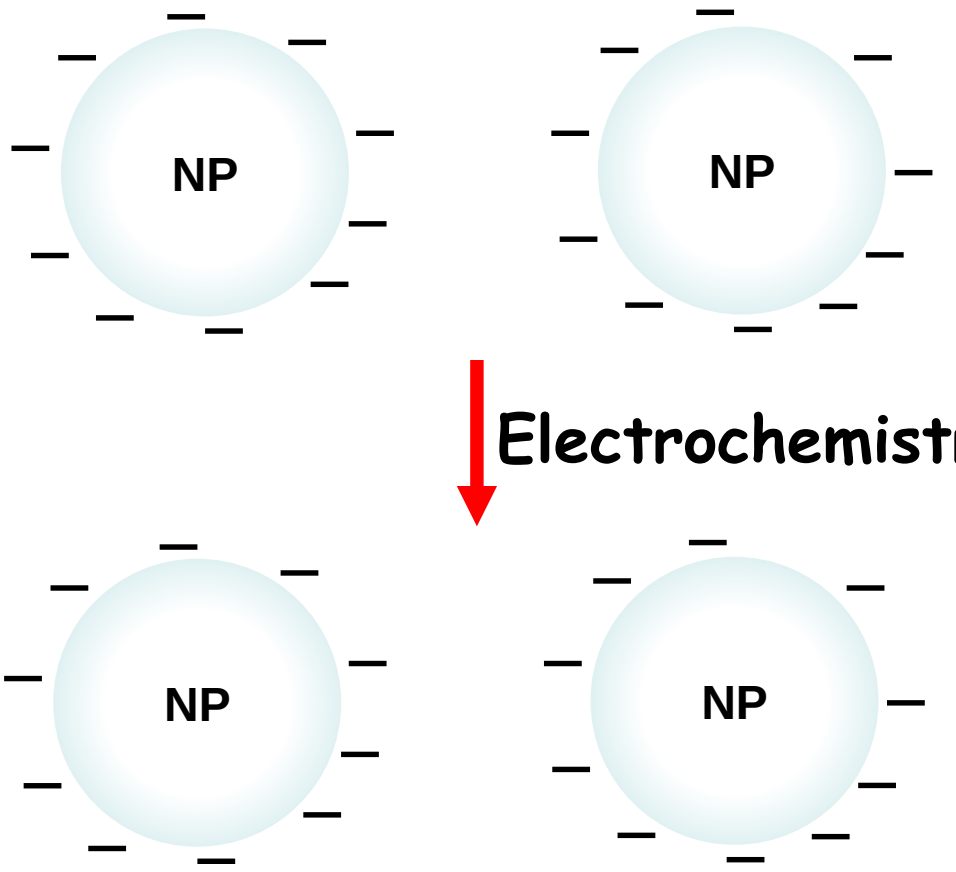


Steric repulsion



Electrochemical Control of the Interparticle Forces

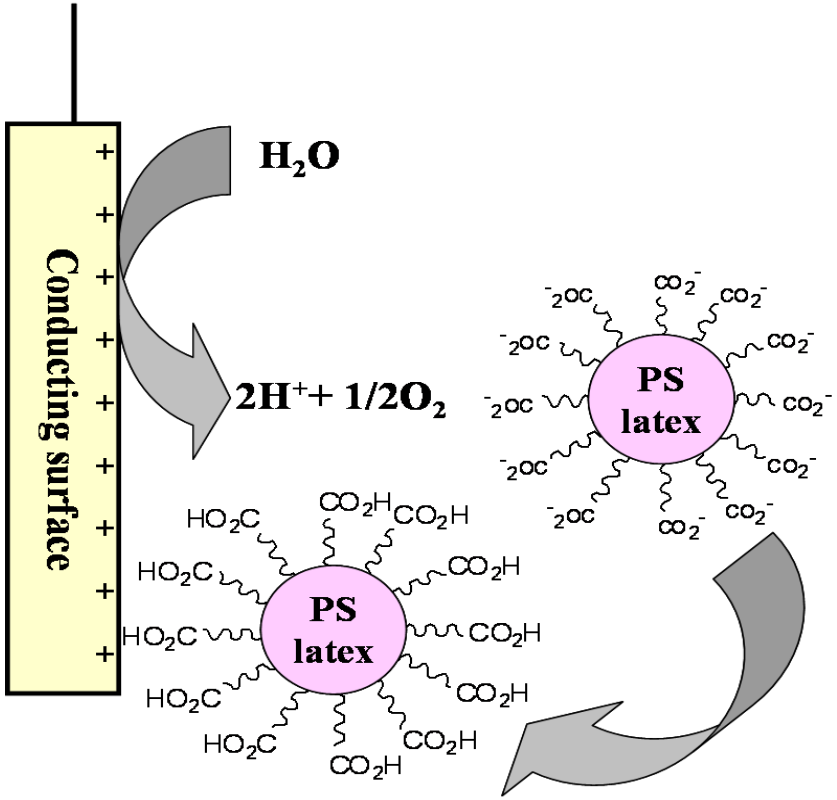
Electrostatic repulsion

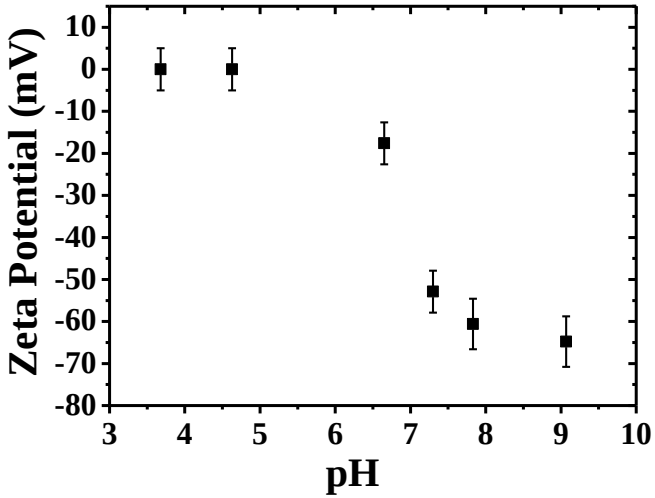


How can electrochemistry diminish the repulsion?

1. Changing the pH!

8. Functionalized Nanoparticles Deposition Potential-Induced Protonation

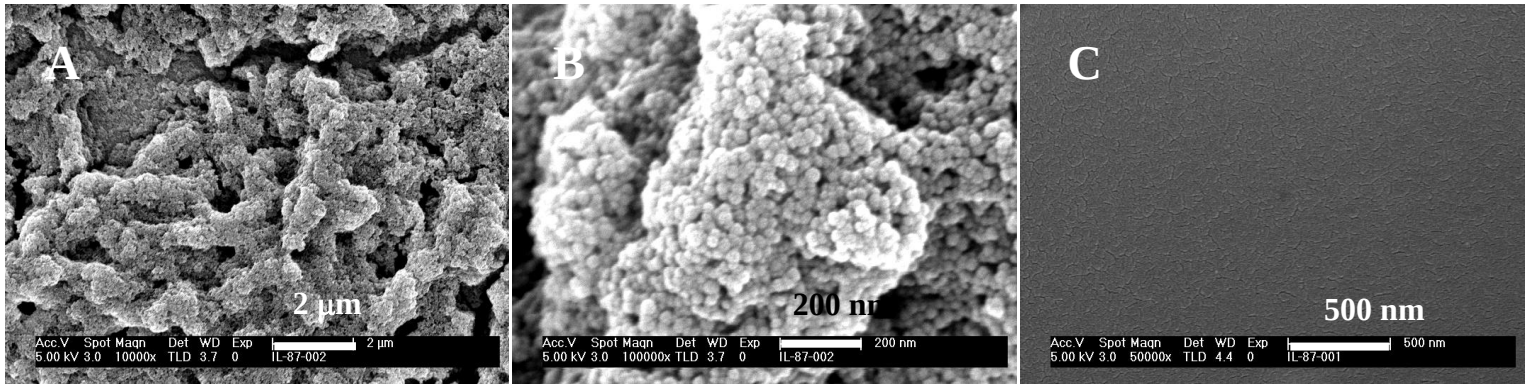




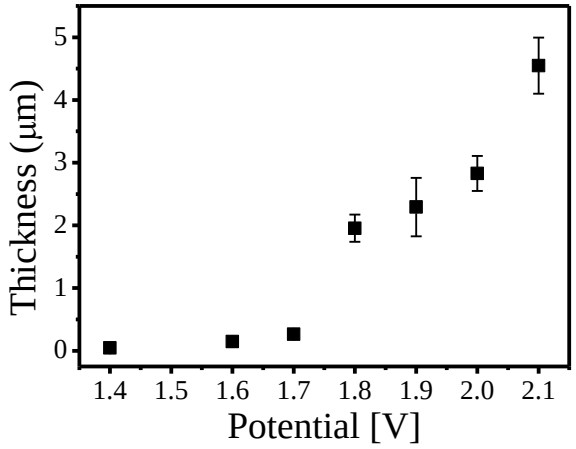
Zeta potential as a function of pH for latex nanoparticles solution

I. Levy et al. Electrochim. Acta, 2010, 55, 8590

Characterization of the Coating

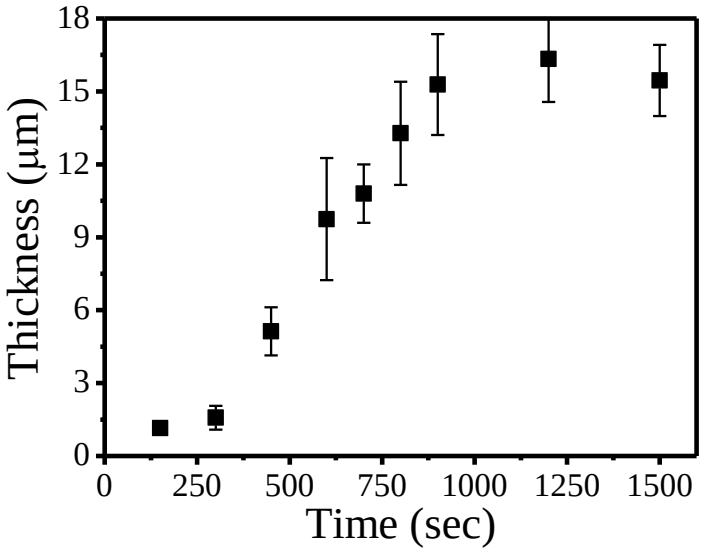


HR-SEM images of electrochemically deposited latex films on an ITO plate. The films were deposited at a constant voltage of 2.0 V for 5 min: (A) and (B) the film as deposited under different magnification; (C) the film after heating to 110 °C for 15 min

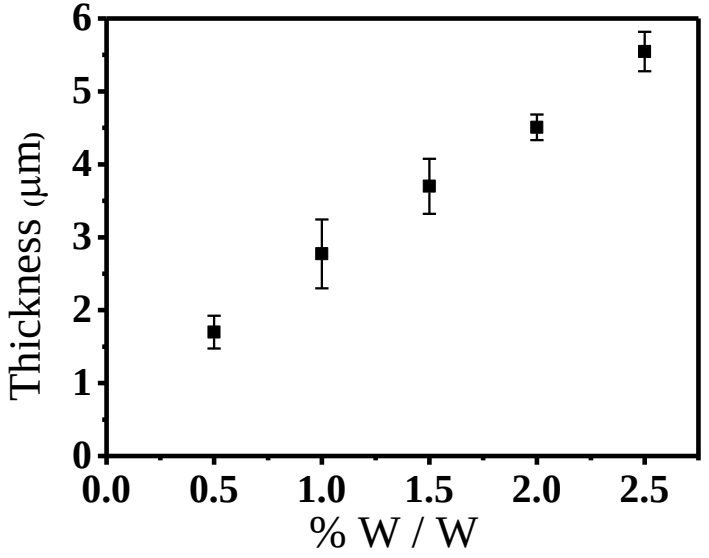


Film thickness of nanoparticles on ITO as a function of the deposition potential. Time of deposition was 5 min and nanoparticles concentration was 0.27% (w/w)

Controlling the Thickness

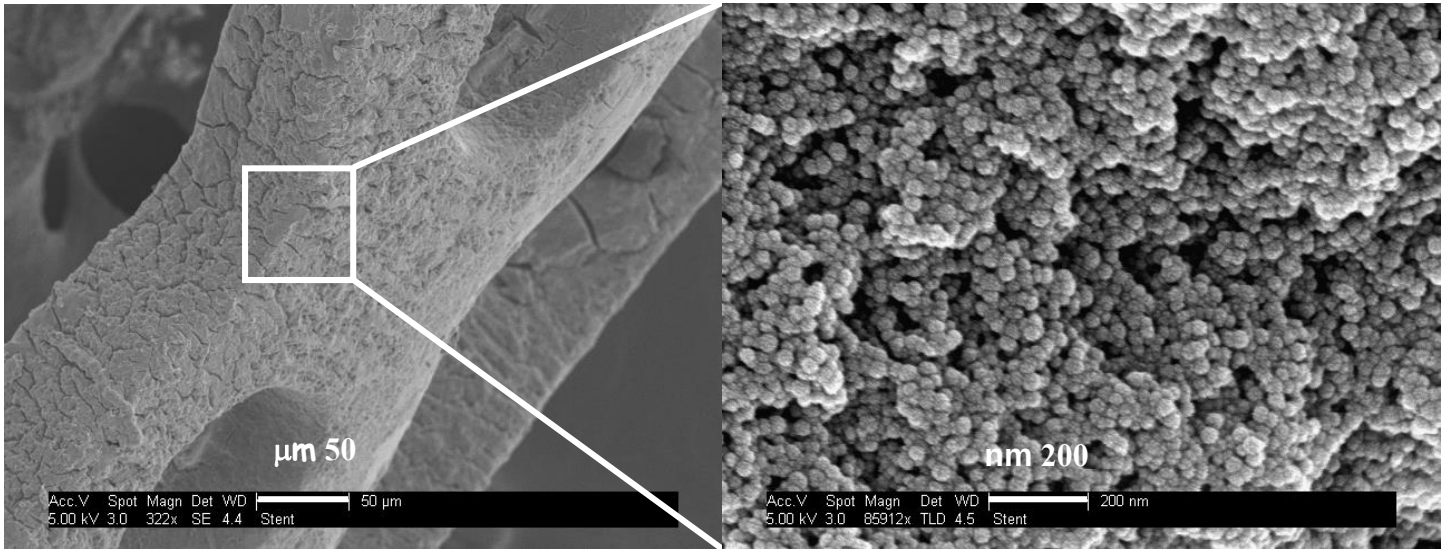


The change in film thickness with time of applied potential. The applied potential was 2.0 V and the nanoparticles concentration 0.27% (w/w)



Film thickness as a function of weight percentage of latex nanoparticles in the deposition solution. Potential and time of deposition are 2 V and 5 min, respectively

Electrochemical Coating of a Stent



HR-SEM images of a latex film electrochemically deposited on a stainless steel stent under a constant potential of 1.3 V for 10 min: (A) The stent after deposition (B) higher magnification of the deposited film

Electrochemical Deposition of Hydroxyapatite (HA) Nanoparticles

Orthopedic implants

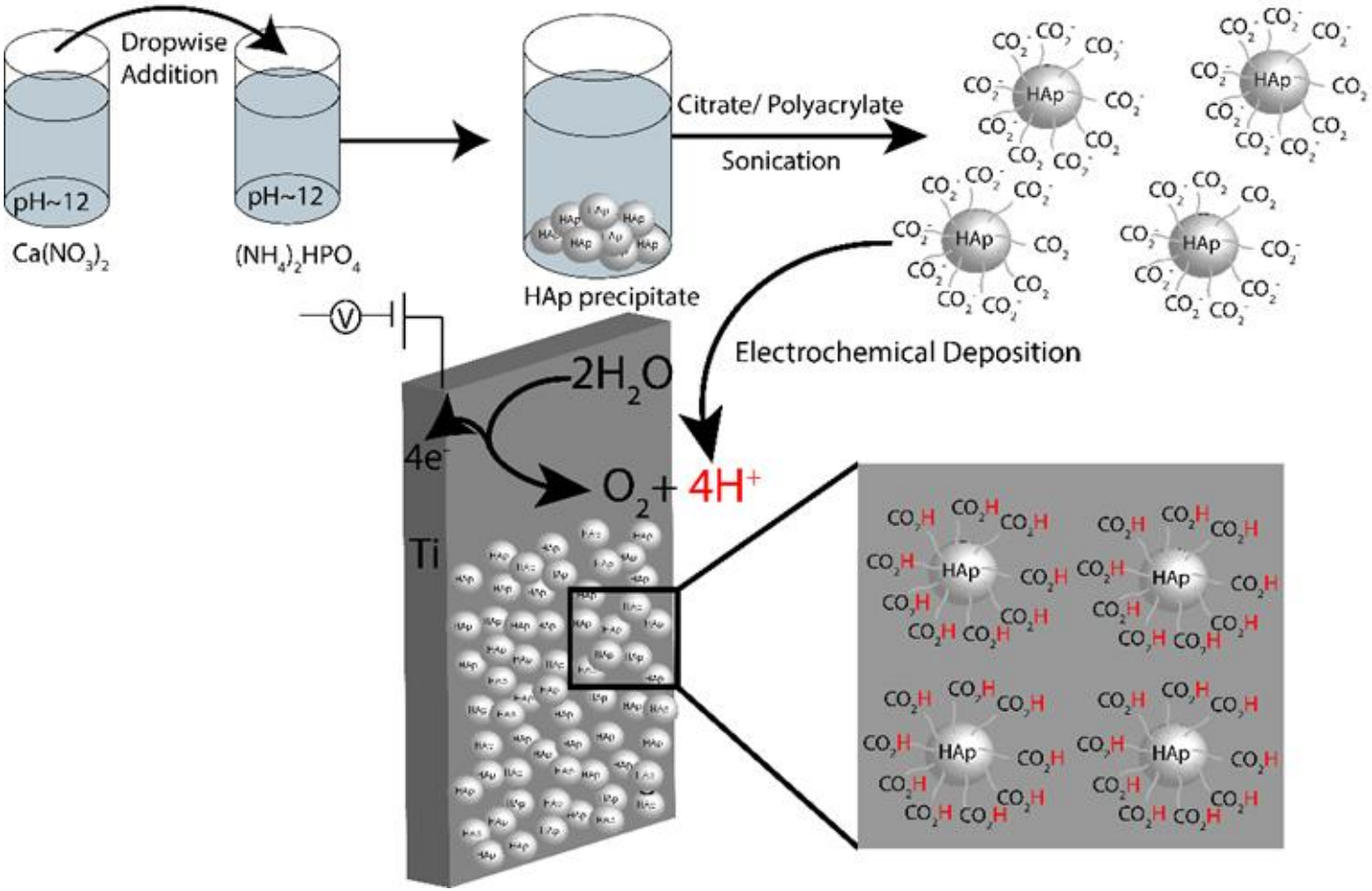
Coating the surface with HA has shown to improve osseointegration

$HA=Ca_5(PO_4)_3(OH)$

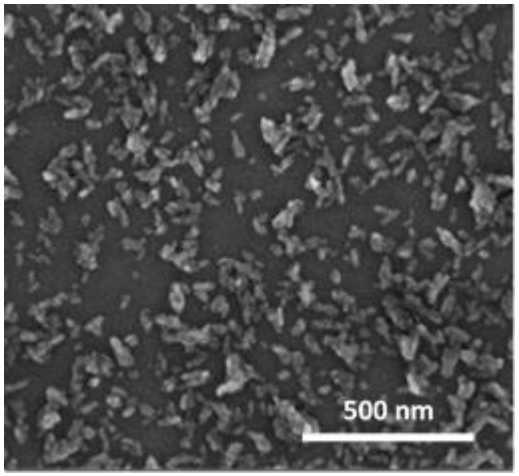
Methods:
Electrospraying at high temp
Electrochemical deposition

Geuli et al., Adv. Funct. Mater. 2016, 26, 8003

The Concept

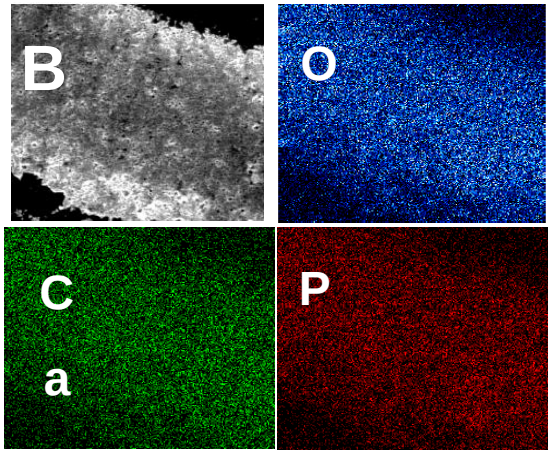

Dropwise Addition
pH~12
pH~12
$Ca(NO_3)_2$
$(NH_4)_2HPO_4$
HAp precipitate
Citrate/ Polyacrylate
Sonication
HAp
Electrochemical Deposition
$2H_2O$
$4e^-$
$O_2 + 4H^+$
Ti
CO_2H

Formation and Characterization of HA NPs

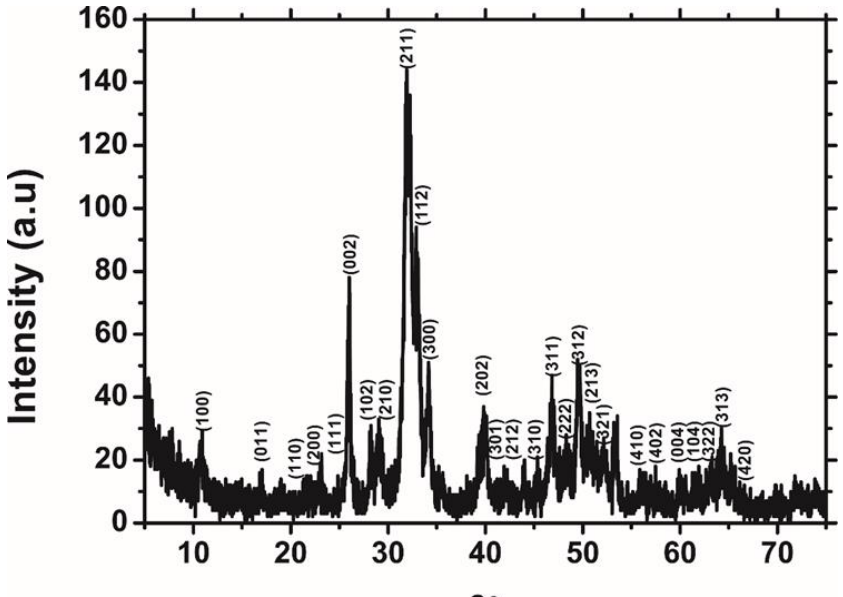


SEM image of HAp NPs

Element	at. %	
	EDS	XPS
Oxygen	68.3±2.5	60.2
Calcium	19.1±1.5	17.9
Phosphorus	12.5±0.1	11.3
Carbon	---	10.6

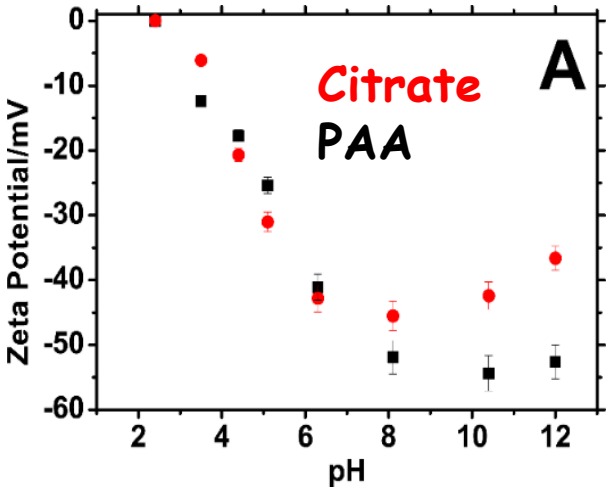


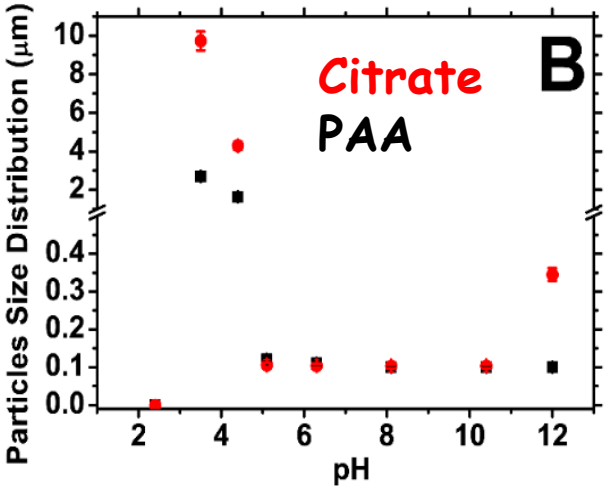
EDS, XPS and imaging

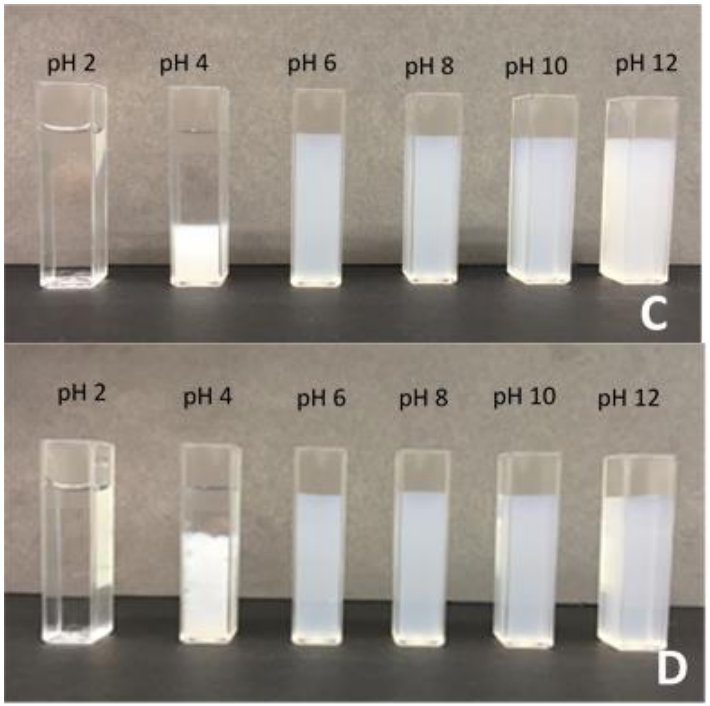


XRD

HA NPs in Water: Effect of pH on ζ-Potential and Aggregation

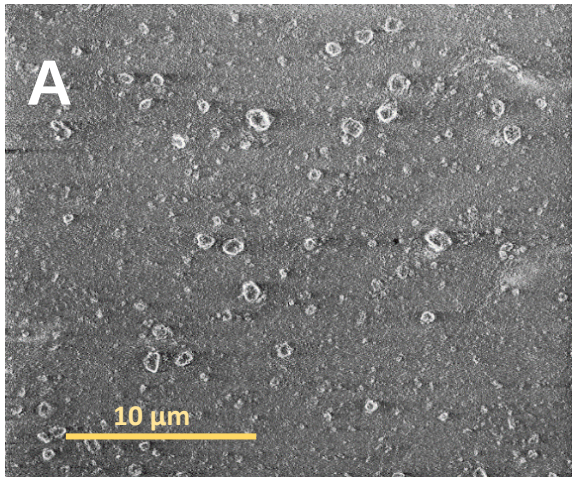


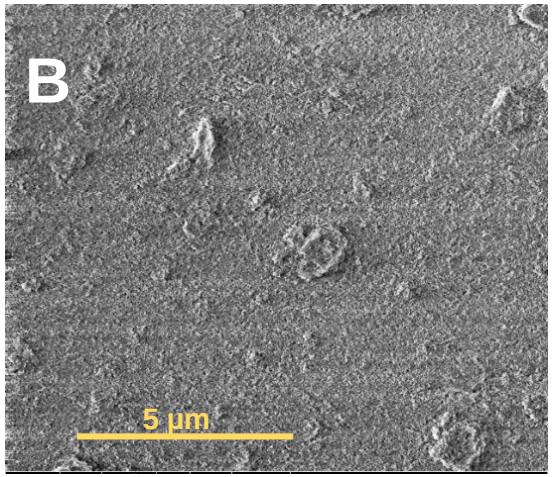


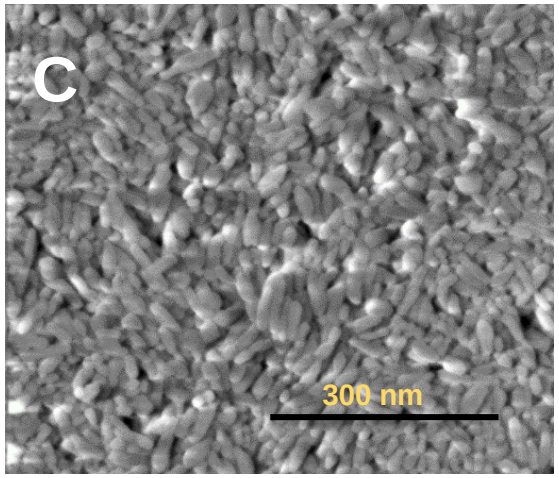


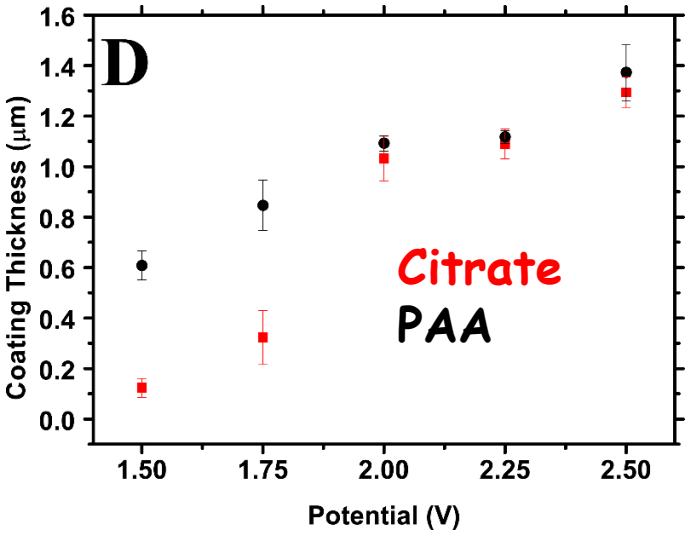
(A) ζ-potential, and (B) particle size distribution of HAp NPs dispersed by Cit (red dots) and PAA (black squares) as a function of pH. (C, D) Images of Cit and PAA (respectively)-stabilized HAp nanoparticle suspensions as a function of pH

Electrochemically Deposited HA NPs



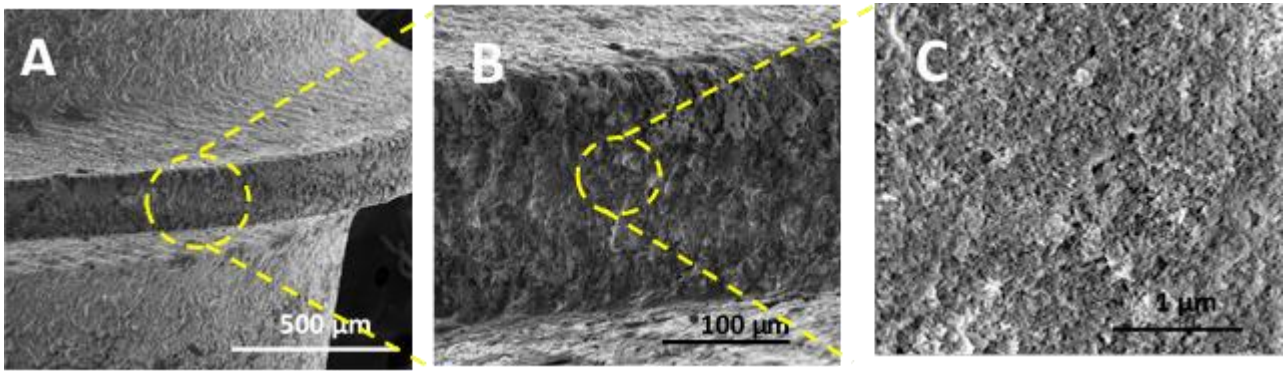




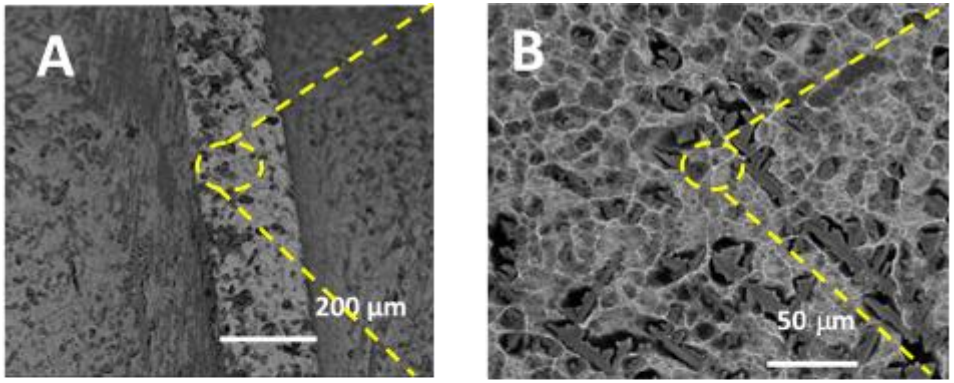


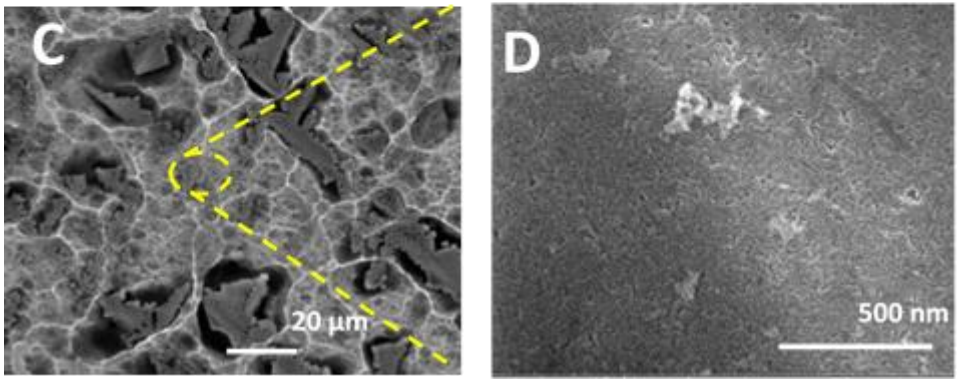
(A, B, C) XHR-SEM images at different magnifications of HAp NPs stabilized with Cit (10 mM) and electrochemically deposited at 2 V for 25 min. D) Thickness of the HAp NPs coating as a function of the applied potential for both dispersions (t = 25 min). Black dots: PAA-stabilized HAp NPs, red dots: Cit-stabilized HAp NPs.

Does it Work?



dental implant electrodeposited with HAp NPs stabilized by Cit at 2 V for 25 min

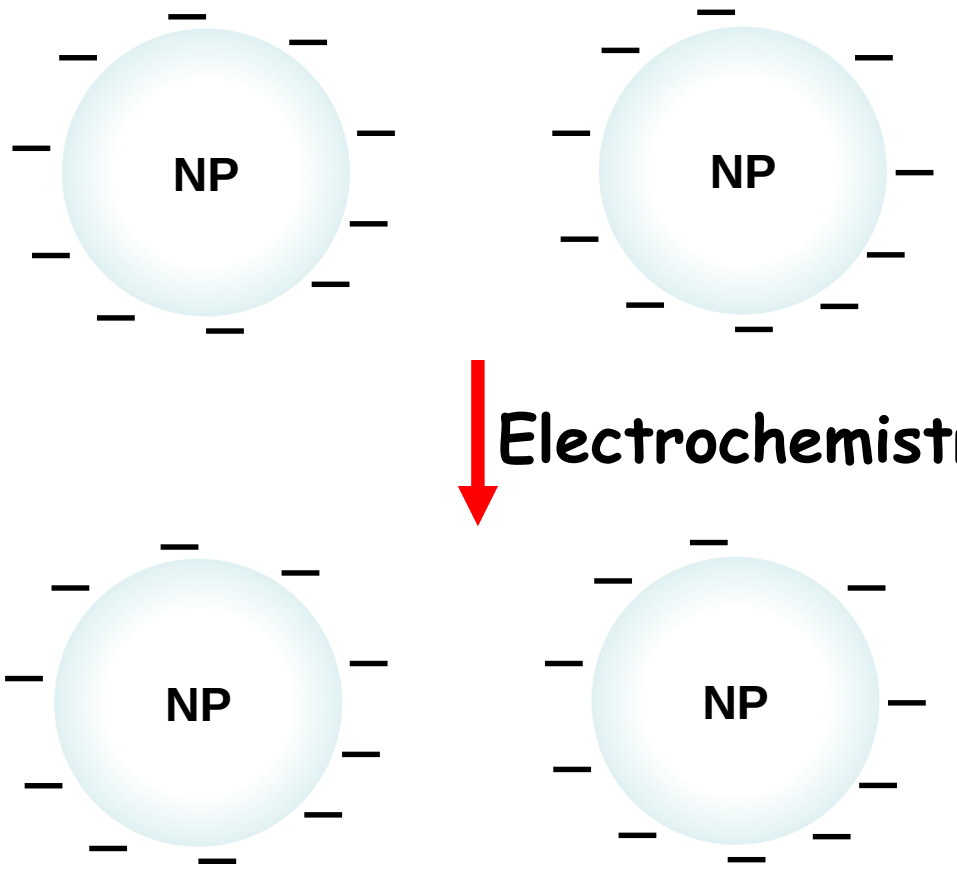




Commercial dental implant coated with HAp NPs after 30 days soaking in SBF at 37 °C

Electrochemical Control of the Interparticle Forces

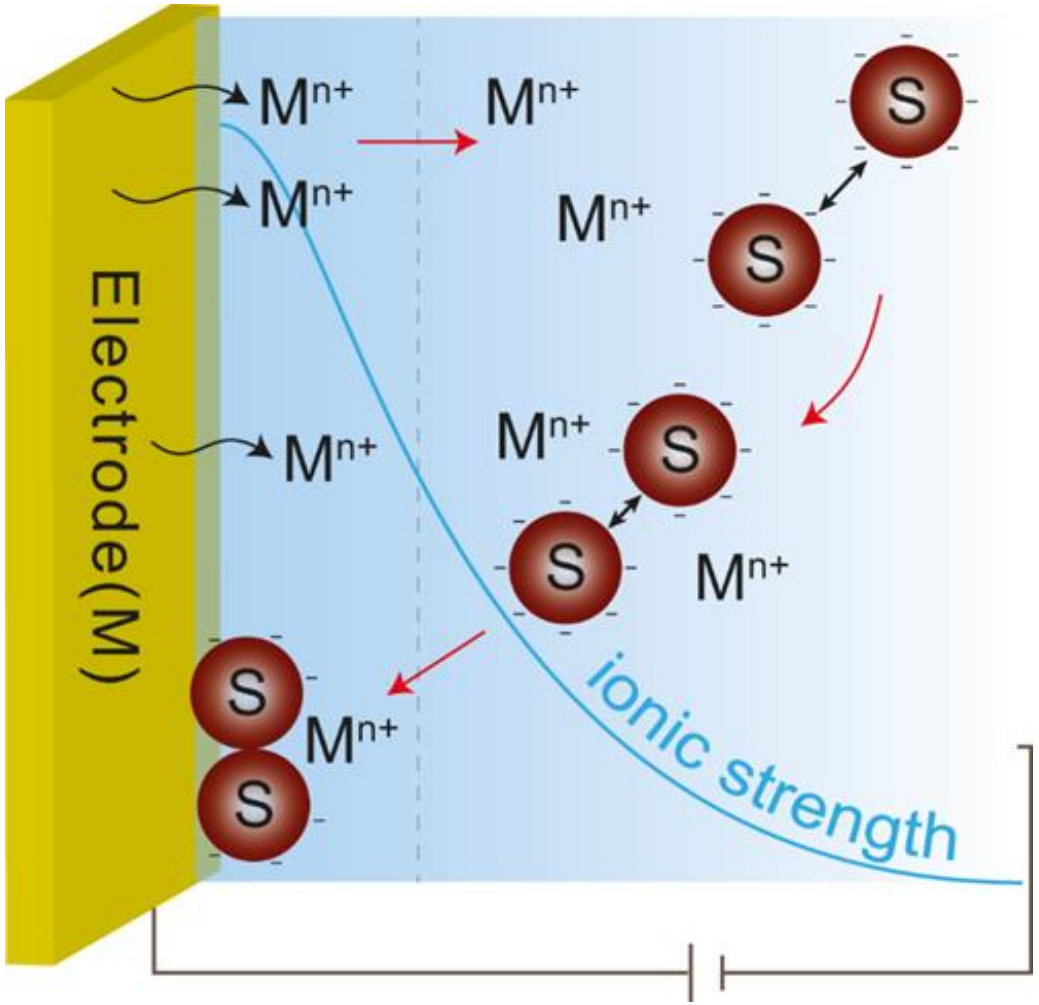
Electrostatic repulsion



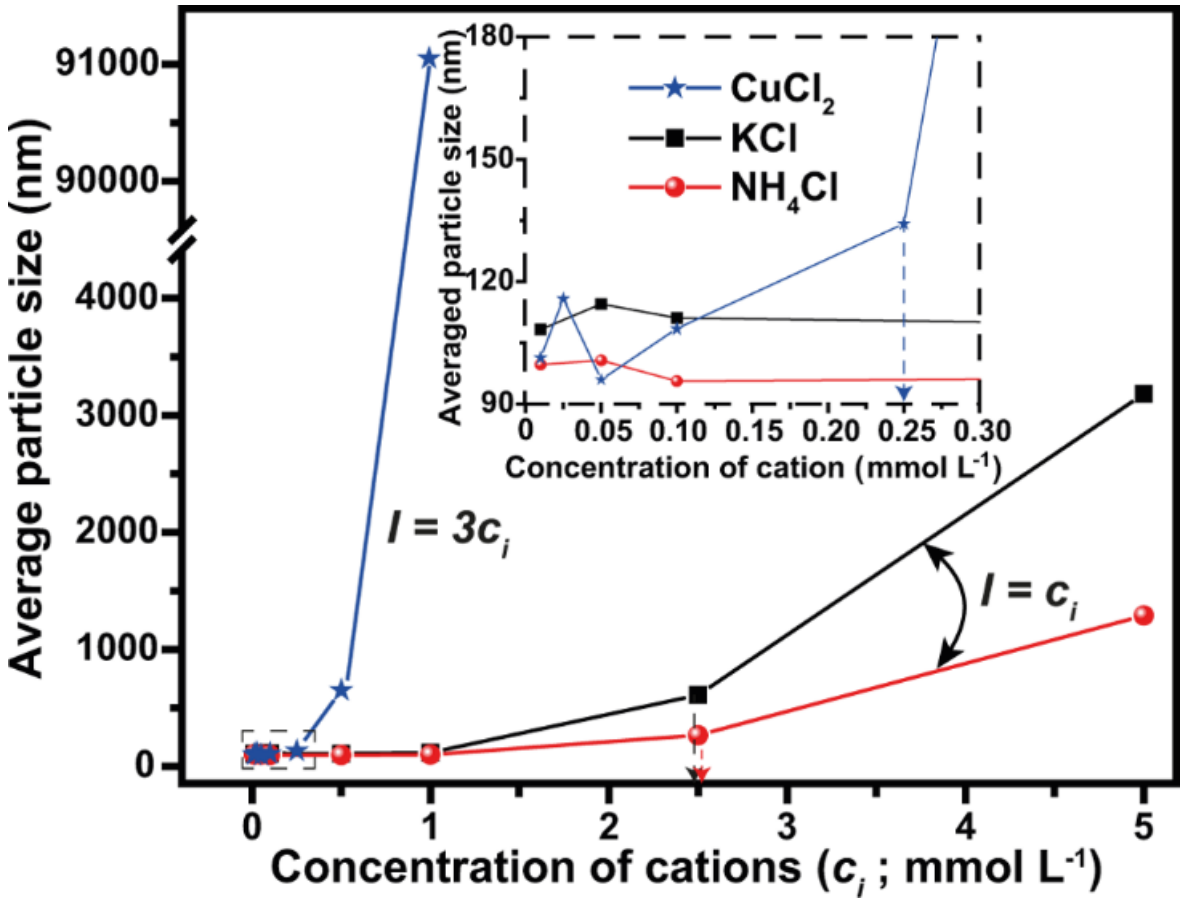
How can electrochemistry diminish the repulsion?

2. Changing the ionic strength

9. Ionic Strength Induced Electrodeposition

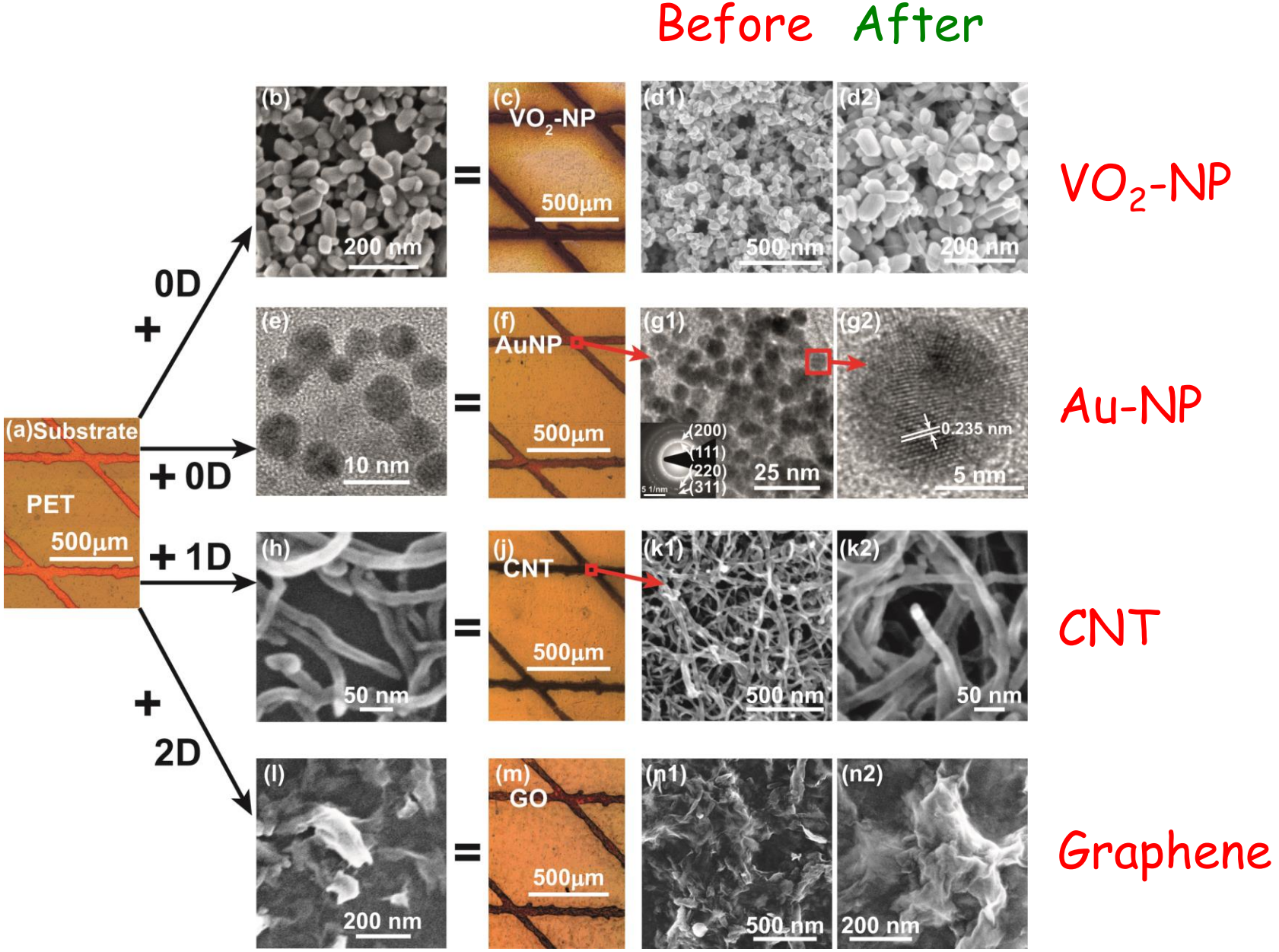


Effect of Ionic Strength on Aggregation

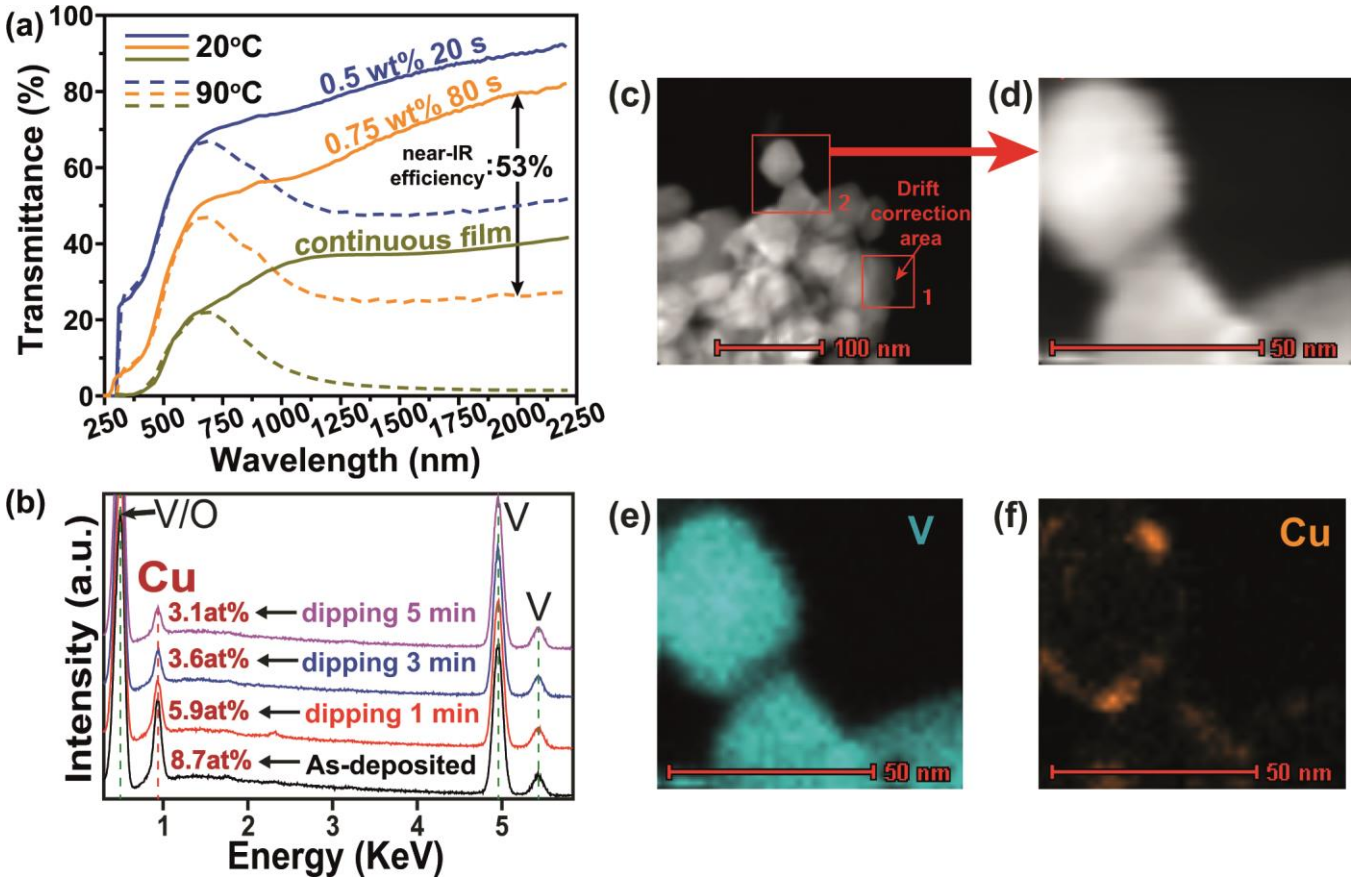


DLS results show the ionic concentration (or ionic strength) effect on the average particle size of VO_2-NP. The inset is the zoom-in image for c_i in the region of 0-0.3 mM.

Applicability of the Approach



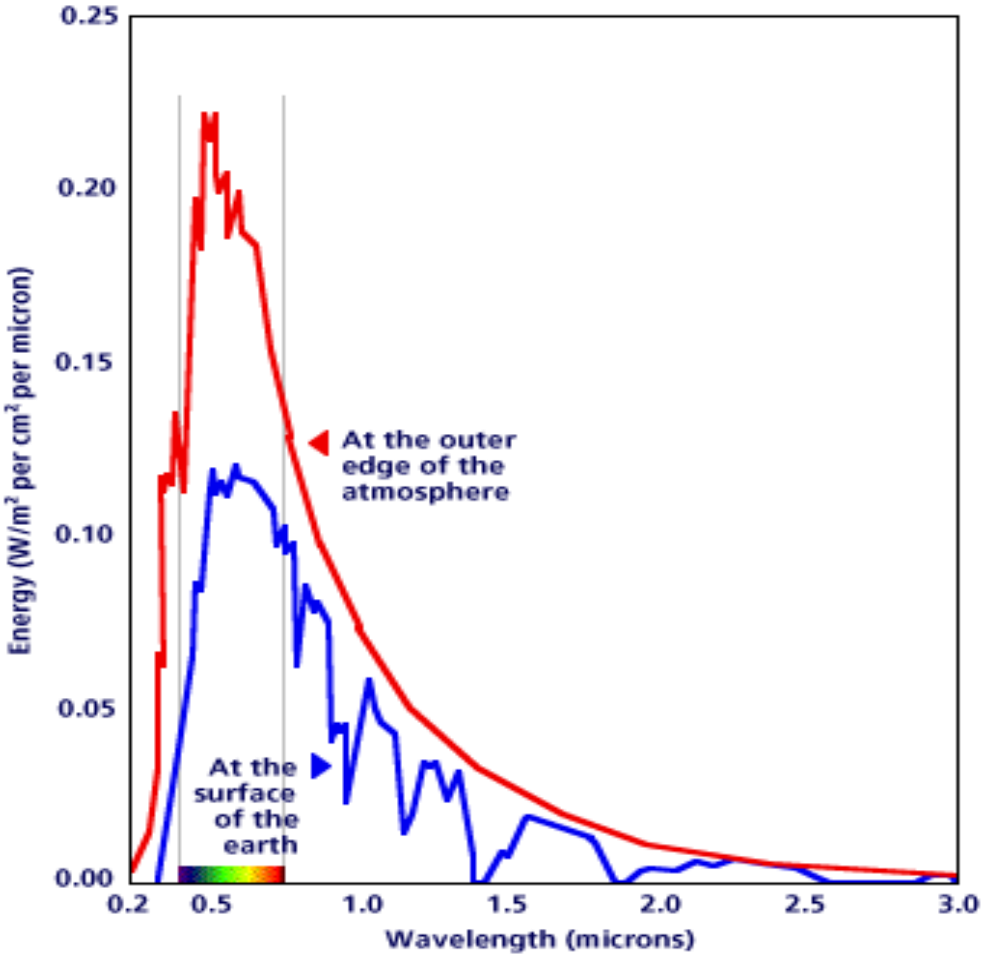
Performance of the VO_2-NP on the Cu Grid



Performance and characterization of VO_2-NP deposits: (a) transmittance spectra for the simulation of the continuous film and the best performing experimental results of the electrodeposited VO_2-NP micro-grid samples; (b) EDX of VO_2-NP deposits before and after immersing in 0.01 M HCl for different durations; (c) TEM image of VO_2-NP deposits; (d) high-angle annular dark-field (HAADF) image of mapping area; (e) EDX mapping of vanadium (in blue color); (f) EDX mapping of copper (in orange color).

10. Inorganic Thin Films – Solar Thermal Conversion

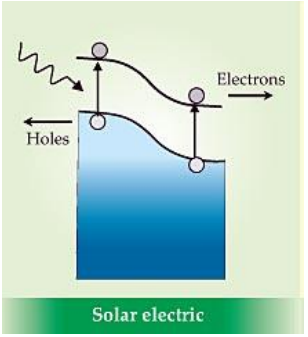
- In one hour, an energy of $4.6 \cdot 10^{20}$ J is delivered by the sun to earth, estimated to be humans annual consumption.
- Solar energy is environment friendly- without pollutant residues.
- Less then 0.1% of world electricity is solar power*.
- The temperature at the surface of the sun is ca. 6000 K. At that temperature, the sun behaves similarly to a black body.



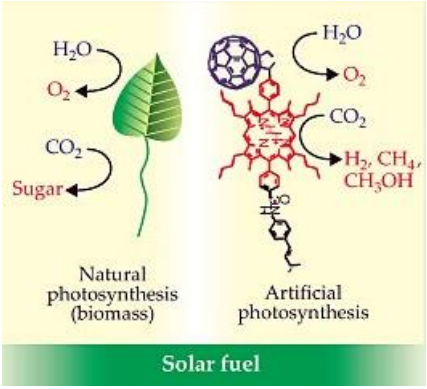
* N.S. Lewis *Basic Research needs for Solar Energy Utilization* 2005, p. 276

Solar Energy Conversion Approaches

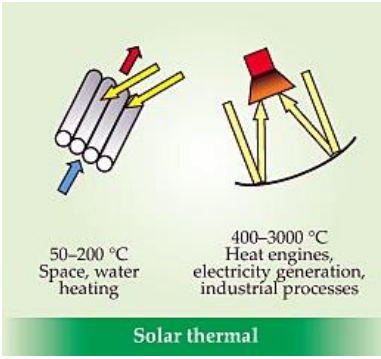
- Photovoltaic



- Solar fuel

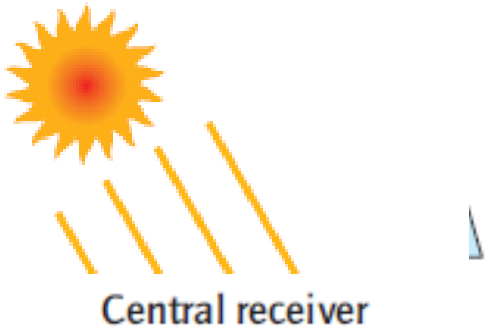


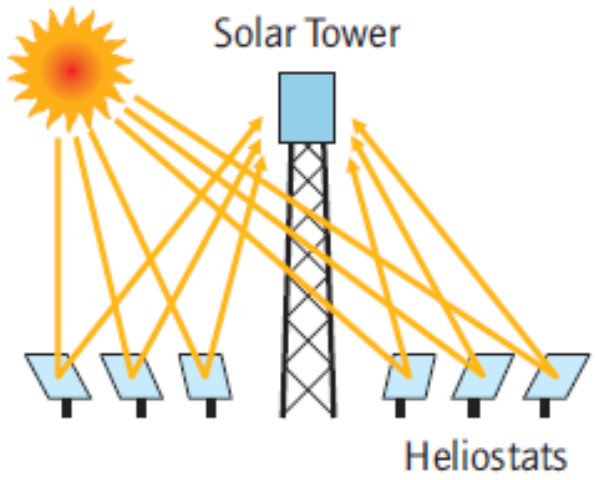
- Photothermal



Photothermal Conversion Methods

- A Parabolic Trough
- Linear Fresnel Reflectors
- Parabolic Dish Systems
- Power Tower Systems

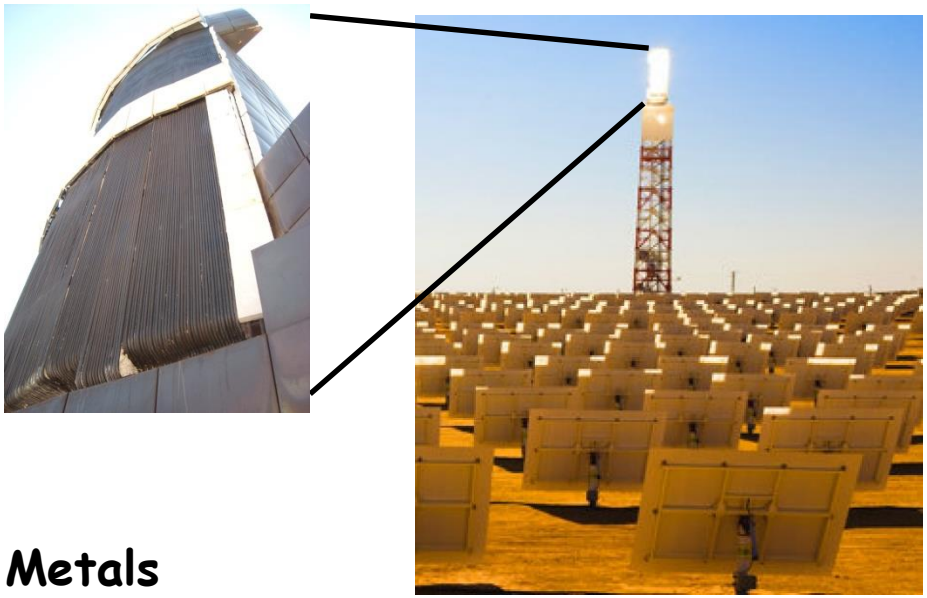




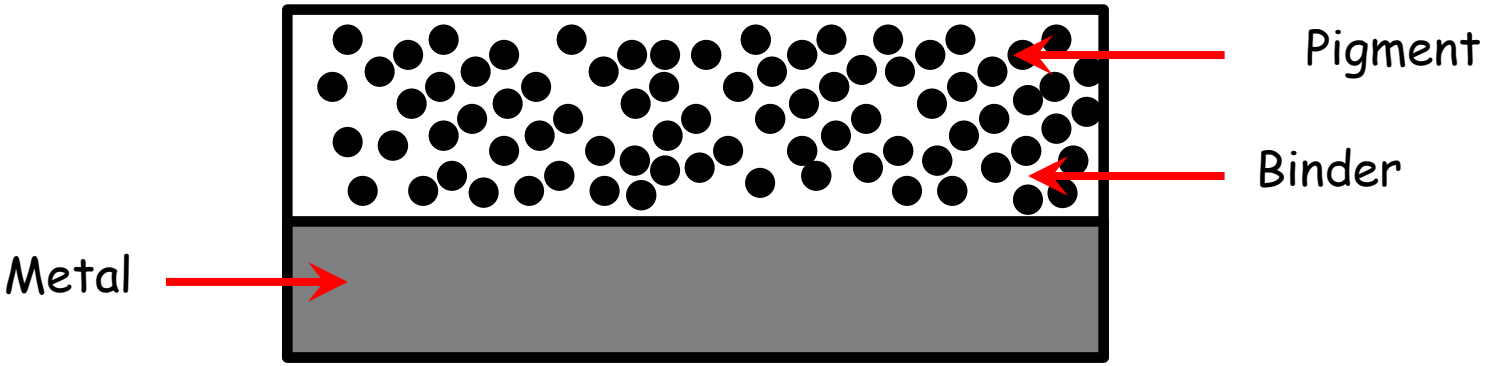
Functionalized Coatings: Photothermal Conversion of Solar Energy

Developing a photothermal coating for high temperatures (stable at 750°C):

- ❑ **High absorptance (95%).**
- ❑ **Corrosion resistance.**
- ❑ **Good adhesion to substrate.**
- ❑ **Inexpensive and easily applied.**



Cermet – Ceramic Metals



Formulation: Preparation of the Coating Dispersion

Typical Formulation	%
Solvent/ water	60-90
Matrix former	2-30
Dispersant	2
Wetting agent	1
Black pigment	2-20

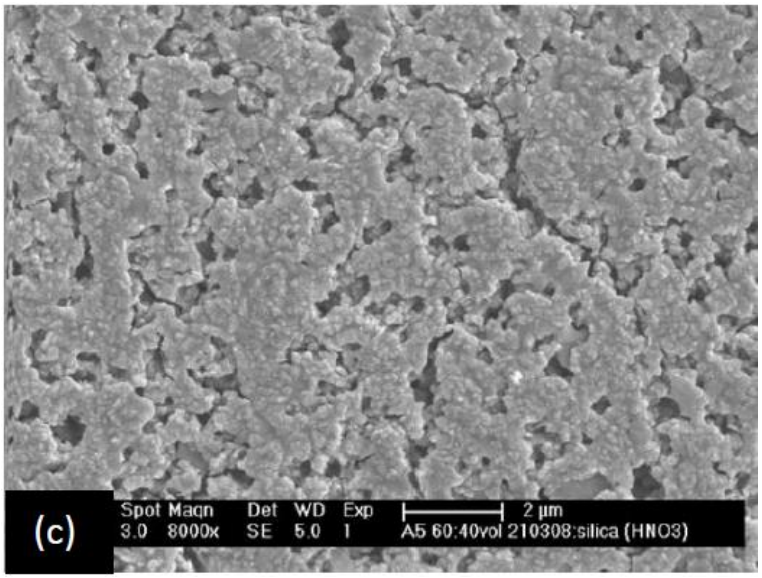
Application methodology:

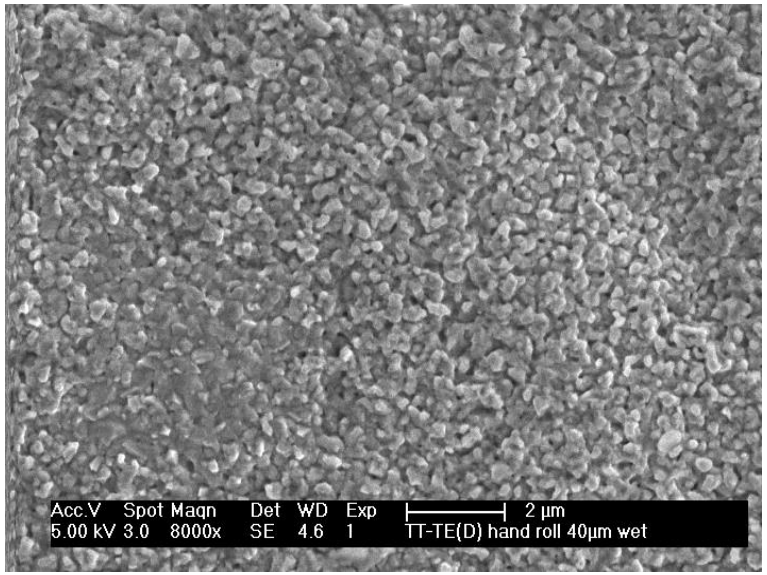
- **Substrate: Inconel (625,718, 740) stainless steel (non-sand blasted)**
- **Coating method: hand roll, brush and spray coating**
- **Curing profile: 5 or 10 °C/min up to 750 °C - 2 hours**

Goals

1. Very high absorptance (>95%)
2. High thermal stability (>1000 hr at 750 °C)
3. Excellent adhesion
4. No corrosion

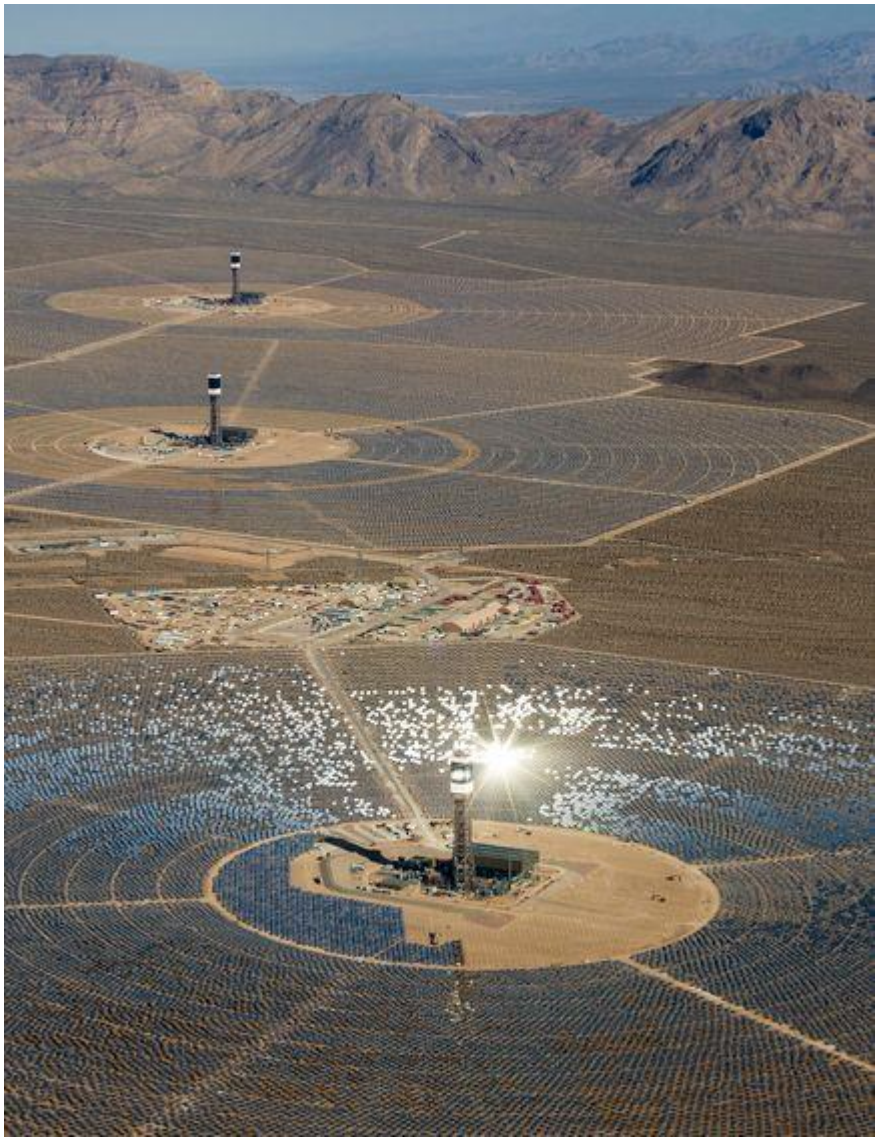
SEM of the coatings after curing





The Ivenpah CSP in California

http://www.brightsourceenergy.com/ivanpah-solar-project



11. Forensic Science: Fingerprint Visualization

The challenge: visualizing fingerprints on wet papers
The reason: the amino acids dissolve

The inorganic and organic constituents present in glandular secretions that may contribute to fingermark residues*

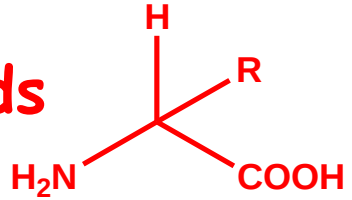
Gland type	Inorganic substituents	Organic substituents
Eccrine	Chlorides	Amino acids
	Sodium	Urea
	Potassium	Lactic acid
	Ammonia	Proteins
	Sulfates	Sugars
		Creatinine
Apocrine	Iron	Proteins
		Carbohydrates
		Cholesterol
Sebaceous		Fatty acids
		Hydrocarbons
		Alcohols
		Glycerides

* J. Almog, Visualization, in: J.A. Siegel, P.J. Saukko, G.C. Knupfer (Eds.), Encyclopedia of Forensic Sciences, Oxford, 2000, pp. 890–900

Composition of the fingermarks

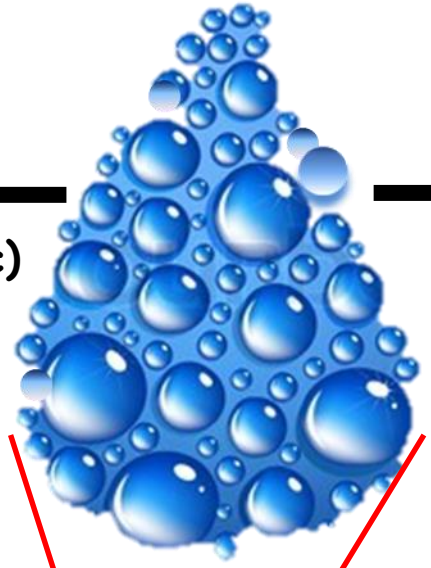
~ 98% water

Amino acids



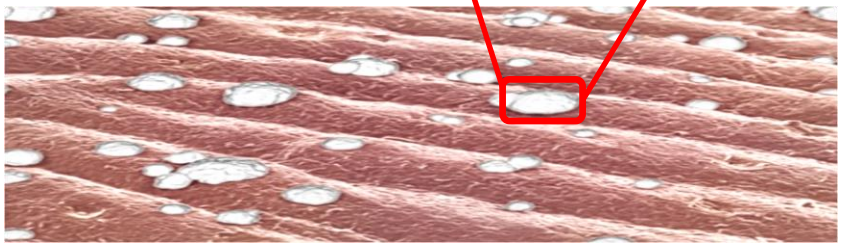
Inorganic

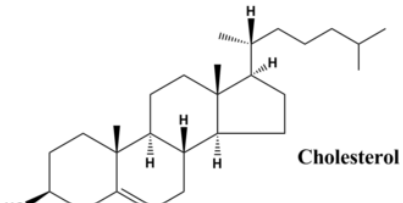
(chlorides, metals ions , etc)

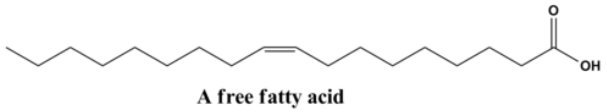


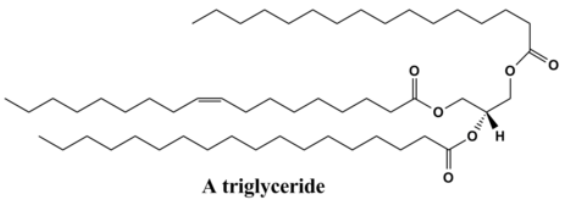
Organic

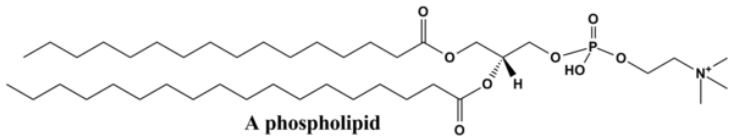
Lipids



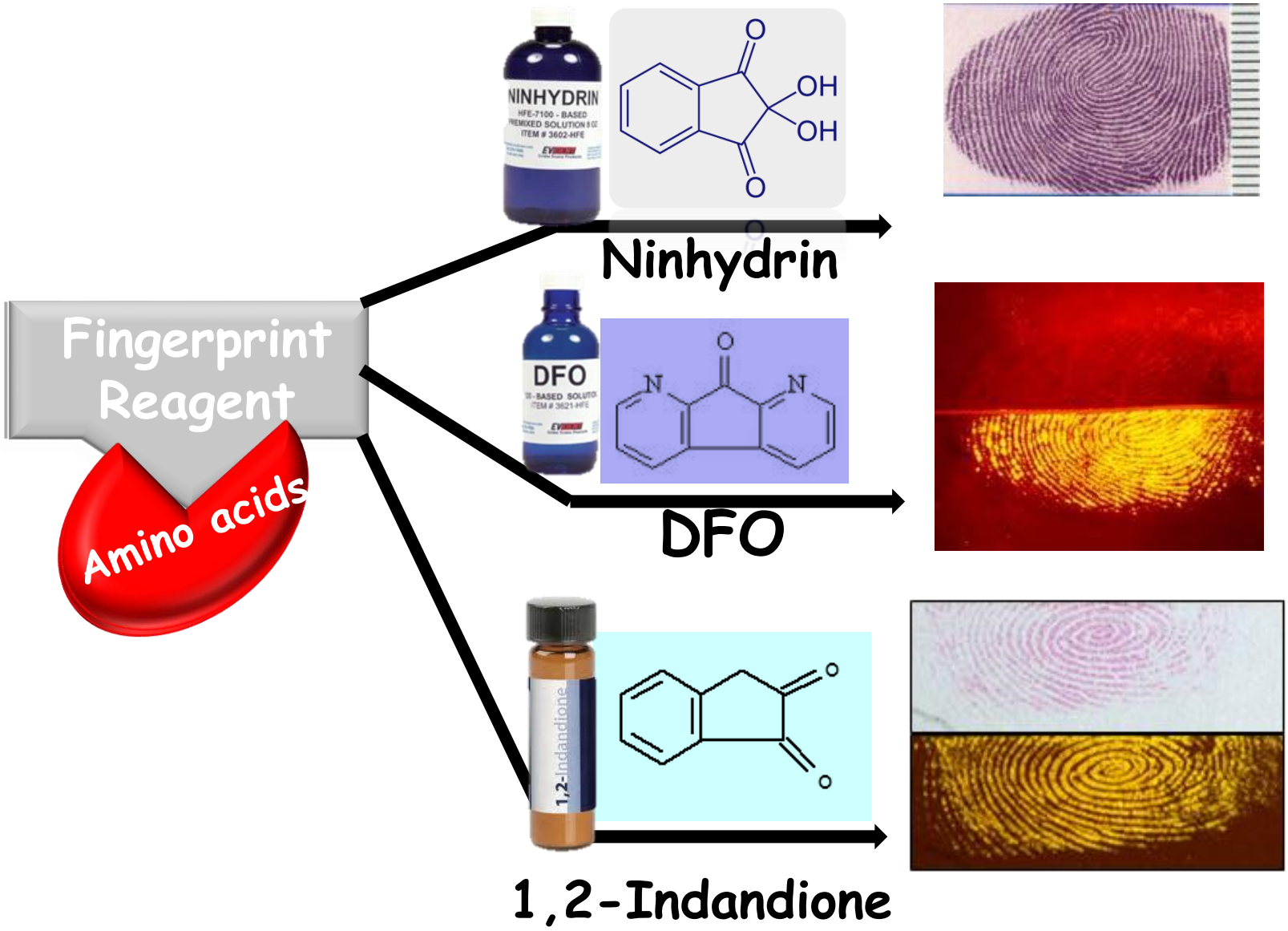




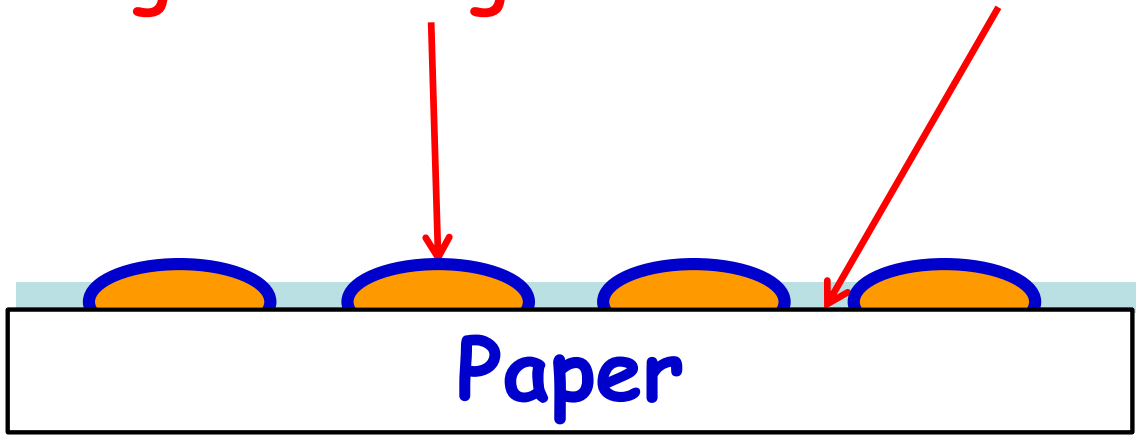




Targeting the Ridges

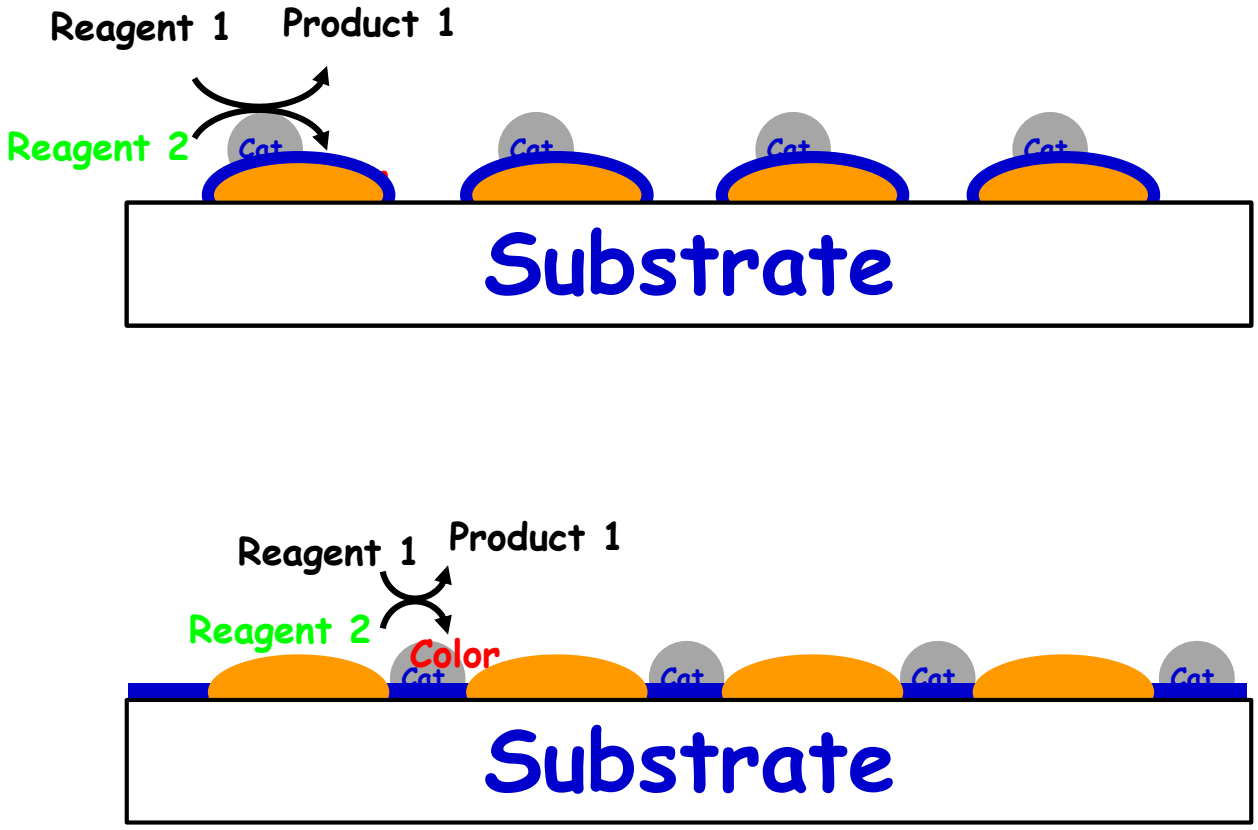


Targeting the Ridges or the Substrate?



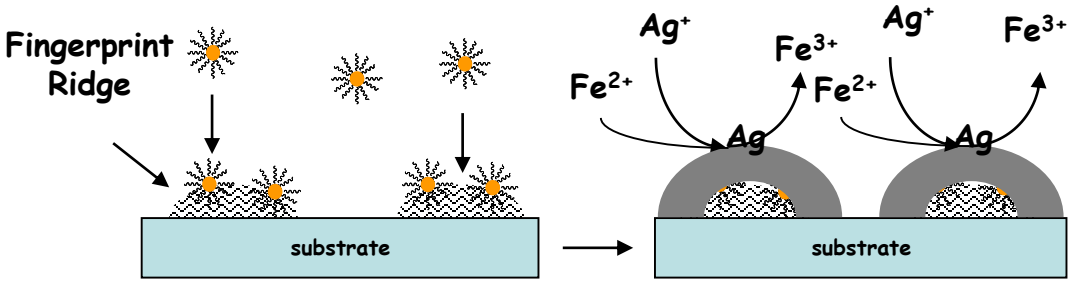
In both cases visualization is limited by the active sites

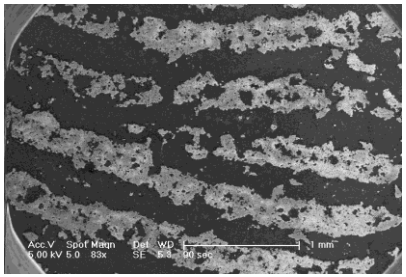
The catalytic (non-stoichiometric) approach



Applying Nanoparticles for Visualizing Latent Fingerprints

$$Ag^{+}+Fe^{2+}\rightarrow Ag+Fe^{3+}$$

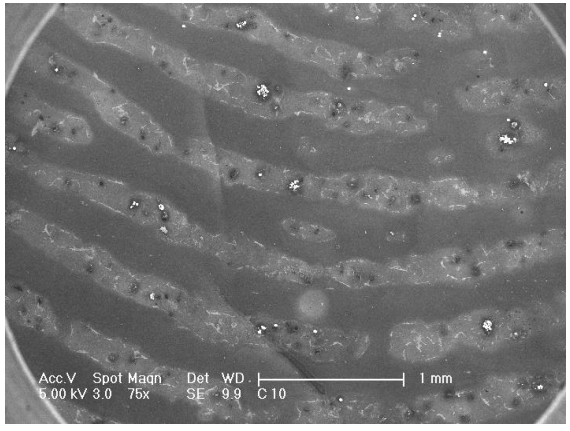


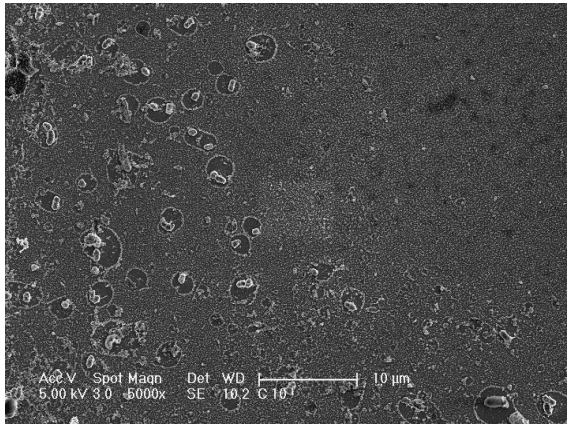


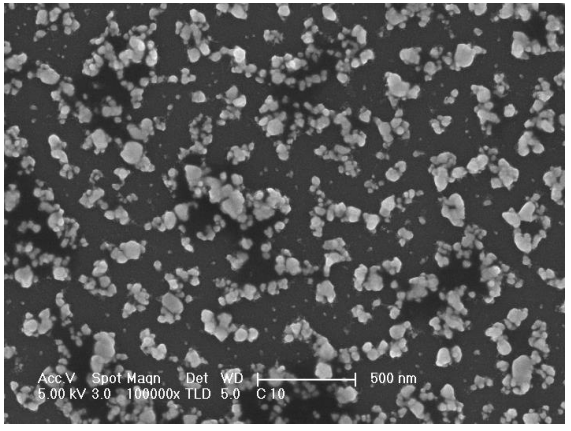
Sametband et al. Chem. Comm. 2007, 1142-1144

Comparison between different chain lengths - silicon surfaces

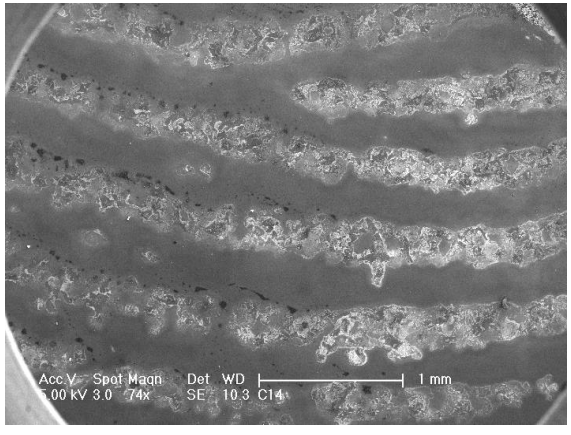
C_{10}

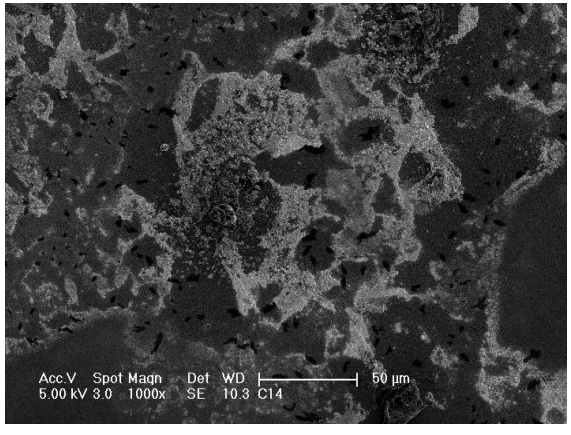


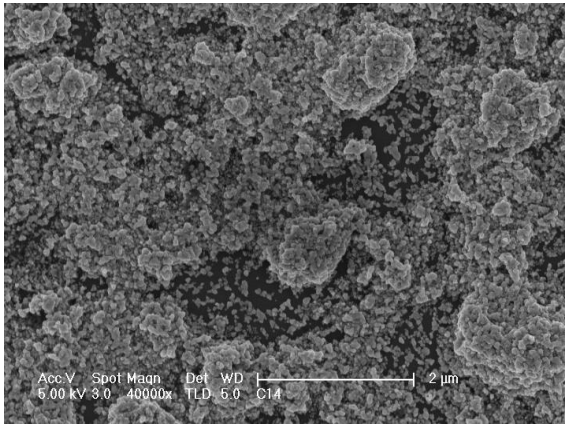




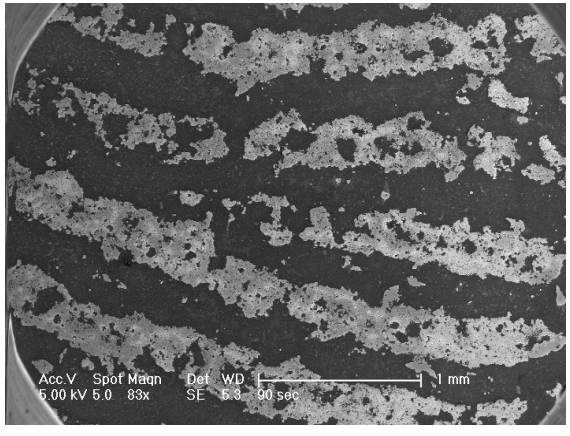
C_{14}

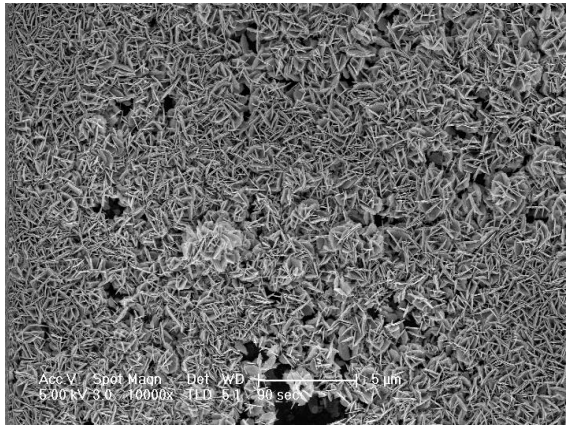


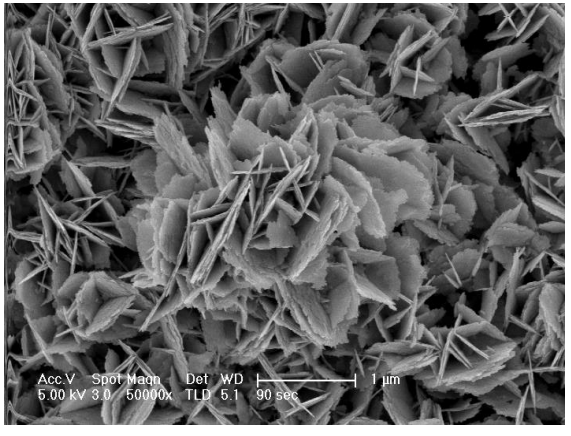




C_{18}







The reverse approach

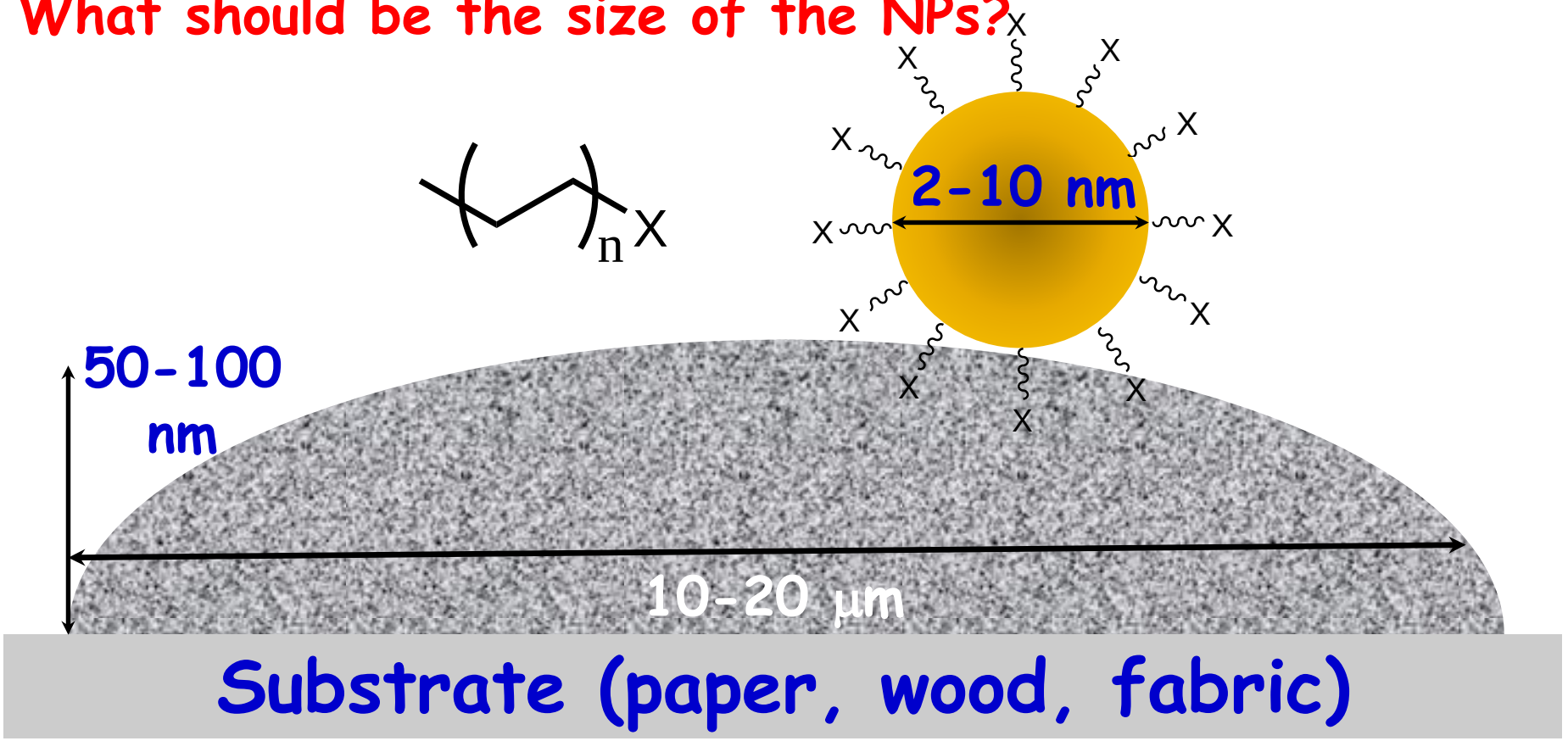
Reaction with the substrate

Advantages:

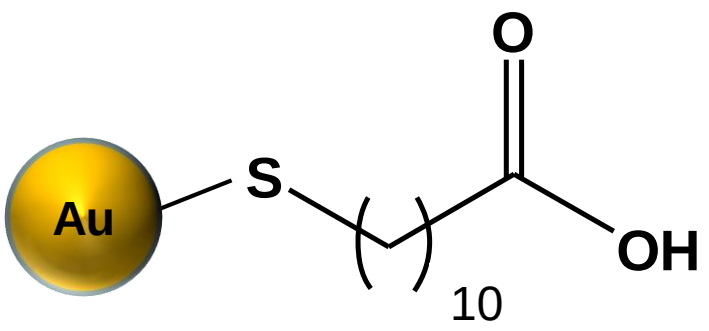
- Generic nature
- Insensitive to the nature of the fingermark
- Should be more sensitive due to higher concentration of active sites
- …

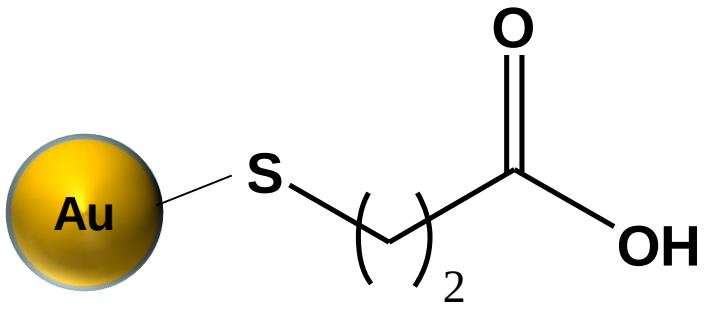
Designing the Catalyst…

- What should be X?
- What should we target?
- What should be the nature of interactions?
- What should be the size of the NPs?

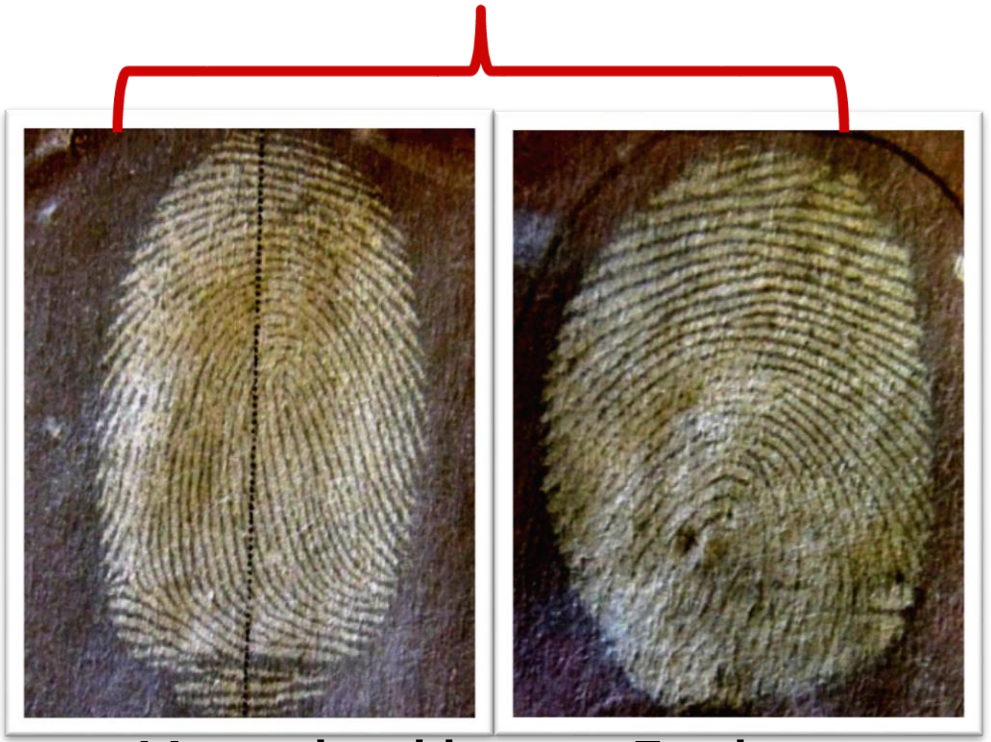


Designing the Catalyst





3-Mercaptopropanoic acid



14 months old

Fresh

Conclusions and Take Home Lessons…

✓ Interfaces can be designed and structured by thin films ranging from monomolecular layers to polymers

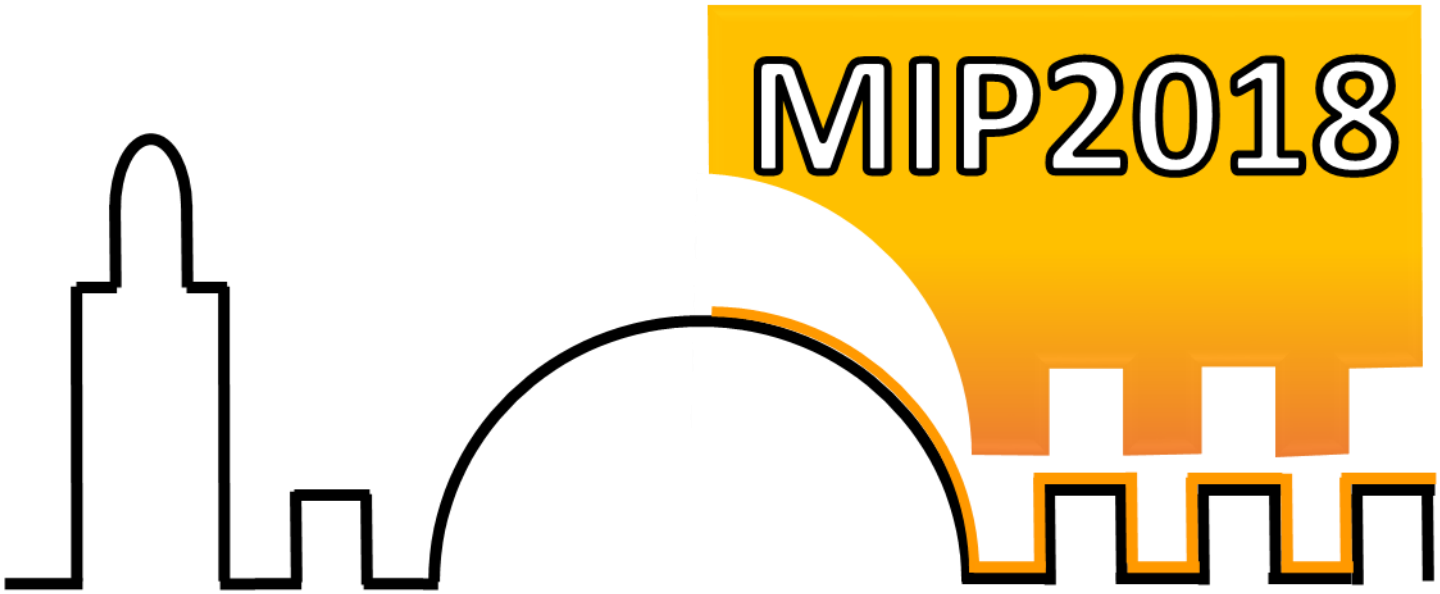
✓ The physical and chemical properties of the surfaces can be tailored by these films

✓ Electrochemistry is an excellent approach for modification, characterization and controlling the deposition as well as the release of a wide variety of materials

✓The future… advanced, smart multifunctional thin films

Acknowledgment

Next MIP Conference



Jerusalem

Save the dates!

June 24-28, 2018

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Thank You!

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