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

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The Pregl Colloquium, November 23, 2017
Slovenia
20,273
2.1

Israel
20,770 (sq.Km)
8.55 (Mpeople)
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

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

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

\[
\text{HS} \xrightarrow{\text{X}} \text{CO}_2\text{H}, \text{NH}_2, \text{SO}_3\text{H}... \\
\text{Ox/Red}
\]
Electrochemical Sensors for Heavy Metals Based on Self-Assembled Monolayers

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

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

1. Metal Deposition (Reduction)
   \[ \text{Hg}^{2+} + 2e^- \rightarrow \text{Hg}^0 \]

2. LSV - Stripping (Oxidation)
   \[ \text{Hg}^0 \rightarrow \text{Hg}^{2+} + 2e^- \]

\[ \text{Ox} + ne^- \rightarrow \text{Red} \]
\[ Q = nFAI \]
1. Sensor for Cd(II): The Under Potential Deposition Effect

Cd stripping

$\text{Cd} \rightarrow \text{Cd}^{2+} + 2e^-$

$\text{Cd}^{2+} + 2e^- \rightarrow \text{Cd}$

CV of 1mM Cd$^{2+}$ in 0.1 M of H$_2$SO$_4$, Au electrode, scan rate 0.1 Vs$^{-1}$

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

![Graph showing the effect of time on Cd UPD on a bare Au electrode. The x-axis represents E/Volt vs Ag/AgCl, and the y-axis represents I/μA. The graph includes data points at 15, 30, 60, 120, 300, and 360 seconds. The y-axis values range from -14 to 8, and the x-axis values range from -0.4 to 0.6. The graph includes a label for 1 ppb Cd⁺², SASV pH2, and Au Electrode.](image-url)
Self Assembled Monolayers (SAM’s)

Head Group : SH

Tail : Alkyl Chain

Functional Group :

- $\text{COOH}$, $\text{SO}_3$, $\text{NH}_2$
The Effect of a Self-Assembled Monolayer (SAM) on the UPD
The height of the peak obtained from subtractive square wave anodic stripping voltammetry (SASV) of Cd$^{2+}$ in buffer pH 2, $E_{\text{dep}}=-0.4$ V $T_{\text{dep}}=360$ sec
Measuring Cd in Tap Water

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 was 320±8 ppm.

ICP-MS result was 320±8 ppt.
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

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

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

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

$\Gamma=4.6 \times 10^{-9} \text{ mol} \cdot \text{cm}^{-2}$

CV (50 mV s$^{-1}$) of the modified ITO in 0.1 M K$_2$SO$_4$ (pH4.0)

CV (50 mV s$^{-1}$) of 1 mM Fe(APT)$_2^{2+}$ in 0.1 M K$_2$SO$_4$ (pH4.0)

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

CV of ITO/Fe(APT)$_2^{2+}$ in 0.1 M K$_2$SO$_4$ (pH4.0) at different scan rates and the dependence of the peak current on scan rate

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

Solution:
- Synthesize a more flexible arm

\[ \text{Fe}^{2+} \quad \text{Fe(tpy)}_2^{2+} \]
Attachment of APOTPY onto ITO

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

CV (50 mV·s⁻¹) of ITO
APOTPY 1 mM and 0.1 M TBATFB in ACN

XPS of APOTPY

Survey - APOTPY E-modification
C 1s
N 1s
Extraction of Fe$^{2+}$ by an ITO/APOTPY

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

XPS of an ITO/APOTPY electrode after extraction of Fe$^{2+}$
**Effect of scan rate**  \[ \Gamma = 2.8 \cdot 10^{-10} \text{mol} \cdot \text{cm}^{-2} \]

**Effect of time of preconcentration (SWV, 0.1 mM Fe}^{2+} \text{)
3. SAM for Increasing the Adhesion

Coating medical implants

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

\[ \text{OPO}_2\text{H}_2 \]
Preparations of Alkyl Phosphonic Acid SAM on Titanium Surface

Chemically prepared

\[ \text{Ru(NH}_3\text{)}_6^{3+} + e^- \rightarrow \text{Ru(NH}_3\text{)}_6^{2+} \]

![Graph A](image1.png)

Electrochemically prepared

\[ I \propto e^{-d} \]

![Graph B](image2.png)
Preparations of Alkyl Phosphonic Acid SAM on Titanium Surface

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemisorbed</th>
<th>Electrochemically prepared</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean Capacitance [(\mu F/cm^2)]</td>
<td>Mean Capacitance [(\mu F/cm^2)]</td>
</tr>
<tr>
<td>Control</td>
<td>39.25±8.14</td>
<td>39.89±1.06</td>
</tr>
<tr>
<td>6C</td>
<td>4.66±1.60</td>
<td>5.42±1.35</td>
</tr>
<tr>
<td>10C</td>
<td>2.98±0.81</td>
<td>2.70±0.27</td>
</tr>
<tr>
<td>13C</td>
<td>1.41±0.22</td>
<td>-</td>
</tr>
<tr>
<td>16C</td>
<td>1.05±0.09</td>
<td>-</td>
</tr>
</tbody>
</table>

\[ C_{dl} = \frac{\varepsilon \varepsilon_0 A}{d} \]
Controlling the Deposition of Hydroxyapatite

\[ \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \]

\[ 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \]

\[ \text{HPO}_4^{2-} + \text{OH}^- \rightarrow \text{PO}_4^{3-} \]

\[ 10\text{Ca}^{2+} + 6\text{PO}_4^{3-} + 2\text{OH}^- \rightarrow \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \]

- Length of chain:
  \[ \text{PO}_3\text{H}_2-(\text{CH}_2)_n-\text{PO}_3\text{H}_2, \ n=3,6,12 \]

- End group charge:
  \[ \text{PO}_3\text{H}_2-(\text{CH}_2)_3-x, \ x= \text{PO}_3\text{H}_2, \text{NH}_2, \text{CH}_3 \]

- Anchoring group:
  \[ x-(\text{CH}_2)_3-x, \ x= \text{PO}_3\text{H}_2, \text{COOH}, \text{OH} \]
Calcium Phosphate Coatings and SAMs

![Graph showing Ca/P ratio with alkyl chain variations](image)

Alkyl Chain: $\text{PO}_3\text{H}_2-(\text{CH}_2)_3-x \times (\text{CH}_2)_x-\text{PO}_3\text{H}_2$
The Effect of the SAM on Stress Failure Test

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stress to failure [MPa] (GB)</th>
<th>Stress to failure [MPa] (NaOH)</th>
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<tbody>
<tr>
<td>No SAM</td>
<td>8.08±0.52</td>
<td>26.18±6.60</td>
</tr>
<tr>
<td>(\text{PO}_3\text{H}_2-(\text{CH}_2)_3-\text{PO}_3\text{H}_2)</td>
<td>48.45±6.12</td>
<td>22.6±4.48</td>
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<tr>
<td>(\text{PO}_3\text{H}_2-(\text{CH}_2)_6-\text{PO}_3\text{H}_2)</td>
<td>37.26±6.86</td>
<td>45.52±16.36</td>
</tr>
</tbody>
</table>

![Diagram](image)

- 5-10 μm
- 7-10 Å
- Ca-P coating
- Ti
It's time to move to thicker films...

- Thin/Thick Films
  - Inorganic Materials
    - Sol-Gel
  - Organic Polymer
  - Nanomaterials

Applications
- Sensors
- Solar Energy
- Medical Coatings
- Fingerprints
The Sol-Gel Process

\[ MX_4 \rightarrow MO_2 \]

\[ M= Si, Zr, W, Ti... \]

\[ X= RO, RO_2, X (halides)... \]

**Hydrolysis**

\[ M(OR)_4 + H_2O \overset{H^+ \text{ or } OH^-}{\rightarrow} M(OR)_3(OH) + ROH \]

**Condensation**

\[ M(OR')_4 + M(OR)_4 \rightarrow (R'O)_3M-O-M(OR)_3 + ROR' \]

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 \( M \).
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)

acid hydrolysis

condensation

TEOS
(tetraethoxy silane)

PTMOS
Phenyl trimethoxy silane

APTES
aminopropyl triethoxy silane

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 0.1 M 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)
Selectivity in Binding Parathion vs. Derivatives

parathion

paraoxon

TEP

parathion-Me

fenitrothion

parathion - Me

fenitrothion

Selectivity in Binding Parathion vs. Derivatives
Selectivity for Parathion

- Imprinted polymer
- Non-imprinted polymer

Relative binding

- Parathion
- Methyl parathion
- Paraoxon
- TEP
- Fenitrothion
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

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

Solid support

Removable barriers

Tanami G. Langmuir 2010, 26, 4239
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·m⁻¹ before (a) and after (b–d) electrochemical dissolution of gold.
LSV of oxidation the Au NPs

LSV of 1–3 deposited NIP (33 nm AuNPs) layers recorded in 0.1 M KCl with a scan rate of 50 mV·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:

\[ \text{Ox}_{(aq)} + ne^- \rightarrow \text{Re} \, \text{d}_{(s)} \]

\[ \text{Cu}^{2+}_{(aq)} + 2e^- \rightarrow \text{Cu}_{(s)} \]

\[ \text{Fe}^{2+}_{(aq)} \rightarrow \text{Fe}^{3+}_{(aq)} + e^- \]

\[ \text{Fe}^{3+}_{(aq)} + \text{OH}^- \rightarrow \text{Fe(OH)}_3_{(s)} \]

Electrochemical polymerization:

![Polymerization Reaction Diagram]

Indirect electrochemical deposition:

\[ \text{Ox}_{(aq)} + ne^- \rightarrow \text{Re} \, \text{d}_{(aq)} \]

\[ \text{Re} \, \text{d}_{(aq)} + \text{A}_{(aq)} \rightarrow \text{P}_{(s)} \]

\[ 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \]

\[ \text{Fe}^{3+}_{(aq)} + 3\text{OH}^- \rightarrow \text{Fe(OH)}_3_{(s)} \]

\[ \text{A} \quad \text{OH}^- \rightarrow \text{P} \]
Advantages of Indirect Electrochemical Deposition

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

\[
\text{Ox} \quad \text{Red}_{(s)} \quad \text{B+Precursor}
\]

Direct ED  Indirect ED
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.

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

Hydrolysis: \[ MX_4 + H_2O \rightarrow MX_3OH + HX \]
Condensation: \[ MX_3OH + M(OH)_4 \rightarrow X_3M - O - M(OH)_3 + H_2O \]
Altering the surface pH by electrochemistry

Reduction

\[ H_2O(1) + e^- \rightarrow \frac{1}{2} H_2(g) + OH^{-}(aq) \]

\[ ROH(1) + e^- \rightarrow \frac{1}{2} H_2(g) + RO^{-}(l) \]

Oxidation

\[ H_2O(1) \rightarrow \frac{1}{2} O_2(g) + 2H^+_{(aq)} + 2e^- \]

\[ RCH_2OH(1) \rightarrow RCHO(1) + 2H^+_{(aq)} + 2e^- \]
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

\[
\text{PEG} + \text{IPTS (2 eq)} \rightarrow \text{PEG diIPTS}
\]

Stent Coated with PEG-Sol-Gel
Platelet Adhesion to Coated and Uncoated Stainless Steel Substrates

X500

Uncoated surface  Coated surface

X2000
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 (Cheap Tubes)
Solvent: 1:1 v/v NMP:H₂O.

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 SEM images of the sol-gel/CNT composite films electrodeposited at $-0.75 \text{ V}$ (A) and $-1.2 \text{ V}$ (B) for 2 min (C): EDX mapping of carbon for (B).
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

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.
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:

- 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
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).
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
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

\[ \text{HA} = \text{Ca}_5(\text{PO}_4)_3(\text{OH}) \]

Methods:
Electrospraying at high temp
Electrochemical deposition

Geuli et al., Adv. Funct. Mater. 2016, 26, 8003
The Concept
Formation and Characterization of HA NPs

<table>
<thead>
<tr>
<th>Element</th>
<th>at. %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EDS</td>
</tr>
<tr>
<td>Oxygen</td>
<td>68.3±2.5</td>
</tr>
<tr>
<td>Calcium</td>
<td>19.1±1.5</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>12.5±0.1</td>
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<tr>
<td>Carbon</td>
<td>10.6</td>
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</table>

SEM image of HA NPs

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?

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

Dental implant electrodeposited with HAp NPs stabilized by Cit at 2 V for 25 min.
Electrochemical Control of the Interparticle Forces

Electrostatic repulsion

Electrochemistry?

How can electrochemistry diminish the repulsion?

2. Changing the ionic strength
9. Ionic Strength Induced Electrodeposition
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

Before | After

0D + 0D: VO$_2$-NP

PET + 0D: Au-NP

CNT + 1D: CNT

2D: Graphene
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 $4.6 \cdot 10^{20} \text{ J}$ 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
Developing a photothermal coating for high temperatures (stable at 750°C):

- High absorptance (95%).
- Corrosion resistance.
- Good adhesion to substrate.
- Inexpensive and easily applied.
Formulation: Preparation of the Coating Dispersion

<table>
<thead>
<tr>
<th>Typical Formulation</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent/ water</td>
<td>60-90</td>
</tr>
<tr>
<td>Matrix former</td>
<td>2-30</td>
</tr>
<tr>
<td>Dispersant</td>
<td>2</td>
</tr>
<tr>
<td>Wetting agent</td>
<td>1</td>
</tr>
<tr>
<td>Black pigment</td>
<td>2-20</td>
</tr>
</tbody>
</table>

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
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*

<table>
<thead>
<tr>
<th>Gland type</th>
<th>Inorganic substituents</th>
<th>Organic substituents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eccrine</td>
<td>Chlorides</td>
<td>Amino acids</td>
</tr>
<tr>
<td></td>
<td>Sodium</td>
<td>Urea</td>
</tr>
<tr>
<td></td>
<td>Potassium</td>
<td>Lactic acid</td>
</tr>
<tr>
<td></td>
<td>Ammonia</td>
<td>Proteins</td>
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<tr>
<td></td>
<td>Sulfates</td>
<td>Sugars</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Creatinine</td>
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<tr>
<td>Apocrine</td>
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<tr>
<td></td>
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<td>Carbohydrates</td>
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<tr>
<td></td>
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<td>Sebaceous</td>
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<tr>
<td></td>
<td></td>
<td>Hydrocarbons</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Alcohols</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Glycerides</td>
</tr>
</tbody>
</table>

Composition of the fingermarks

~ 98% water

Inorganic (chlorides, metals ions, etc)

Amino acids

Organic

Lipids

*H2N*  \[\text{COOH}\]

\[\text{H}_2\text{N}\text{COOH}\]

\(\text{R}\)

Cholesterol

A free fatty acid

A triglyceride

A phospholipid
Targeting the Ridges

Fingerprint Reagent

Amino acids

1,2-Indandione

DFO

Ninhydrin
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

\[ \text{Ag}^+ + \text{Fe}^{2+} \rightarrow \text{Ag} + \text{Fe}^{3+} \]

Fingerprint Ridge

Substrate

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?

Substrate (paper, wood, fabric)
Designing the Catalyst

\[ \text{3-Mercaptopropanoic acid} \]

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

MIP2018

Jerusalem

Save the dates!

June 24-28, 2018

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