Heavy points of Organic Nanoparticles

- Easy to synthesized
- Easy to process
- Easy to deposit
- Just of Nanometric size
- Interesting optical/electrical properties
Different types of Nanoparticles
- Metallic Nanoparticles
- Semiconducting Nanoparticles

Different Materials
- Au, Ag, CdSe, CdS, PbS, ...

Different synthesis procedures
- Liquid Phase
- Solid Phase
- Within a Precursor Matrix

NANOPARTICLES by Liquid Phase
Preparation via a chemical route

- Au$^{3+}$ Salt
- Reducing agent
- Capping agent
- Au nanoparticles
Direct Solution-Phase Synthesis

\[
\text{AuCl}_4^{-}(\text{aq}) + \text{N}(\text{C}_8\text{H}_{17})_4^{+}(\text{toluene}) \rightarrow \\
\text{N}(\text{C}_8\text{H}_{17})_4^{+}\cdot \text{AuCl}_4^{-}(\text{toluene})
\]

\[
\text{mAuCl}_4^{-}(\text{toluene}) + \text{nC}_2\text{H}_5\text{SH}(\text{toluene}) + 3\text{me}^{+} \rightarrow \\
4\text{mCl}^{-}(\text{aq}) + (\text{Au}_n(\text{C}_2\text{H}_5\text{SH})_m)_{(\text{toluene})}
\]

Single step synthesis for thiol-capped Au nanocrystals based on the reduction of AuCl4- by NaBH4 in the presence of Cl2H25SH in a two-phase toluene/water solution over a period of 4 h. Their reaction scheme involves first a transfer of the AuCl4- moiety from aqueous to organic phase (reaction 1) and then its reduction (reaction 2) in the presence of a long-chain thiol. Brust and coworkers found that their particles were stable, were easily precipitated by the addition of ethanol to the toluene product mixture, and readily dissolved back into toluene. Whetten and coworkers have shown that nanoparticles produced by this method are equivalent in quality to clusters synthesized by the gas-phase method.

GOLD NANOPARTICLES

Biphasic reduction procedure

1. Add ligand molecules (+)
2. Add phase transfer reagent e.g. tetraoctyl ammonium bromide (TOAB)
3. Metal cations in solution

In the real world two-phase droplets will form

Not so easy
GOLD NANOPARTICLES

Add Reducing agent

electron donor
NaBH₄

Stabilized Metal particles in solution

Isolation in solid form

Stabilized Metal particles in solution

Radius by TEM

1.2 nm or 2.6 nm

Radius by SAXS

= 3.1 nm

4.4 nm

S. Carnes, et al., in press.
Gold crystalline cores encapsulated in a compact thiol molecular coating absorbed on the surface: novel “molecules” that manifest special properties

Natural size-selection following a series of “magic numbers”

The size control

Synthesis of gold nanoparticles

Sodium citrate method — 12 – 64 nm

To an initial solution of 0.01% (w/v) HAuCl4 that is a boil is added a solution of 1% (w/v) of Na3citrate → smaller is the amount of citrate, bigger is the diameter of nanoparticles.

Table 2. Results from Modeling of Gold Core Sizes, Shapes, and Alkanethiolate Coverages, and of Size-Dependent f2 Broadening of Proton NMR of Citrate Resonances

<table>
<thead>
<tr>
<th>Alkanethiolate</th>
<th>Core, nm</th>
<th>Surface atoms/ % of surface area</th>
<th>TGA % uptake/ % of added thiol</th>
<th>B NMR, ppm</th>
<th>C NMR, ppm, Hz</th>
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</thead>
<tbody>
<tr>
<td>70 (TOH)</td>
<td>0.65</td>
<td>4980.4/6.39</td>
<td>33.4/856/83</td>
<td>2.8</td>
<td>13</td>
</tr>
<tr>
<td>140 (TOH)</td>
<td>0.71</td>
<td>14881/0/11.85</td>
<td>33.4/856/83</td>
<td>2.8</td>
<td>16</td>
</tr>
<tr>
<td>201 (TOH)</td>
<td>0.87</td>
<td>129470/0/15.22</td>
<td>33.4/856/83</td>
<td>2.8</td>
<td>18</td>
</tr>
<tr>
<td>325 (TOH)</td>
<td>0.98</td>
<td>164082/9/55.13</td>
<td>33.4/856/83</td>
<td>2.9</td>
<td>19</td>
</tr>
<tr>
<td>500 (CO)</td>
<td>1.1</td>
<td>1625/62/99/15.44</td>
<td>33.4/856/83</td>
<td>3.0</td>
<td>22</td>
</tr>
<tr>
<td>614 (TOH)</td>
<td>1.6</td>
<td>21461/10/16.46</td>
<td>33.4/856/83</td>
<td>3.0</td>
<td>25</td>
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<tr>
<td>690 (TOH)</td>
<td>1.9</td>
<td>234649/0/21.64</td>
<td>33.4/856/83</td>
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<td>24</td>
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<tr>
<td>807 (TOH)</td>
<td>2.1</td>
<td>26481/0/35.86</td>
<td>33.4/856/83</td>
<td>3.2</td>
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<tr>
<td>906 (TOH)</td>
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<td>29010/0/40.92</td>
<td>33.4/856/83</td>
<td>3.4</td>
<td>28</td>
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<tr>
<td>1029 (C10)</td>
<td>2.5</td>
<td>32427/0/49.02</td>
<td>33.4/856/83</td>
<td>3.5</td>
<td>30</td>
</tr>
<tr>
<td>1206 (C10)</td>
<td>2.6</td>
<td>35957/0/59.66</td>
<td>33.4/856/83</td>
<td>3.5</td>
<td>31</td>
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<tr>
<td>1260 (C10)</td>
<td>2.8</td>
<td>38692/0/69.38</td>
<td>33.4/856/83</td>
<td>3.8</td>
<td>41</td>
</tr>
<tr>
<td>1500 (C12)</td>
<td>3.3</td>
<td>43847/0/79.44</td>
<td>33.4/856/83</td>
<td>4.0</td>
<td>47</td>
</tr>
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<td>1500 (C12)</td>
<td>3.4</td>
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<td>1500 (C12)</td>
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<td>33.4/856/83</td>
<td>4.0</td>
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</table>

* CO = cuboctahedron; TO = ideal truncated octahedron (all sides equal); TO = truncated octahedron in which 0 < n ≤ m ≤ 4, where n is the number of atoms between (111) facets and m is the number of atoms between (110) facets; TO = truncated octahedron in which −4 ≤ n − m ≤ 0. The second value in the righthand column is the reduced width for the methylene peak.
Gold NANOPARTICLES via Gas-Phase

Gold atoms evaporated from a carbon crucible in a resistively heated carbon tube are entrained in He and induced to condense into nanoclusters by mixing the hot flow from the oven with a room temperature stream of He. Controlling conditions in the oven and the flow downstream from the oven (see 1) controls the mean cluster size. The clusters are melted (see 2) and recrystallized (see 3) while still in the gas phase. They are scrubbed from the gas phase by contact with a mist of organic solvent containing 1-dodecanethiol and collected as a stable colloidal suspension (see 4).
Many possibilities

Can be made from

- Noble metals: Au, Ag, Pd, Pt
- Semiconductor: CdS, PbS, Ag2S, CdSe, TiO2
- Multiple core-shell structures:
  - Ag, Pd, Pt, TiO2, Fe, Zn,
  - Cu, ZrO2, CdS, Fe2O3
- Different shell functionalization:
  - Hydroxy-, Carboxil-, Amino-, DNA-, …

One of the most important for Nano-Bio-Technology

Nanoparticles functionalization by means of DNA

(a), Au; (b), Au–DNA; (c), Au–DNA with DNA stained by uranyl acetate (UA), which further increased the diameter of the complex.

(d), scattering spectra of Au (green line) and Au–DNA (red line).
Different types of Semiconducting Nanoparticles means different Activation Energies

Group 14 (old group IV) Si, Ge

III-V Materials: GaN, GaP, GaAs, InP, InAs

II-VI Materials: ZnO, ZnS, ZnSe, CdS, CdSe, CdTe

SEMICONDUCTING NANOPARTICLES

with CdSe

Stock solutions of cadmium acetate (Cd(OAc)₂) in tri-n-octylphosphine (TOP) and selenium (Se) in TOP were prepared in a dry box. In a fume-cupboard tri-n-octylphosphine oxide (TOPO) was dried and degassed by heating under vacuum. The capping agents, hexadecylamine (HAD) and n-tetradecylphosphonic acid, were then added and the solution was again dried under vacuum. Next, the Se-TOP stock solution was added and the solution heated to 300°C. Then, under vigorous stirring, the Cd-TOP solution was rapidly injected into the vessel. Particles were then grown at 260°C until the size required was achieved. Once the particles had reached the size desired, as judged by UV-visible spectroscopy, growth was quenched by rapid cooling.

NANOPARTICLES

TEM image of CdSe nanoparticles

Sulfide nanoparticle

Particles were formed by exposing the deposited films to H₂S atmosphere for 24 h according to the following reaction [1,6]

(CH₃(CH₂)₇COO)ₓM + H₂S → 2(CH₃(CH₂)₇COOH) + MS

How to prepare
GOLD NANOPARTICLES

The nanoparticle formation

Arachidic Acid

Cd

CdS

Sulfide based NANOPARTICLES

\[ (\text{CH}_3(\text{CH}_2)_3\text{COO})_2\text{Cd} + \text{H}_2\text{S} \rightarrow 2\text{CH}_3(\text{CH}_2)_3\text{COO} + \text{CdS} \]

Mass variation during the growth of CdS nanoparticles in H2S atmosphere
Sulfide based NANOPARTICLES

STM image of CdS Nanoparticles

NANOPARTICLES CHARACTERISTICS

They have the character of Quantum Dots

QUANTUM DOT

- Tunnelling barrier
- Potential hole for the charge carriers
**NANOPARTICLES CHARACTERISTICS**

They act as electron-traps

**QUANTUM DOT**

- Tunnelling barrier
- Potential hole for the charge carriers

---

**NANOPARTICLES CHARACTERISTICS**

The inside electron states are quantized

- Trapped electron
- Stationary Waves

\[ E_n = E_0 + \frac{n^2\varepsilon t}{2R} \]
Photon Energy related to R

\[ E = h \nu \]
\[ c = \frac{\lambda}{T} = \left( \frac{1}{T} \right) \lambda = \nu \lambda \]
\[ E = \hbar \frac{c}{\lambda} = \hbar \frac{nc}{R} \]

\[ \lambda = \frac{R}{n} \]

The role of Nanoparticles Size

Quantum dots are semiconductors particles that has all three dimensions confined to the 1-100 nm length scale.

Colloidal CdSe quantum dots dispersed in hexane.

The size changes the color.

\[ E_n = E_0 + \frac{n^2 e^2}{R} \]
Una teoria semi-classica

Il ruolo della dimensione
Spettroscopia STM su Nanostrutture

Figure 1. The scheme of the experimental set-up for measuring STM $V-I$ characteristic.

Immagini da microscopia STM

Nanoparticelle di Solfuro di Cadmio (dimensioni tipiche 3 nm)
CVs of methylviologen in 0.1 M Na2SO4 at (a) EC roughened electrode, and (b) NP array electrode.

Surface Properties

Couple 1: -0.66 V & 0.72 V; $\Delta E_p = 60 \text{ mV}$

Couple 2: -0.53 V & -0.55 V; $\Delta E_p = 60 \text{ mV}$

(a)

(b)

No adsorption of MV!

No active sites for adsorption of MV on nanoparticle array.

Surface Comparison

SEM images of (A) EC roughened electrode and (B) NP array electrode.

Ag Electrode polished, then roughened by potential steps in 0.1 M KCl.

NP array made by dipping an Indium-Tin Oxide (ITO) electrode in poly-L-lysine for two hours, then into a colloidal silver solution overnight.

Defect sites on the EC roughened electrode must be active for MV adsorption.

The Applications of Nanoparticles

- Conducting nanostructured Layers
- Ampérometric Biosensor Improvements
- Biosensors by aggregates formation
ASSEMBLY ON SILICON OXIDE

Fabricating two-dimensional arrays of Au NPs on a silicon substrate in combination with self-assembly of an (aminopropyl)triethoxysilane monolayer, immobilization of nanoparticles, alkanethiol treatment, and solvent evaporation technique.

1) substrates are cleaned and then derivatized by 3-aminopropyl-dimethylethoxysilane.
2) After the substrates are washed with toluene and treated with a solution of Au nanoparticles in toluene.
3) The substrates are washed again with toluene, and treated with linker solution of alkanedithiol.
4) And so on….

LAYER BY LAYER TECHNIQUE

USING DITHIOLS AS THE DERIVATIZING SPACER UNITS FOR AMINO-STABILIZED NANOPARTICLES:

Fig. 3: Schematic representation of the layer by layer construction of nanomaterials from gold nanoparticles and a dithiol.
Electrode gaps size related phenomenon

Micro-contacts

![Micro-contacts Diagram]

Conducting Layers

Nano-contacts

![Nano-contacts Diagram]

Single Electron Device

Current/voltage characteristic of a Organic interconnections on micro-contacts

![Current/voltage Characteristic Diagram]

1. Voltammetric Measurements: range -5 V; +5 V
2. Step Measurements: $V_{ox} = +5$ V

- Measurements at different sample concentrations:
  
  1mg/ml - 0.75mg/ml - 0.5mg/ml - 0.25mg/ml - 0.1mg/ml - 0.075mg/ml - 0.05mg/ml
MICRO-ELECTRODES

Electrode matrix fabricated using conventional photolithographic technique

Electrode geometry

DATA Analysis

<table>
<thead>
<tr>
<th></th>
<th>P1 1 mg/ml</th>
<th>P2 0.75 mg/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1 [ohm]</td>
<td>2.49E+12</td>
<td>2.49E+12</td>
</tr>
<tr>
<td>C1 [pF]</td>
<td>0.728</td>
<td>0.748</td>
</tr>
<tr>
<td>R2 [ohm]</td>
<td>1.26E+13</td>
<td>1.28E+13</td>
</tr>
<tr>
<td>C2 [pF]</td>
<td>2.16</td>
<td>2.11</td>
</tr>
<tr>
<td>R3 [ohm]</td>
<td>4.84E+13</td>
<td>2.06E+14</td>
</tr>
</tbody>
</table>
Enhancement of Biosensors performance by using gold Nanoparticles

The principle:

Cholesterol + O₂ → Pregnenolone + isooctapic aldehyde

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

Cytochrome P450scc (CYP11A1) catalyzes the cholesterol side chain cleavage reaction, the initial and key step in the regulation of steroid hormone biosynthesis. Cytochrome P450scc is a mono-oxygenase located in the inner mitochondrial membrane of most steroidogenic tissues. The complex of cytochrome P450scc and substrate (cholesterol + oxygen) accepts electrons from NADPH via an electron transfer pathway of adrenodoxin reductase and adrenodoxin. Adrenodoxin reductase is a flavoprotein containing the flavin nucleotides FMN and FAD, in order to improve the connection between the electrode and the cytochrome P450 system, the electron transfer reaction is effectively transferred through electrodes in the presence of such mediator.
Enhancement of Biosensors performance by using gold Nanoparticles

Cholesterol Biosensor based on P450 scc and improved by thiols encapsulated gold nanoparticles used as electron transfer mediator

Biosensors by Nanoparticles Aggregation

Oligonucleotides

Thiol-capped oligonucleotides:
- Strand 1 - 12 mer TAIL 1
  TCAGGTCGCGG
- Strand 2 - 12 mer TAIL 2
  GGTCGACCTAG

Linker
- Strand 3 - 52 mer BRIDGE
  CTACGCTCGACCTTTT……..TTTCCGCGAAGCTAG

CHANGE IN COLOR!
Assembly of nanoparticles

TAIL1 modified Nps + TAIL2 modified Nps

BRIDGE

Target molecules

CHANGE IN COLOR!

Biosensors by Nanoparticles Aggregation

To control the disassembly of a nanostructure in response to an external stimuli, for example a DNA molecule.
Uses for magnetically labeled cells

A: Cell sorting

B: Magnetic Fluid Hyperthermia


CONCLUSIONS

- Organic Nanoparticles are nice objects to use for built nano-bio-structures.
- Organic Nanoparticles could act as quantum dots in arrays and store electrical charges
- Hybrid structures with organic nanoparticles layers could be considered to enhance Ampérometric Biosensors performance
- Organic nanoparticles could be considered to invent new kind of Optical Biosensors
Thank you for your attention!

from

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