LASER PROCESSING LABORATORY

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http://LPL.phys.polymtl.ca
FEL Workshop 8-10 March 2005
LPL’s Research activities

Mission:
Develop and model new laser material processes for:
microelectronics, nanotechnologies, biotechnologies, photonics and MEMS

Laser-materials interaction:
Theory and simulation of laser-materials interaction

Laser microengineering of materials:
Laser trimming of microelectronics circuits (LTRIM process);
Femtosecond laser micromachining.
3D laser micromachining of photosensitive glasses
3D laser fabrication of photonics components

Laser nanoengineering of materials:
Laser fabrication of nanostructured thin films, nanoparticles and nanotubes.
Applications to biosensing and nanobiophotonique

Personnel: ~20
1 Professor, 1 senior researcher, 3 research associates,
12 graduate students and 4 undergraduate students.
Colloidal metal nanoparticles synthesized by femtosecond laser ablation in liquids

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Laser Processing Laboratory, École Polytechnique, Montréal, Canada

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Content

Colloids
Whys laser ablation?
Why femtosecond laser ablation?
Mechanism of femtosecond laser ablation in liquids and formation of nanoparticles
Chemistry of gold nanoparticles in water, KCl, NaOH, Cyclodextrin and Dextran
Conclusion
Use of FEL?
**Colloidal Gold Nanoparticles**

**Absorption spectra:** Surface plasmon resonance (520 nm)

**Biosensing and pharmacology applications**
Antibodies are detected by a change of optical characteristics of gold nanoparticles

**Desired characteristics of nanoparticles:**
- Small (< 30 nm), with narrow size distribution
- Availability of reactive chemical groups for further attachment to biomolecules

**Conventional chemical fabrication method**
Reduction of chloroaauric acid (HAuCl₄) with citrate in water
Control size by adding a stabilizing agent (thiol- (-SH) containing molecules.)

**Disadvantages: Contamination** (impurities; Cl on surface, …)
Why laser ablation of solids in liquids?

Laser ablation in vacuum leads to highly energetic species and particles.

Laser ablation in neutral gas (few Torrs) results in the cooling of species and formation of “cold” nanoclusters.

Laser ablation in liquids:
- Rapid quench of hot species and formation of cold nanoclusters
- Direct formation of colloidal solution
  - Biosensor
  - Spin-on

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“Long” pulse laser ablation in liquids

In distilled water:
~5-200 nm particles with broad size distribution
Reasons:
- Ablation is mainly due to shock wave
- Post-ablation: large quantity of ‘low’ but sufficient energetic particles that coalesce to form large particles

<table>
<thead>
<tr>
<th>Transmitted energy (%)</th>
<th>ns</th>
<th>fs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Few %</td>
<td>20-45</td>
</tr>
<tr>
<td>Mechanical energy (%)</td>
<td>~80%</td>
<td>15 %</td>
</tr>
</tbody>
</table>

In surfactants:
Surfactant (sodium dodecyl sulfate or SDS) covers some ablated particles, thus limiting coalescence (big particles) and aggregation.

Exemple: Nd:YAG laser (1064 nm, 532 nm) with SDS
5-10 nm Au particles (size dispersion - 5 nm)

Disadvantages: - SDS terminates gold surface making it hardly useful for bioimmobilizations
- SDS is not biocompatible (denaturation of proteins)

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# Metal colloids in aqueous media

<table>
<thead>
<tr>
<th>Authors</th>
<th>Laser</th>
<th>Materials</th>
<th>Aqueous media</th>
<th>Size distributions</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Henglein (1993)</td>
<td>Rubis, 694 nm</td>
<td>Au, Ni and C</td>
<td>Pure H$_2$O</td>
<td>2-4 nm for Au</td>
<td>Ablation of thin films (few nm)</td>
</tr>
<tr>
<td>Cotton (1993)</td>
<td>Nd:YAG, 1064 nm</td>
<td>Ag, Au, Pt, Pd and Cu</td>
<td>Pure H$_2$O</td>
<td>10-50 nm for Ag</td>
<td>Sound during ablation</td>
</tr>
<tr>
<td>Stepanek (1997), (1998)</td>
<td>Nd:YAG, 1064 nm, 20ns and 40 ps</td>
<td>Ag</td>
<td>Pure H$_2$O, NaCl, phtalazine</td>
<td>6-140 nm for ns 6-80 nm for ps</td>
<td>Size reduction effect of Cl⁻ and adsorbing molecules (pht)</td>
</tr>
<tr>
<td>Shafeev (2001), (2002)</td>
<td>Cu vapor laser, 511 nm, 20 ns</td>
<td>Ag, Au, Ti and Si</td>
<td>Pure H$_2$O</td>
<td>20-200 nm for Au and Ag</td>
<td>Partial oxidation of Ti and Si prepared in water</td>
</tr>
<tr>
<td>Compagnini (2002)</td>
<td>Nd:YAG, 532 nm</td>
<td>Ag and Au</td>
<td>Pure H$_2$O</td>
<td>10-30 nm for Ag and Au</td>
<td></td>
</tr>
<tr>
<td>Tsuji (2002), (2003)</td>
<td>- Nd:YAG, 1064, 532 and 355 nm (ns) - Ti:saphire, 800 nm, 120 fs</td>
<td>Ag</td>
<td>Pure H$_2$O, 5-160 nm for ns 5-90 nm for fs</td>
<td>Size dispersion of particles is reduced using femtosecond laser</td>
<td></td>
</tr>
<tr>
<td>Kabashin JCPB, JAP (2003), Sylvestre JACS (2004)</td>
<td>- Ti:saphire, 800 nm, 120 fs</td>
<td>Au, Ag</td>
<td>Pure H$_2$O, CDs</td>
<td>$3.5 \pm 1$ nm for Au at small fluences 2.5± 1 nm for Au in CDs at high fluence</td>
<td>Size of particles is dependant of laser fluence, CDs reduces particles size</td>
</tr>
</tbody>
</table>

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**Experimental setup**

**Femtosecond laser:**
110 fs FWHM, 800 nm, 1 kHz

**Aqueous solutions:**

1. Pure water
2. Cyclodextrins (α-CD, β-CD and γ-CD) (Biologically compatible glucose-containing compounds)
3. Molecules containing an amine group (-NH₂)


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fs laser ablation in water: fluence effects

\[ F = 30 \text{ J/cm}^2 \]

Ablation threshold:
\[ \sim 5 \text{ J/cm}^2 \]

Relative Abundance (arb. units)

\[ 3.5 \pm 1 \text{ nm} \]

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fs laser ablation in water: fluence effects

- Diameter increases with fluence
- For intermediate fluences, size distributions can be fitted by two Gaussian functions
- Evidence for two different mechanisms of nanoparticle production

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Two size distributions are present. Two different mechanisms of particle formation.

fs laser ablation in water: craters on gold after femtosecond ablation in water (5000 pulses)

30 J/cm²

- Molten layer
- Optical breakdown of the water above the gold substrate leading to hot plasma generation and mechanical effect (cavitation bubble, shock wave) affecting the surface.

200 J/cm²
Experimental setup

Optical breakdown of the liquid → A sound is generated due to generation of shock wave and collapse of cavitation bubble

Sound can be recorded by a microphone connected to a computer to better control the production of particles
Mass loss

Mass loss of gold substrate and sound intensity vs. position of focal plane relatively to the surface target

0.35 mJ/pulse,
20 min, rotation of target

Mass loss is maximal when sound intensity is maximal

Indication for ablation mechanism related to optical breakdown effects
Optical Extinction

Optical extinction of Au colloids vs. position of focal plane relatively to the surface target

- Experimental conditions: 0.35 mJ/pulse, 5 min, rotation of target
- Positions are relative to the point of maximal sound intensity

Focal positions away from the focal position generating maximal sound intensity results in less ablation and smaller particles.
Effect of focusing position

Optical breakdown

Sound maximum and ablation due to optical breakdown of water maximum
Large nanoparticles and broad plasmon peak

Energy density decreases and optical breakdown effects (ablation + sound) decreases and disappears.
Direct photon ablation, smaller nanoparticle and finer plasmon peak

Optical breakdown is too far from surface: ablation efficiency decreases.
Few nanoparticles and plasmon peak disappears.

Further away

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fs laser ablation in water: mechanisms of particle formation

A) “Low” fluence

- Direct fs laser ablation

No other ablation mechanism when optical breakdown of water is avoided.

Narrow size distribution with mean particle size between 3.5 and 12 nm

Conclusion:
fs laser radiation at low fluences is unique in obtaining fine nanoparticles size

B) “High” fluence

optical breakdown of water = hot plasma generation

1) First few picoseconds

- Direct fs laser ablation

2) Micro- millisecond range

- Cavitation bubble boundary

- Vapor

- Hot plasma

3) Fractions of a millisecond later

- Collapse of the cavitation bubble

- Ablation related to plasma or mechanical effects or both ???

Broad size distribution with mean particle size 20 – 120 nm

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Summary on mechanism

• **Two different mechanisms:**
  – «pure» laser ablation at «low» fluence: very fine small nanoparticles
  – «optical breakdown» induced ablation at «high» fluence: large nanoparticles

• **Few nm nanoparticles** can be produced by fs laser ablation in WATER (impossible with ns lasers) (absence of any chemicals)

• **Stability:** For fine nanoparticles (5-7 nm) even after two years in water, no clustering is seen!
Chemistry of gold nanoparticles

Nanoparticles fabricated in deionized water

XPS Au4f (substrat HOPG)
- Nanoparticles are basically composed of Au$^0$
- Nanoparticles are partially oxidized (Au$^{+1}$ et Au$^{+3}$)
Effect of OH\textsuperscript{-} et Cl\textsuperscript{-} ions

Gold nanoparticles were produced under identical conditions

Deionized water

10 mM KCl

NaOH pH 9.4

Size reduction when the ablation is performed in the presence of KCl and NaOH

Chemical interaction between Cl\textsuperscript{-} and OH\textsuperscript{-} with the gold surface

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Effect of OH⁻ et Cl⁻ ions

Zeta potential measurements: surface charge of nanoparticles

**Methodology:** Mobility of particles prepared in 10 mM of NaCl was measured, while an electric potential was applied.

**Conclusions**
- Particle surface exchanges protons (H⁺) with aqueous medium.
- OH groups are responsible for the negative charge of nanoparticles.

\[ \text{Au-OH} \leftrightarrow \text{Au-O}^- + \text{H}^+ \]

![Graph showing the effect of pH on Zeta potential](image)

Acid basic

Faster Au nanoparticle agglomeration

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Effect of cyclodextrins

**Effect of α, β et γ-CD**
Chemistry: oligosaccharide cyclique containing 6, 7 et 8 alpha-D-glucoses forming a toroidal

0.01M β-CD solution: 2.3 ± 1 nm
A.V. Kabashin, M. Meunier et.al,

How do cyclodextrins react with gold?

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Conclusion

• The size of nanoparticles can be controlled by changing conditions of ablation.

• Two different mechanisms: pure and optical breakdown ablation

• Fs laser ablation of Au in liquids:
  “Low” fluence in water: 3.5 ± 1 nm
  “High” fluence in water: > 20 nm
  In Cyclodextrins 2.3 ± 1 nm

• The nanoparticles are mainly metallic, but their surface is partially oxidized

• It is possible to achieve interactions of gold nanoparticles during their formation in order to control the nanoparticle size and surface chemistry. Examples:
  - Ions (OH⁻ et Cl⁻)
  - Cyclodextrines
  - Dextran

• Fine QDs can be made
<table>
<thead>
<tr>
<th>First author</th>
<th>Title</th>
<th>Journal</th>
</tr>
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</table>

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