ÉCOLE
POLYTECHNIQUE
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LASER PROCESSING LABORATORY

Michel Meunier

Canada Research Chair

Department of Engineering Physics

École Polytechnique de Montreal

http://LPL.phys.polymtl.ca

FEL Workshop 8-10 March 2005

LPL's Research activities

<u>Mission</u>:

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

<u>Laser-materials interaction</u>:

Theory and simulation of laser-materials interaction

<u>Laser microengineering of materials</u> :

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

<u>Laser nanoengineering of materials</u>:

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

<u>Personnel: ~20</u>

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

M. Meunier,
A. V. Kabashin, J.-P. Sylvestre, S. Besner,
F. Winnik and E. Sacher
Laser Processing Laboratory,
École Polytechnique, Montréal, Canada

FEL Workshop 8-10 March 2005

Content

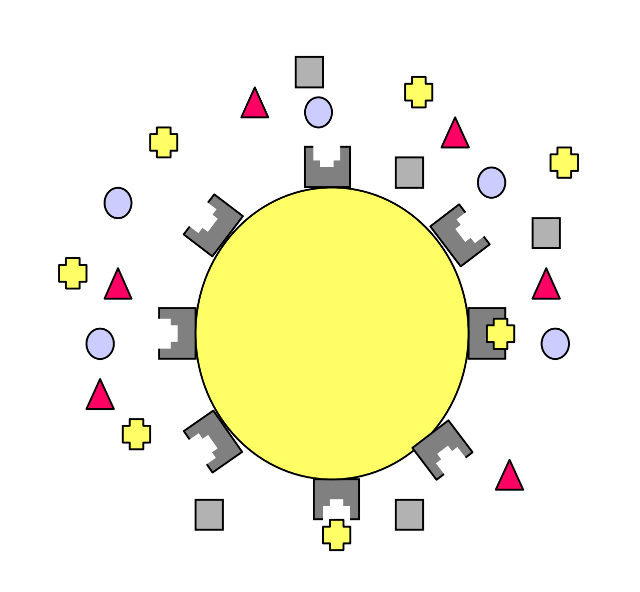
Colloids
Whys laser ablation?
Why femtosecond laser ablation?
Mechanism of femtosecond laser ablation in liquids
and formation of nanoparticles
Chemistry of gold nanoparticles in water, KCl, NaOH,
Cyclodextrin and Dextran
Conclusion
Use of FEL?

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 chloroauric acid ($HAuCl_4$) with citrate in water

Control size by adding a stabilizing agent (thiol- (-SH) containing molecules.)

Disadvantages: Contamination (impurities; Cl on surface, …)

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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

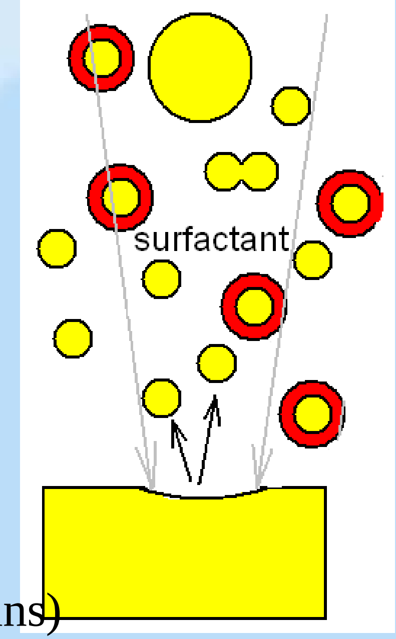
Reasons:

- Ablation is mainly due to shock wave
- Post-ablation: large quantity of 'low' but sufficient energetic particles that coalesce to form large particles

	ns	fs
Transmitted energy (%)	**Few %**	**20-45**
Mechanical energy (%)	**~80%**	**15 %**

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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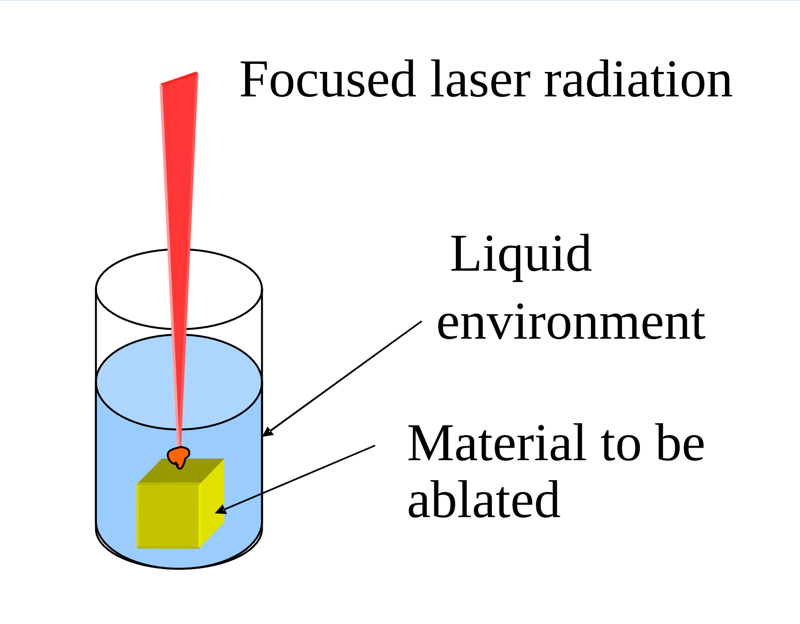
Metal colloids in aqueous media

Authors	Laser	Materials	Aqueous media	Size distributions	Comments
Henglein (1993)	Rubis, 694 nm	Au, Ni and C	Pure H_2O	2-4 nm for Au	Ablation of thin films (few nm)
Cotton (1993)	Nd:YAG, 1064 nm	Ag, Au, Pt, Pd and Cu	Pure H_2O	10-50 nm for Ag	Sound during ablation
Stepanek (1997), (1998)	Nd:YAG, 1064 nm, 20ns and 40 ps	Ag	Pure H_2O, NaCl, phtalazine	6-140 nm for ns 6-80 nm for ps	Size reduction effect of Cl^- and adsorbing molecules (pht)
Yeh (1998), (2002)	Nd:YAG, 1064 and 532 nm	Ag	Pure H_2O, SDS, CTAB	4-120 nm	Size reduction effect of surfactants (2002)
Kondow (2000),(2001), (2002), (2003)	Nd:YAG, 1064 and 532 nm	Au, Ag and Pt	SDS	5-50 nm	Size reduction effect of surfactants
Shafeev (2001), (2002)	Cu vapor laser, 511 nm, 20 ns	Ag, Au, Ti and Si	Pure H_2O	20-200 nm for Au and Ag	Partial oxidation of Ti and Si prepared in water
Compagnini (2002)	Nd:YAG, 532 nm	Ag and Au	Pure H_2O	10-30 nm for Ag and Au	
Tsuji (2002), (2003)	- Nd:YAG, 1064, 532 and 355 nm (ns) - Ti:saphire, 800 nm, 120 fs	Ag	Pure H_2O,	5-160 nm for ns 5-90 nm for fs	Size dispersion of particles is reduced using femtosecond laser
Kabashin JCPB, JAP (2003), Sylvestre JACS (2004)	- Ti:saphire, 800 nm, 120 fs	Au, Ag	Pure H_2O, CDs	3.5 ± 1nm for Au at small fluences 2.5± 1 nm for Au in CDs at high fluence	Size of particles is dependant of laser fluence, CDs reduces particles size

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 (-NH_2)

A.V. Kabashin, M. Meunier, C. Kingston and J. H.T. Luong « Fabrication and Characterization of Gold Nanoparticles by Femtosecond Laser Ablation in Aqueous Solution of Cyclodextrins » J. Phys. Chem. B, 107, 4527-4531 (2003)

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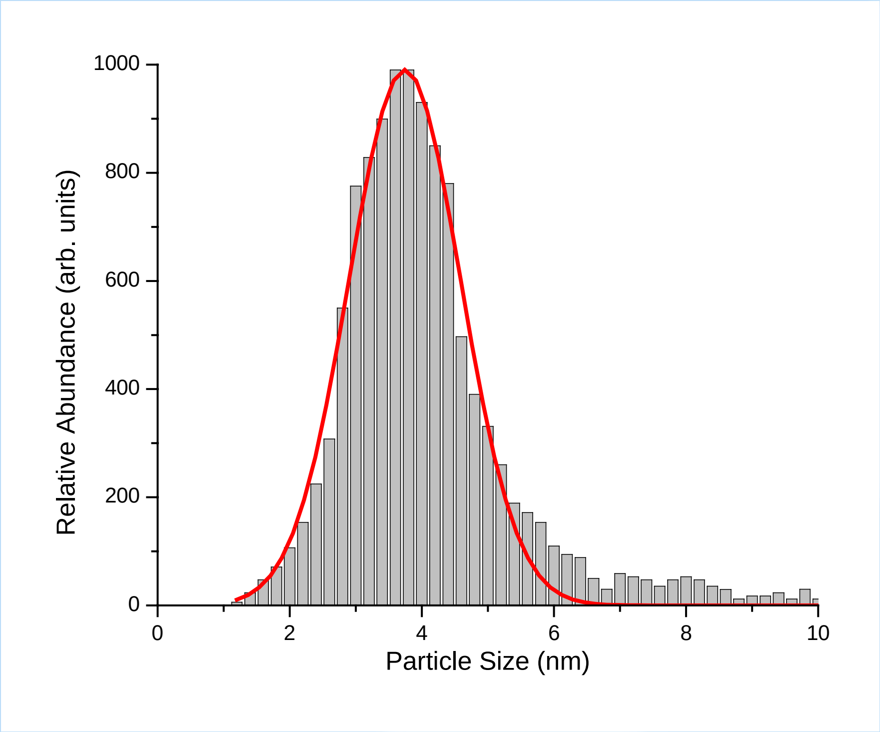
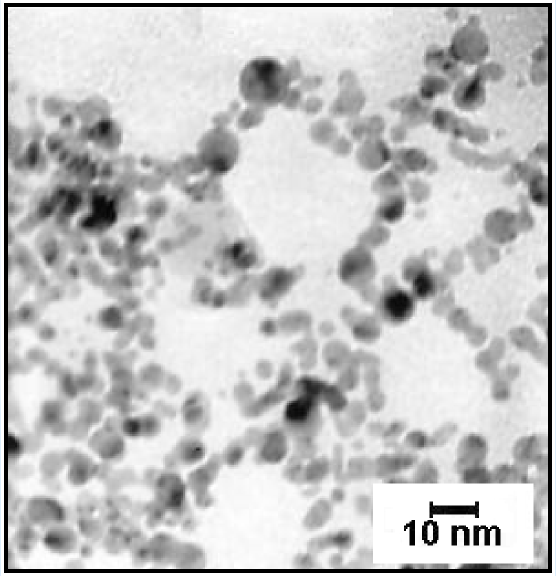
fs laser ablation in water: fluence effects

F = 30 J/cm^2



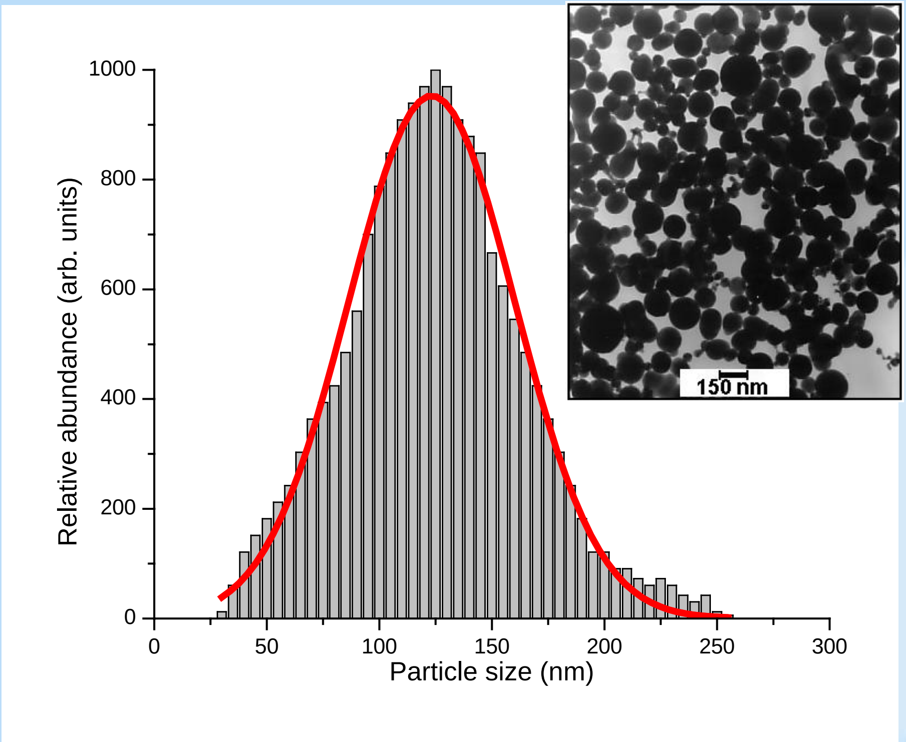


3.5 ± 1 nm

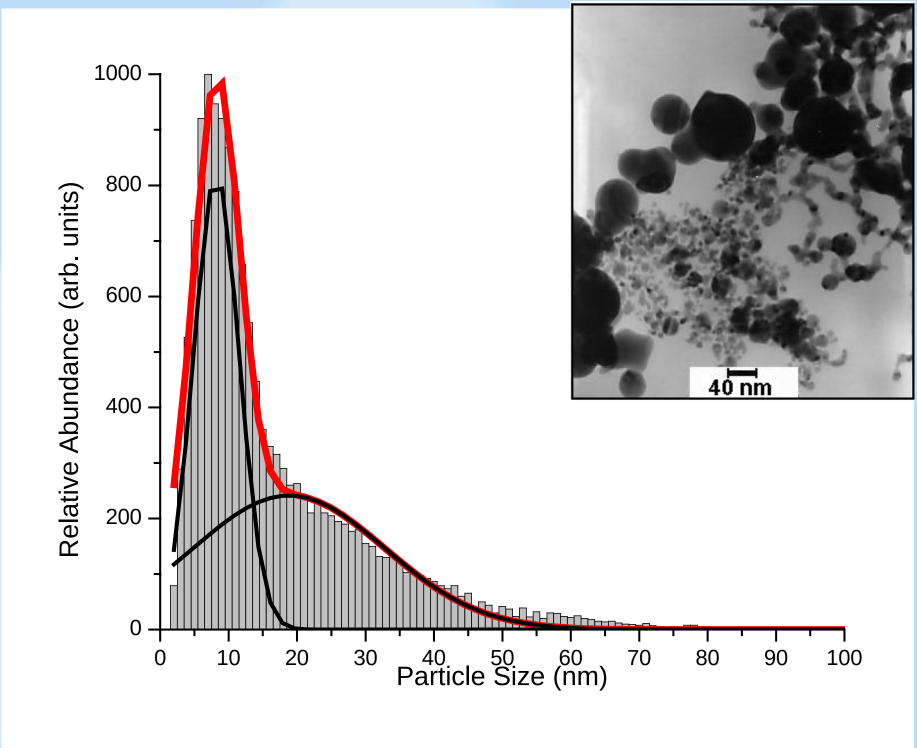
Ablation threshold:
~5 J/cm^2

fs laser ablation in water: fluence effects

F = 1000 J/cm^2



F = 160 J/cm^2

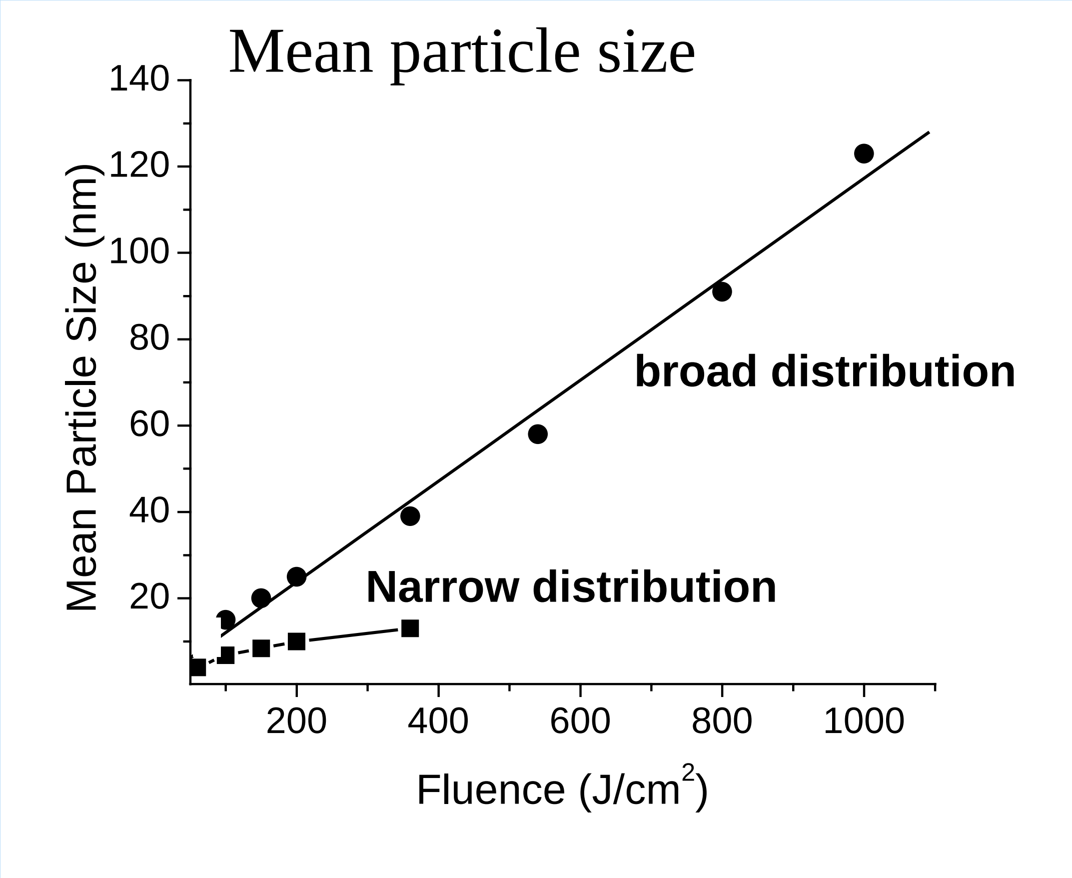


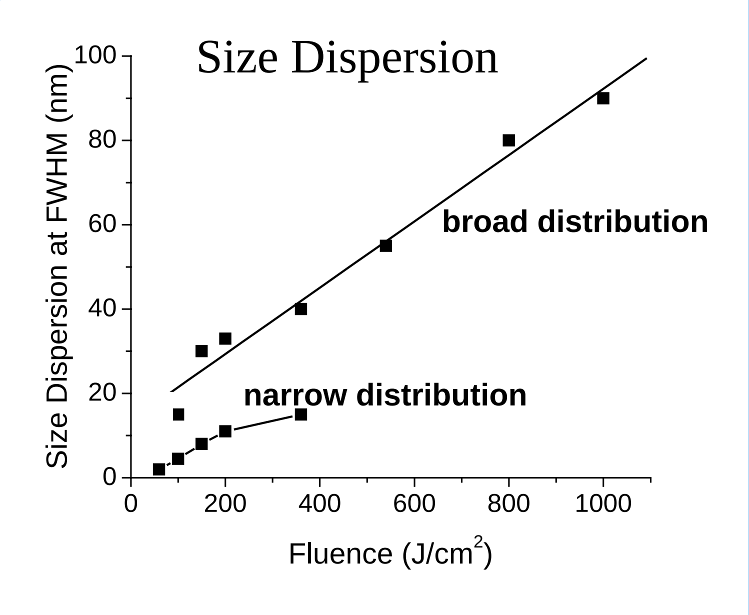
- Diameter increases with fluence

- For intermediate fluences, size distributions can be fitted by two Gaussian functions

- Evidence for two different mechanisms of nanoparticle production

fs laser ablation in water: fluence effects



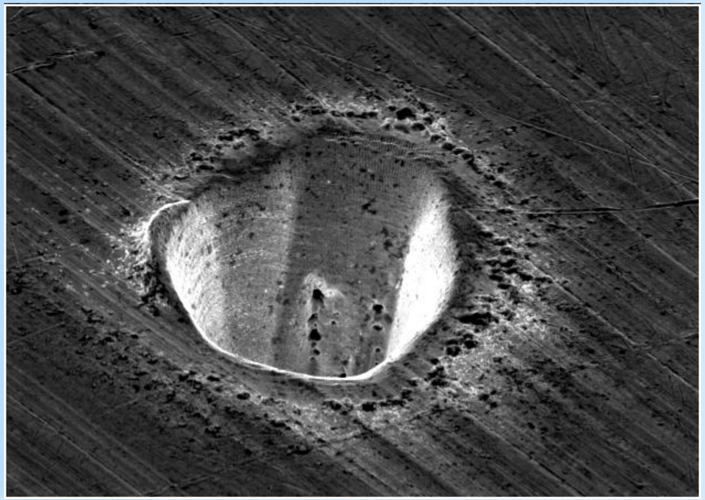


Two size distributions are present → Two different mechanisms of particle formation

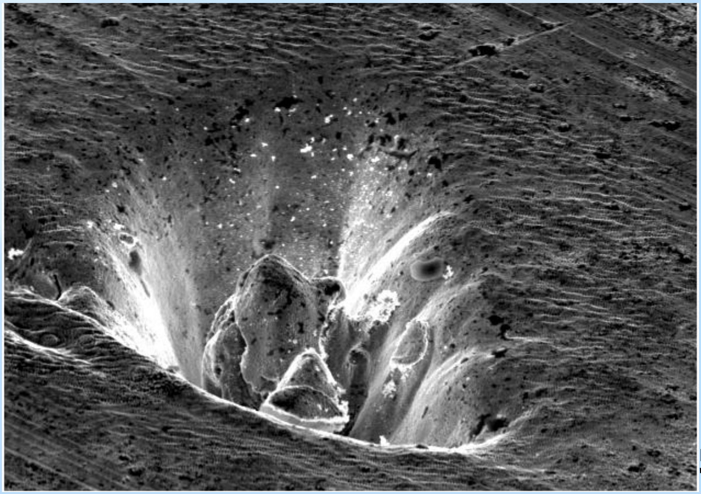
Kabashin and Meunier « Properties of femtosecond laser ablation in liquid environment and formation of gold nanoparticles» J. Appl. Phys., 94, 7941 (2003)

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

30 J/cm^2



200 J/cm^2

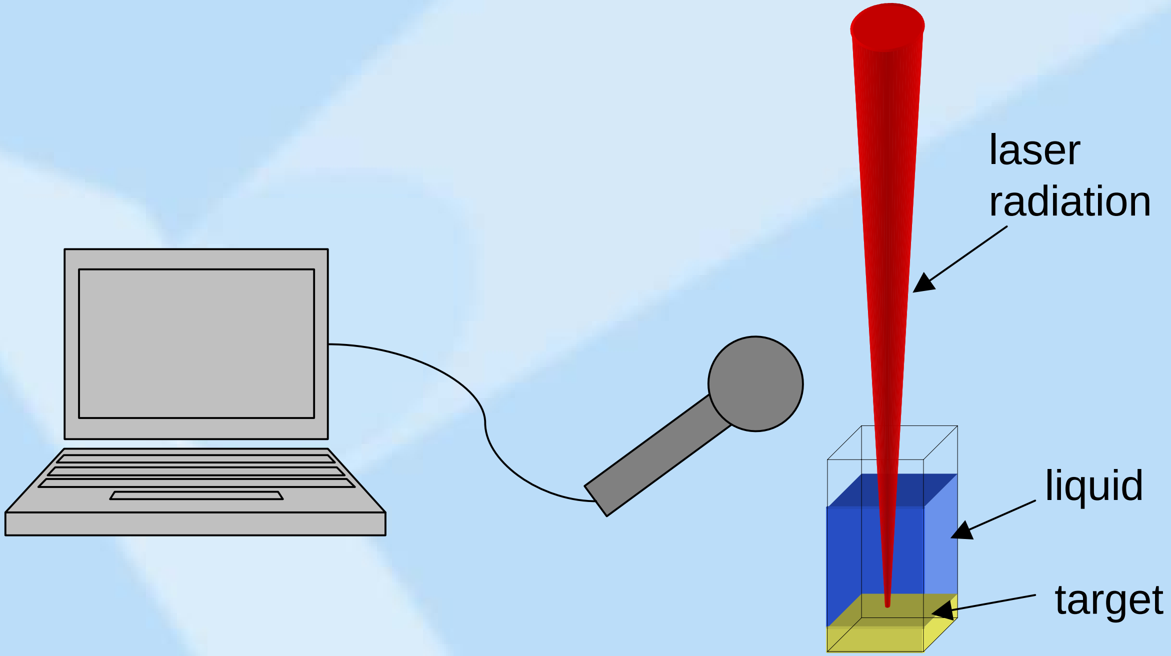


- Molten layer
- Optical breakdown of the water above the gold substrate leading to hot plasma generation and mechanical effect (cavitation bubble, shock wave) affecting the surface.

Experimental setup

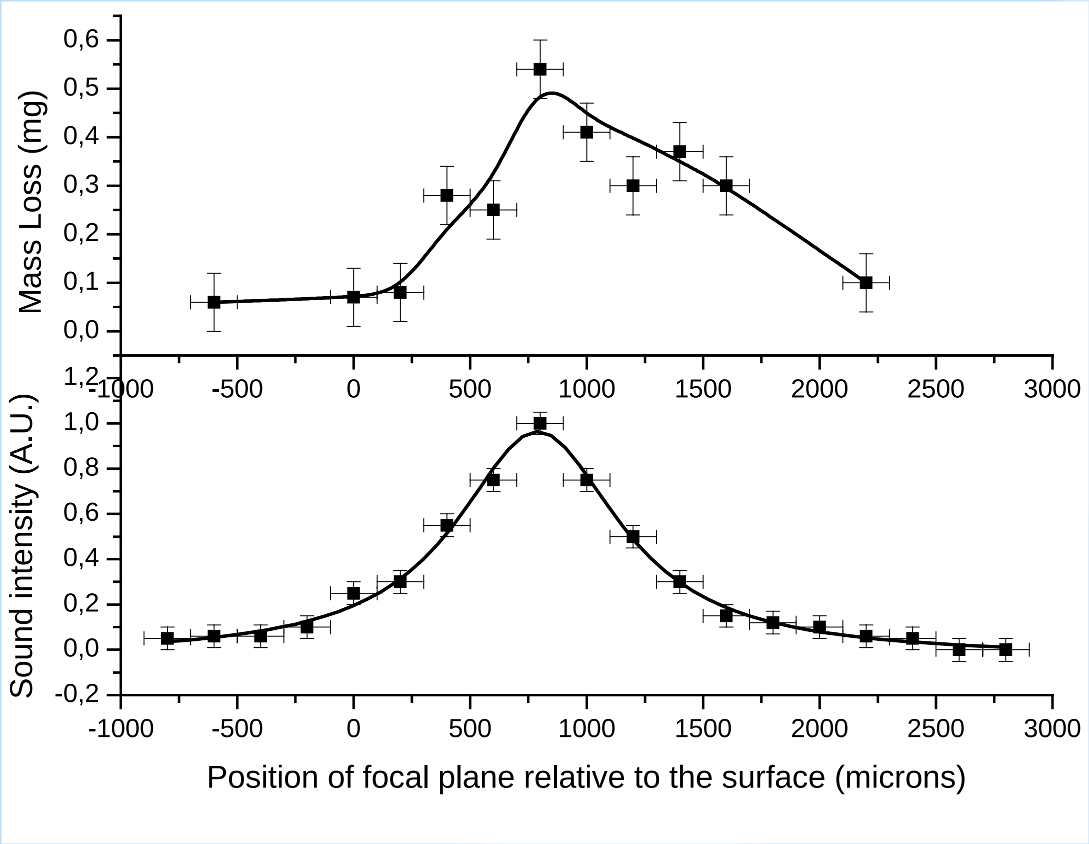
Optical breakdown of the liquid → A sound is generated due to generation of shock wave and collapse of cavitation bubble

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

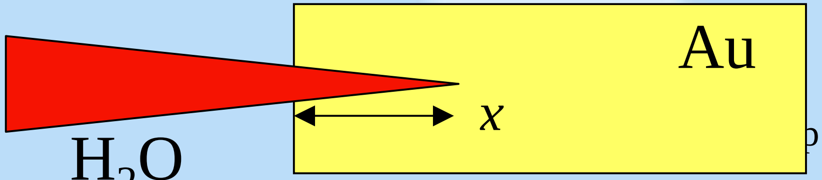


0.35 mJ/pulse,

20 min, rotation of target

Mass loss is maximal when sound intensity is maximal

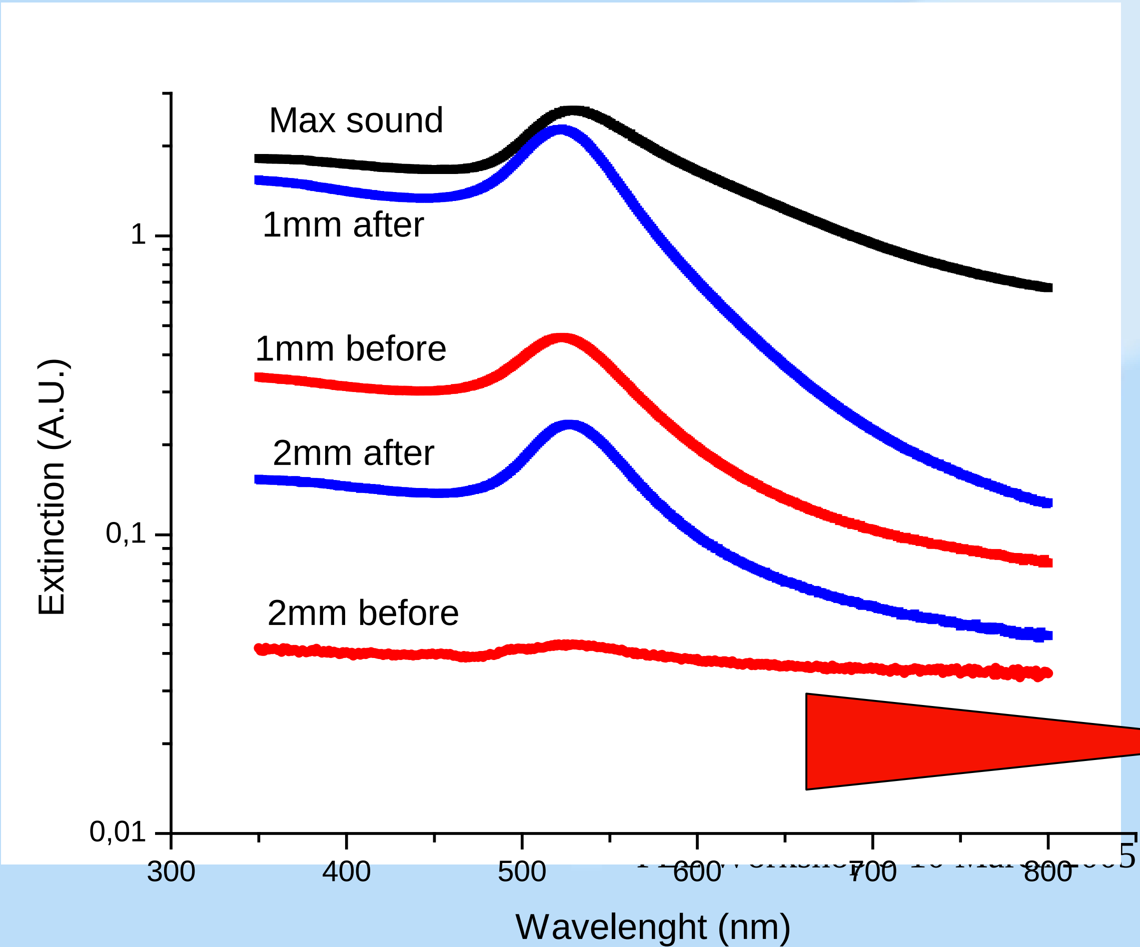
Indication for ablation mechanism related to optical breakdown effects



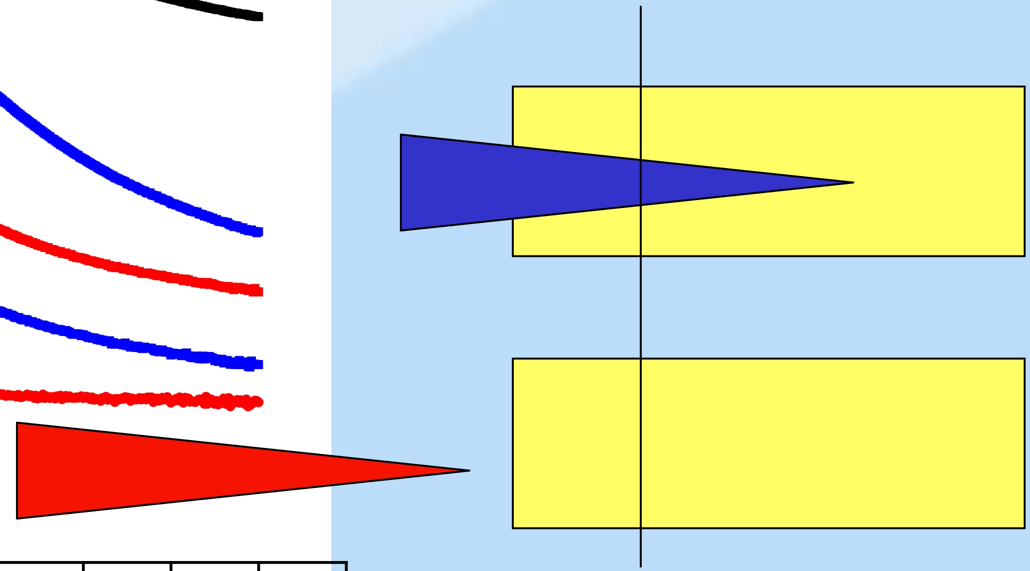
Optical Extinction

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

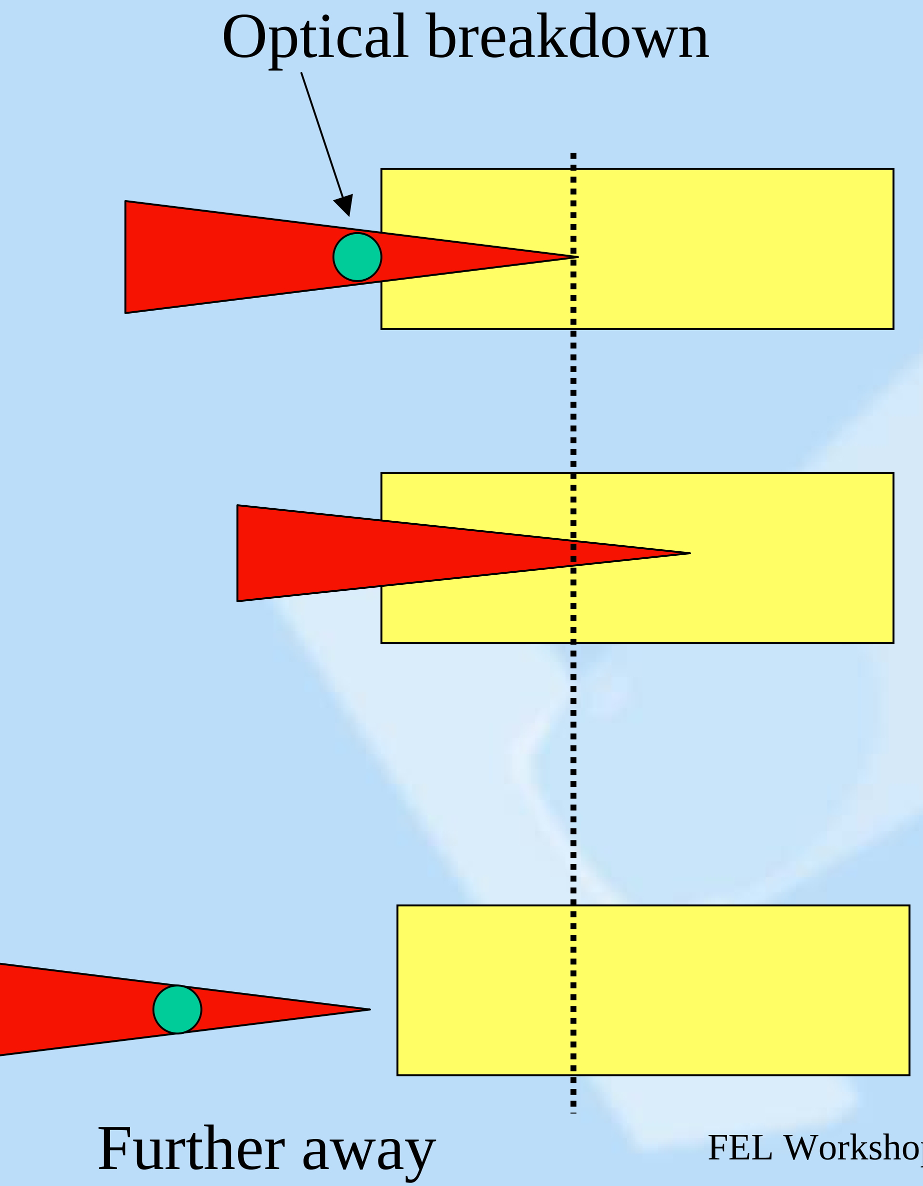
- Experimental conditions: 0.35 mJ/pulse, 5 min, rotation of target
- Positions are relative to the point of maximal sound intensity



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



Effect of focusing position



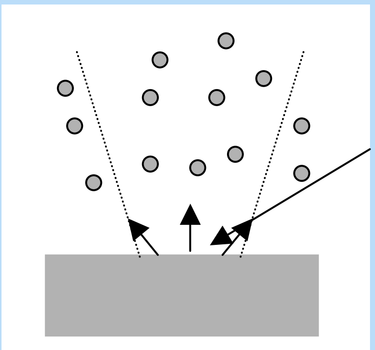
Sound maximum and ablation due to optical breakdown of water maximum
Large nanoparticles and broad plasmon peak

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

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

fs laser ablation in water: mechanisms of particle formation

A) "Low" fluence



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

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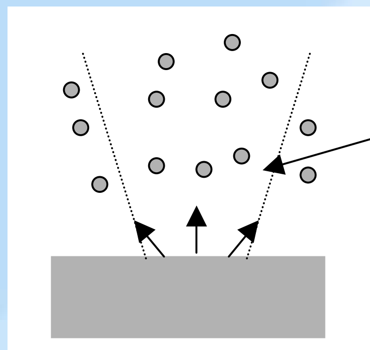
Narrow size distribution with mean particle size between 3.5 and 12 nm

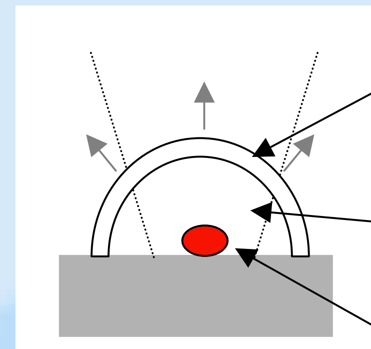
B) "High" fluence

optical breakdown of water = hot plasma generation

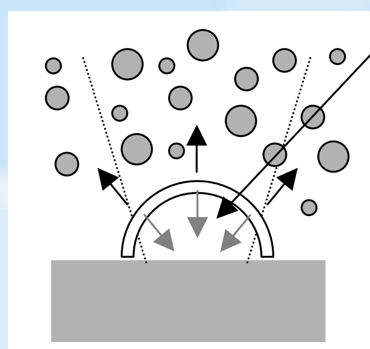
1) First few picoseconds



2) Micro- millisecond range



3) Fractions of a millisecond later



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

Broad size distribution with mean particle size 20 – 120 nm

Conclusion:

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

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!

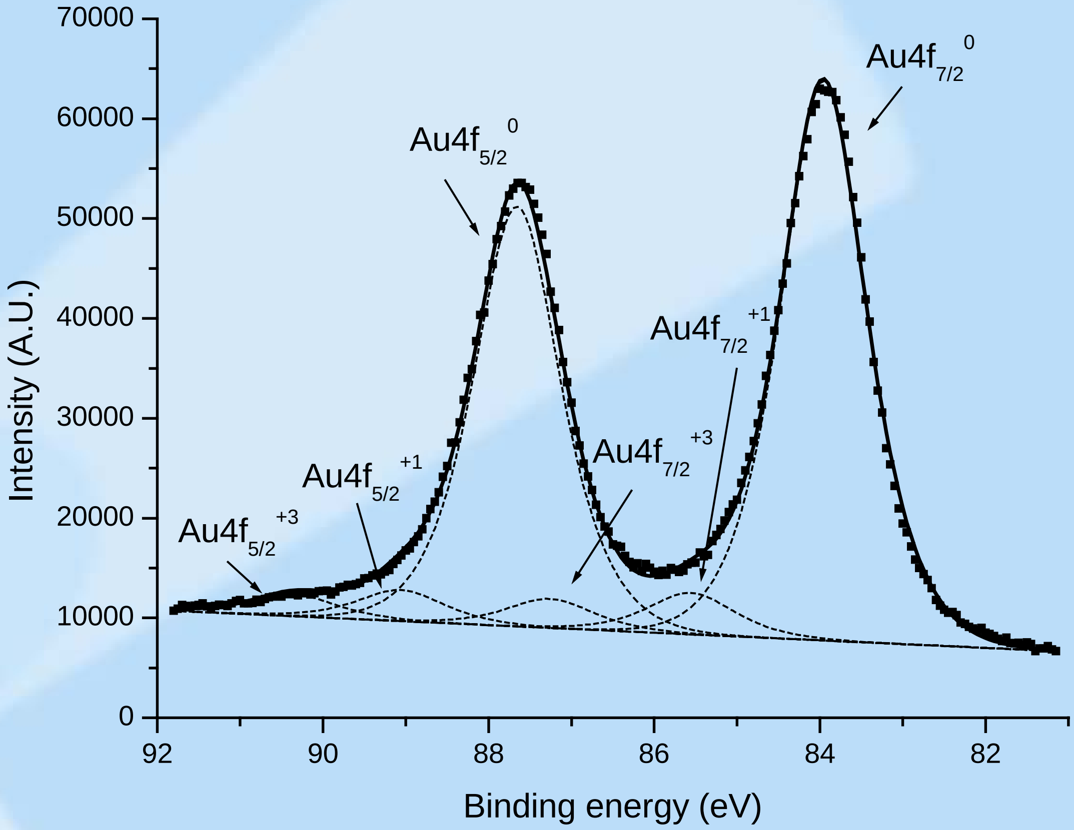
Chemistry of gold nanoparticles

Nanoparticles fabricated in deionized water

XPS Au4f (substrat HOPG)

- Nanoparticles are basically composed of Au^0

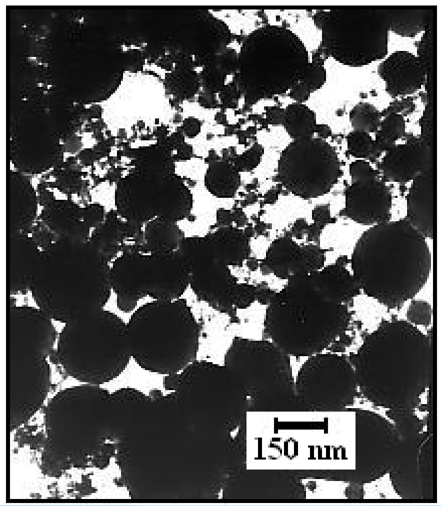
- Nanoparticles are partially oxidized (Au^{+1} et Au^{+3})



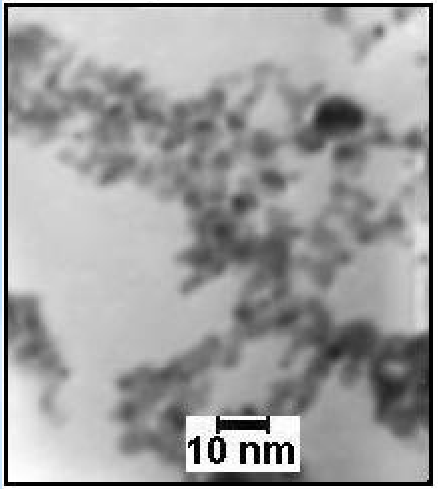
Effect of OH^- et Cl^- ions

Gold nanoparticles were produced under identical conditions

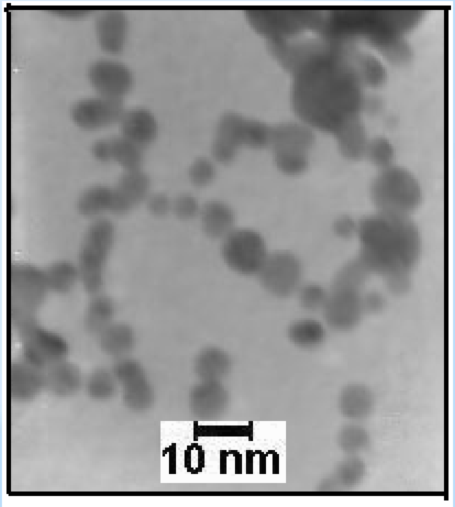
Deionized water



10 mM KCl



NaOH pH 9.4



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

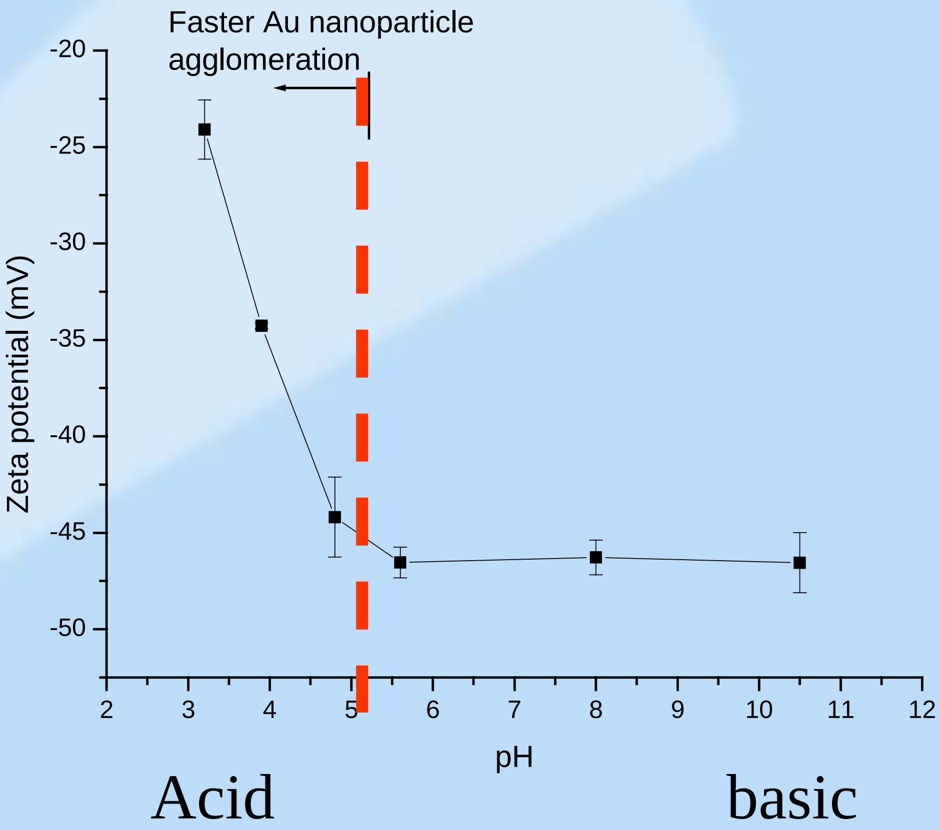
↓

Chemical interaction between Cl^- and OH^- with the gold surface

Effect of OH^- et Cl^- ions

Zeta potentiel 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

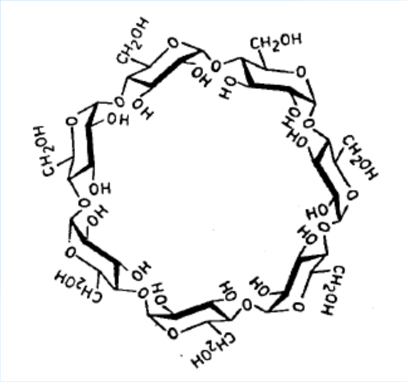
$$Au\text{-}OH \leftrightarrow Au\text{-}O^- + H^+$$

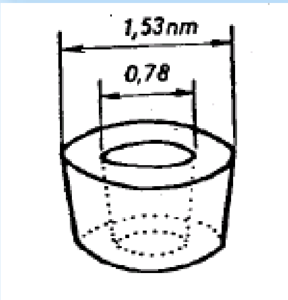
Effect of cyclodextrins

Effect of α, β et γ-CD

Chemistry: oligosaccharide cyclique containing 6, 7 et 8 alpha-D-glucoses forming a toroidal

J. Szejtli, Chem. Rev., **98**, 1743 (1998)





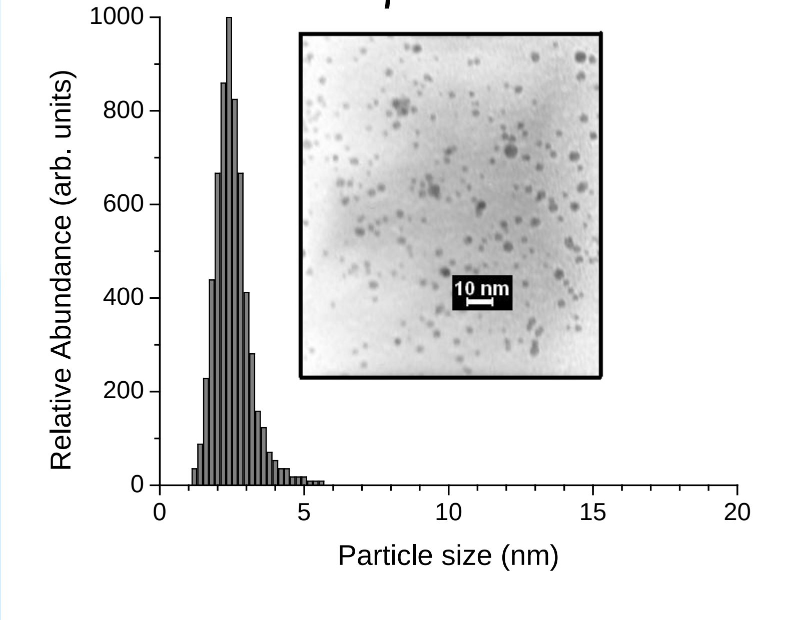
0.01M β-CD solution: 2.3 ± 1 nm

A.V. Kabashin, M. Meunier et.al,

J. Phys. Chem. B 107, 4527 (2003)

How do cyclodextrins react with gold?

0.01 M β-CD



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

References (M. Meunier)

First author	Title	Journal
J-P. Sylvestre	Femtosecond laser ablation of gold in water: influence of the laser-produced plasma on the nanoparticle size distribution	Applied Physics A. 80, 753-758 (2005)
J.-P. Sylvestre	Surface chemistry of gold nanoparticles produced by laser ablation in aqueous media	Phys. Chem. B. 108, 16864-16869 (2004)
J.-P. Sylvestre	Stabilization and Size Control of Gold Nanoparticles during Laser Ablation in Aqueous Cyclodextrins	J. Am.. Chem. Soc. 126, 7176-7177 (2004)
A. V. Kabashin	Synthesis of colloidal nanoparticles during femtosecond laser ablation of gold in water	J. Appl. Phys. 94, 7941-7943, (2003)
A. V. Kabashin	Fabrication and Characterization of Gold Nanoparticles by Femtosecond Laser Ablation in Aqueous Solution of Cyclodextrins	J. Phys. Chem. B, 107, 4527-4531 (2003)

WEB site of LPL http:// lpl.phys.polymtl.ca/