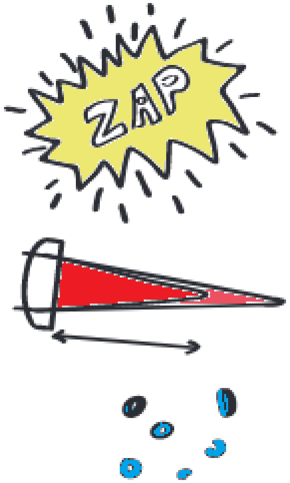
UMONS
Université de Mons

LPMO
Materials physics and Optics

Pulsed laser ablation in liquids: engineering low dimensionality systems



Physics of Materials and Optics unit
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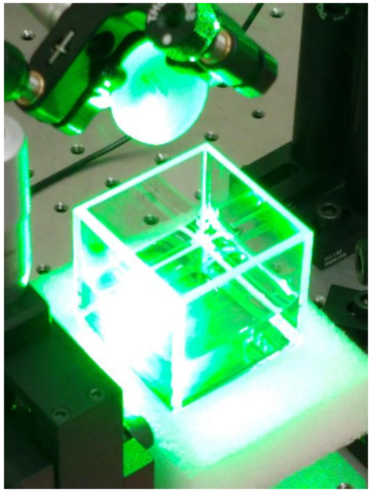


Cartoon from Barcikovski, 2019

Outlook of today's presentation

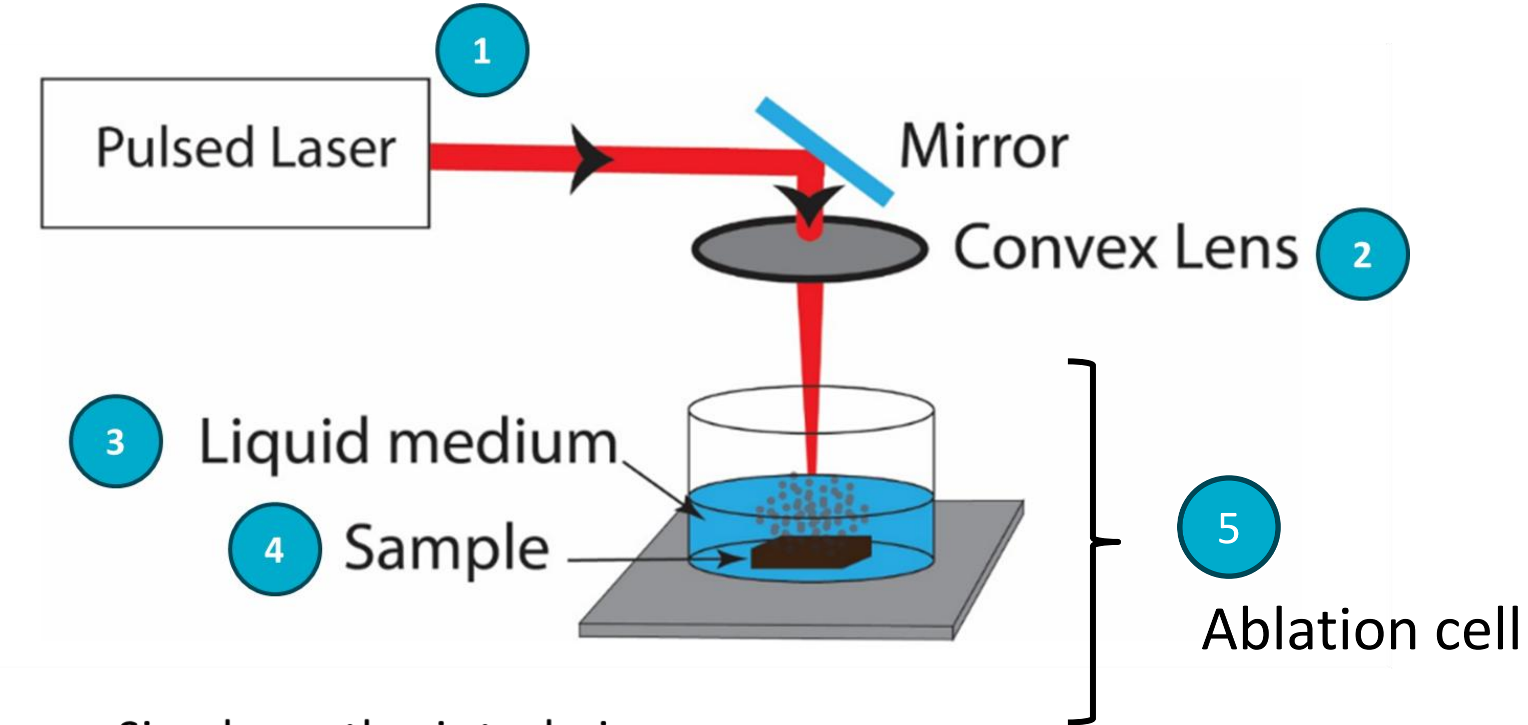
OVERVIEW OF LAL TECHNIQUES

THERMODYNAMICS OF NANOPARTICLES RESHAPING AND ENGINEERING

LAL AND 2D MATERIALS

TAKE HOME MESSAGES

Basics of LAL (*)



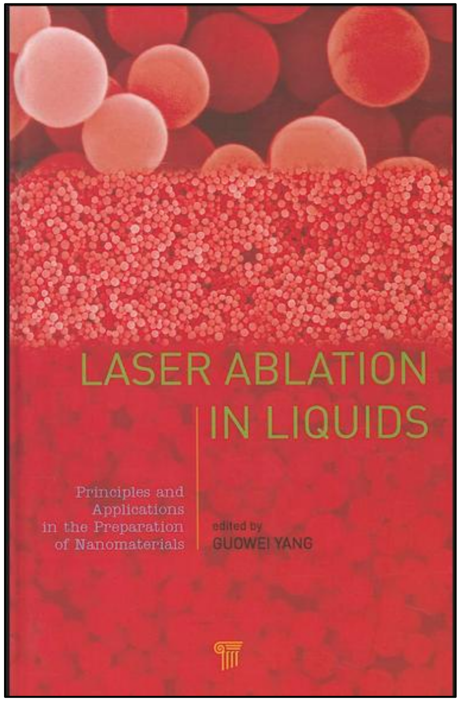
- Simple synthesis technique
- Usually with non reproducible results when you run it for the first times

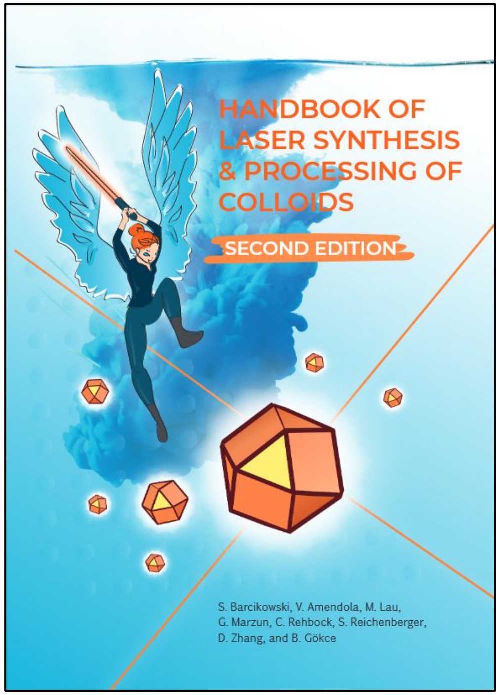
From Shaheen, 2025

Use of laser beams to generate a dispersion of NPs in a liquid environment

(*) LAL = LASiS (Laser Ablation Synthesis in Solution)

Literature



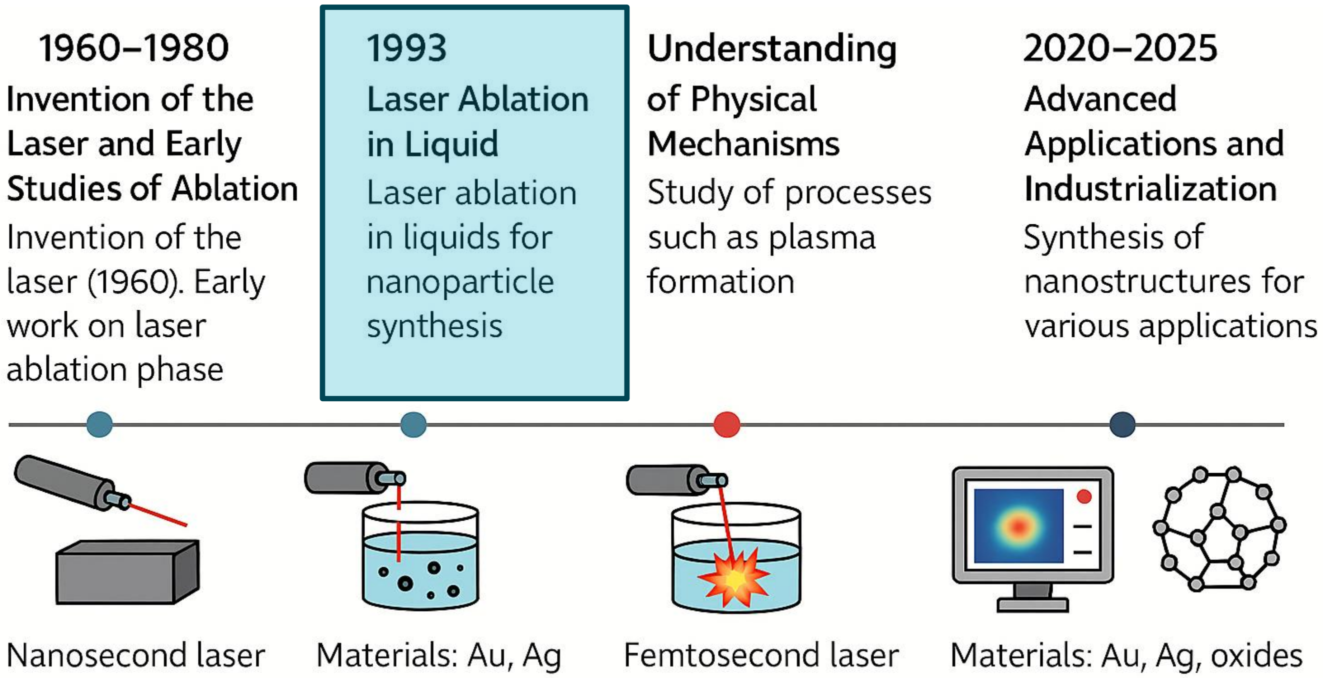


Yang, G. (Éd.). (2012). *Laser ablation in liquids : Principles and applications in the preparation of nanomaterials*. Pan Stanford Publishing.

Barcikowski, S., Amendola, V., et al (2019). *Handbook of Laser Synthesis & Processing of Colloids*. DuEPublico: Duisburg-Essen Publications online, University of Duisburg-Essen, Germany. https://doi.org/10.17185/DUEPUBLICO/70584

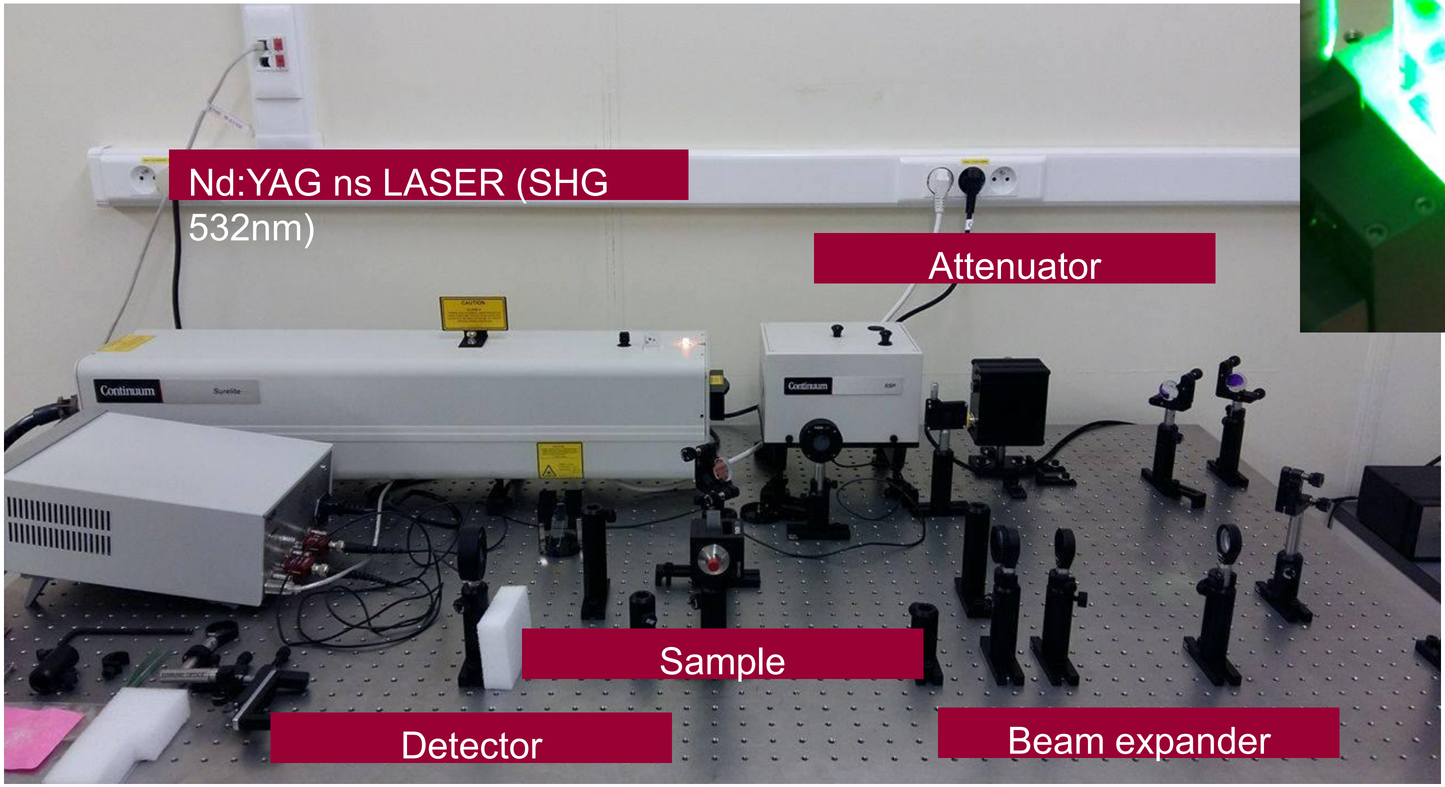
Key historical developments in LAL

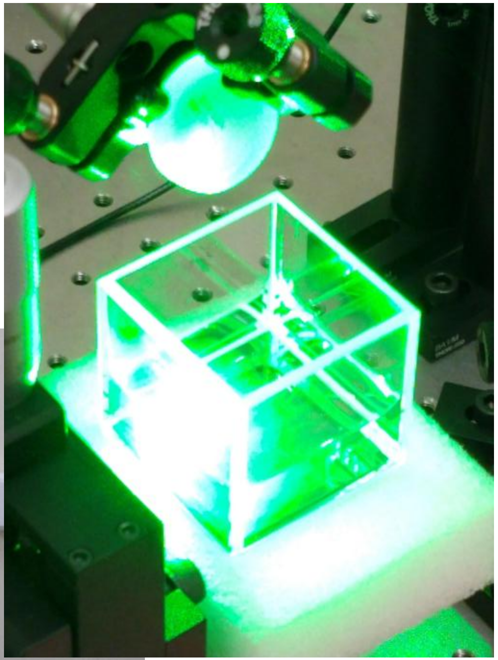
Approx. 15000 articles since 1995



Fojtik, A.; Henglein, A.
Laser Ablation of Films and Suspended Particles in a Solvent: Formation of Cluster and Colloid Solutions.
Berichte der Bunsen-Gesellschaft für Physikalische Chemie, **97**(2), 252–254 (1993).

Experimental setup at LPMO



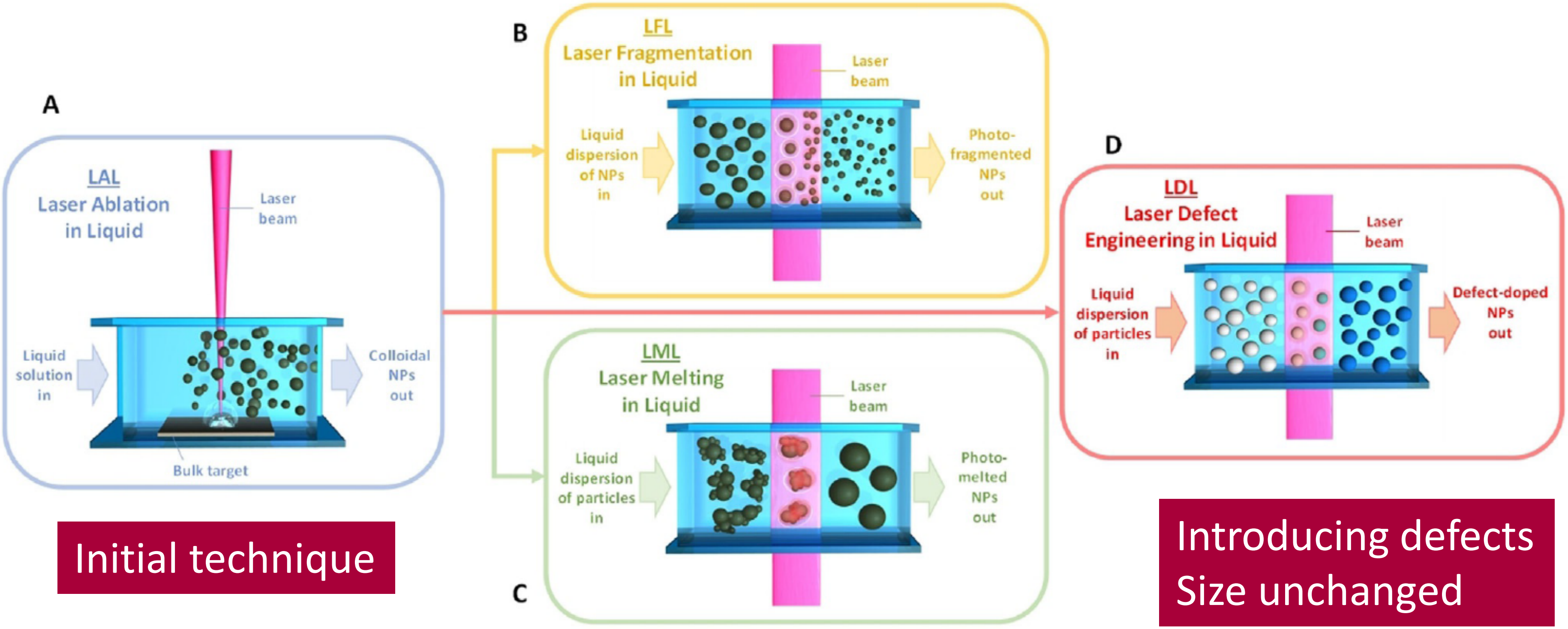


Why LASER ablation ?

- Optical properties of plasmonic nanocomposites
- Usually : bottom-up approach for NP synthesis
- But : **LAL provides top-down ways of producing NPs**

- Plasmonic nanocomposites : interesting for their linear and non-linear optical properties (3rd order susceptibility)

Multiple facets of LAL



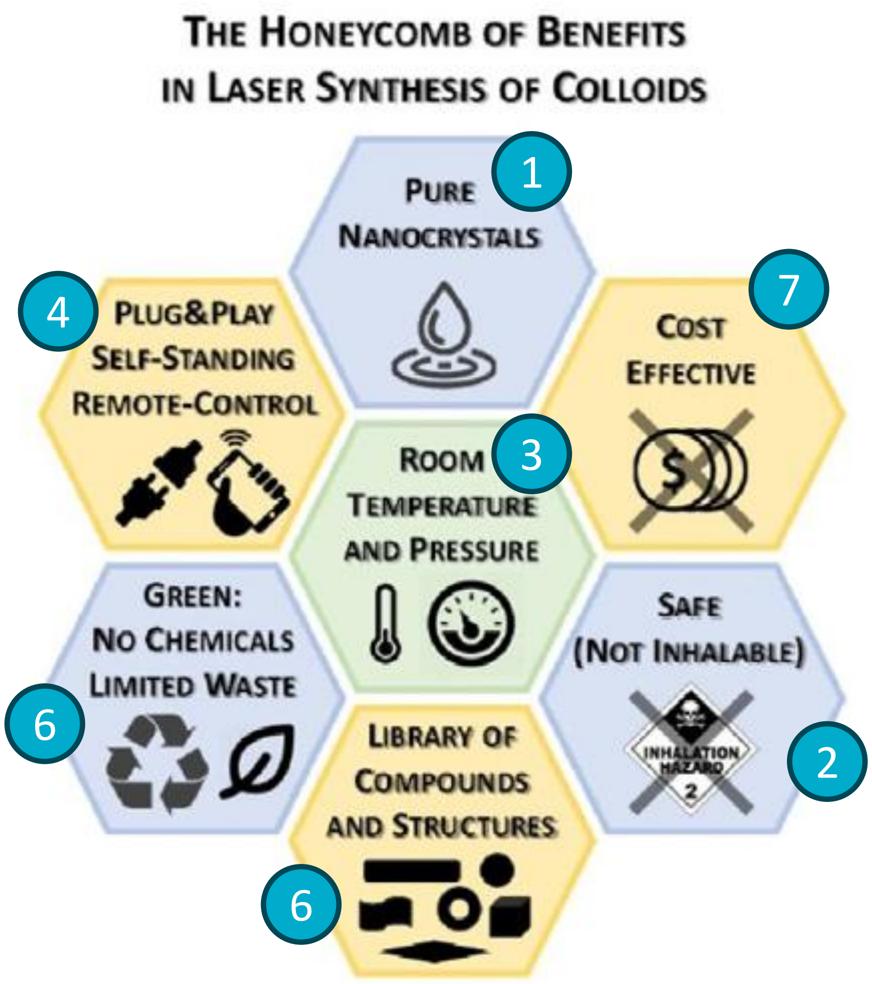
Initial technique

Introducing defects
Size unchanged

Photo-fragmentation (LFL)
- Reduction of size
- Control of polydispersity

Photothermal fusion (LML)

Benefits of LAL

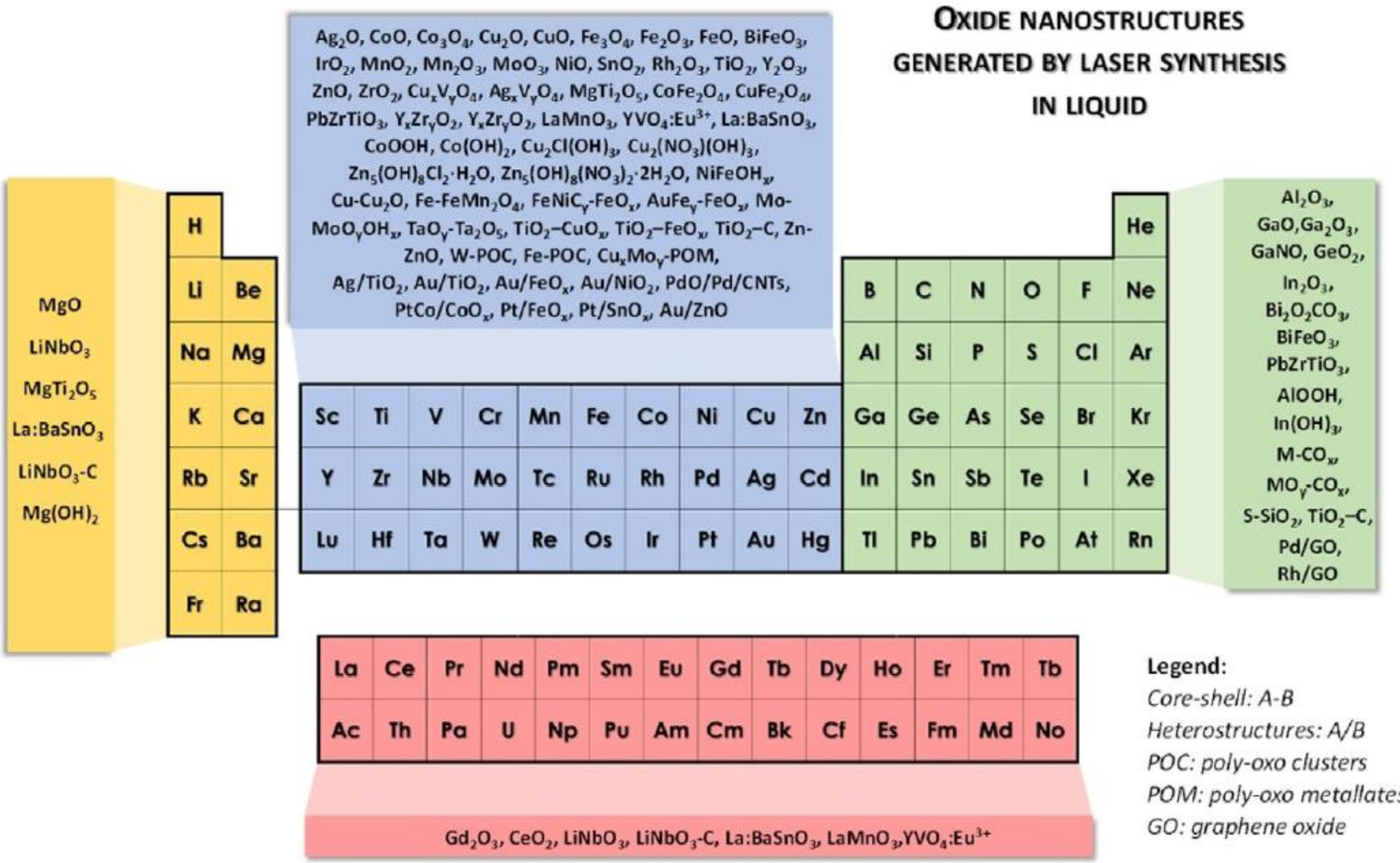


1. Extremely pure and stable colloids (ligand free, uncoated surface, no ligands, no chemical precursors, non chelating agents)
2. Minimized chemical risks
3. Large number of components under the same conditions of temperature and pressure
4. Easy way to switch from one process to another
5. Large number of compounds and structures
6. Chemically improved in terms of absence of waste
7. Cost effective but linearly scalable : productivity linearly scales with both laser power and time, at constant liquid flow operation

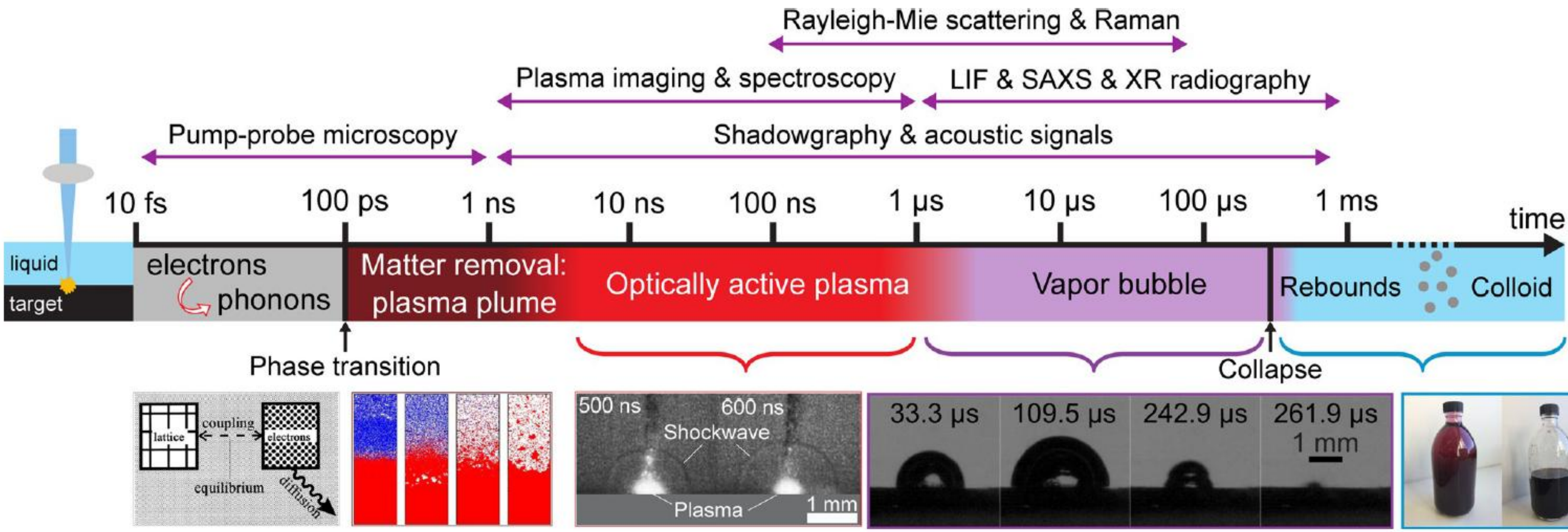
Amendola et al, 2020

Synthesis of nanomaterials: comparison

	Elements	Green synthesis	Synthesis Purity	Inhalation	Productivity	Complexity	Remote Control
Chemical Methods	–	✗	✗	–	✓	✓	–
Nanomaterials Biosynthesis	✗	✓	✗	–	✗	–	✗
Physical Methods	✓	✓	–	–	✓	✓	–
Laser synthesis	✓	✓	✓	✓	✗	✓	✓

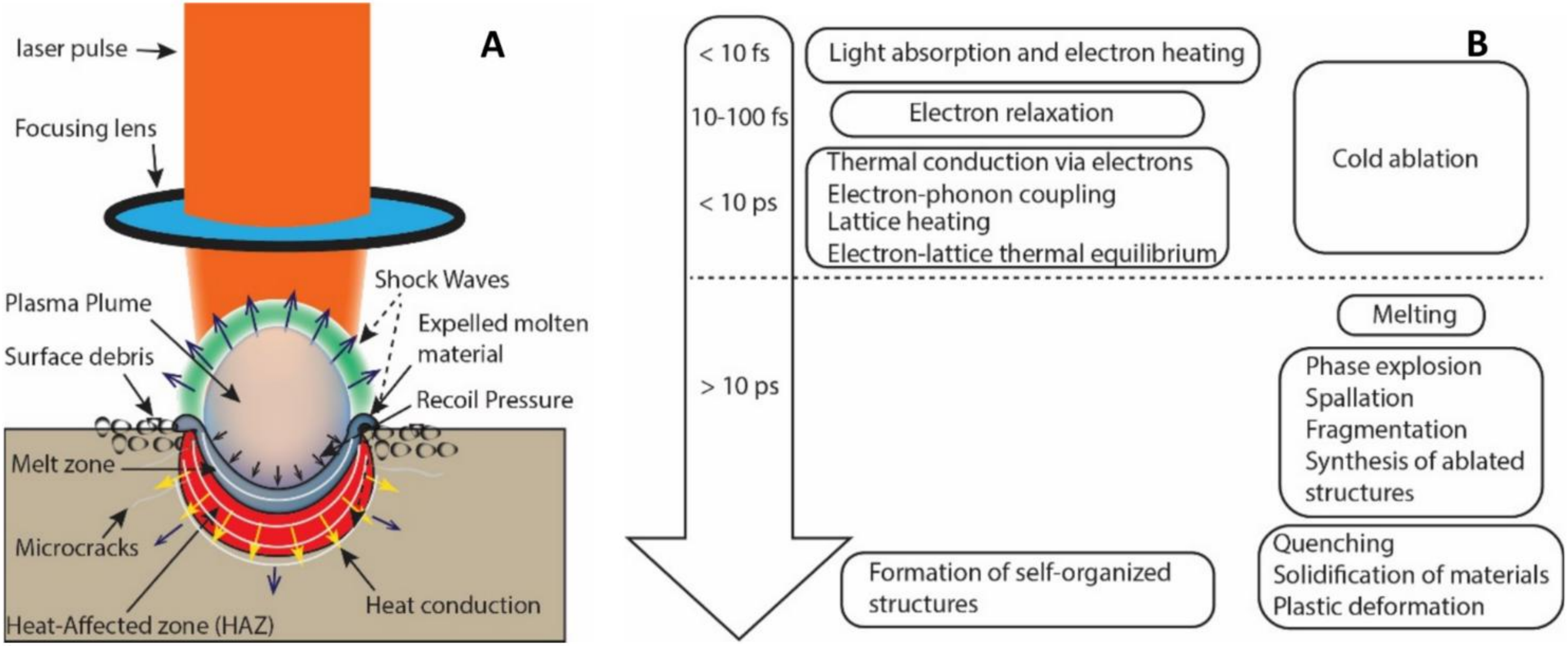

OXIDE NANOSTRUCTURES
GENERATED BY LASER SYNTHESIS
IN LIQUID
Ag2O, CoO, Co3O4, Cu2O, CuO, Fe3O4, Fe2O3, FeO, BiFeO3, IrO2, MnO2, Mn2O3, MoO3, NiO, SnO2, Rh2O3, TiO2, Y2O3, ZnO, ZrO2, CuxVyO4, AgxVyO4, MgTi2O5, CoFe2O4, CuFe2O4, PbZrTiO3, YxZryO2, YxZryO2, LaMnO3, YVO4:Eu3+, La:BaSnO3, CoOOH, Co(OH)2, Cu2Cl(OH)3, Cu2(NO3)(OH)3, Zn5(OH)8Cl2·H2O, Zn5(OH)8(NO3)2·2H2O, NiFeOHx, Cu-Cu2O, Fe-FeMn2O4, FeNiCy-FeOx, AuFey-FeOx, Mo-MoOyOHx, TaOy-Ta2O5, TiO2–CuOx, TiO2–FeOx, TiO2–C, Zn-ZnO, W-POC, Fe-POC, CuxMoy-POM, Ag/TiO2, Au/TiO2, Au/FeOx, Au/NiO2, PdO/Pd/CNTs, PtCo/CoOx, Pt/FeOx, Pt/SnOx, Au/ZnO
MgO
LiNbO3
MgTi2O5
La:BaSnO3
LiNbO3-C
Mg(OH)2
Al2O3, GaO, Ga2O3, GaNO, GeO2, In2O3, Bi2O2CO3, BiFeO3, PbZrTiO3, AlOOH, In(OH)3, M-COx, MOy-COx, S-SiO2, TiO2–C, Pd/GO, Rh/GO
H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba Lu Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Tb
Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No
Gd2O3, CeO2, LiNbO3, LiNbO3-C, La:BaSnO3, LaMnO3, YVO4:Eu3+
Legend:
Core-shell: A-B
Heterostructures: A/B
POC: poly-oxo clusters
POM: poly-oxo metallates
GO: graphene oxide

Timeline in LAL : a multiple steps process



- Liquid must be transparent and liquid breakdown avoided at the fluence of the experiment (challenging due to self focusing and filamentation effects)

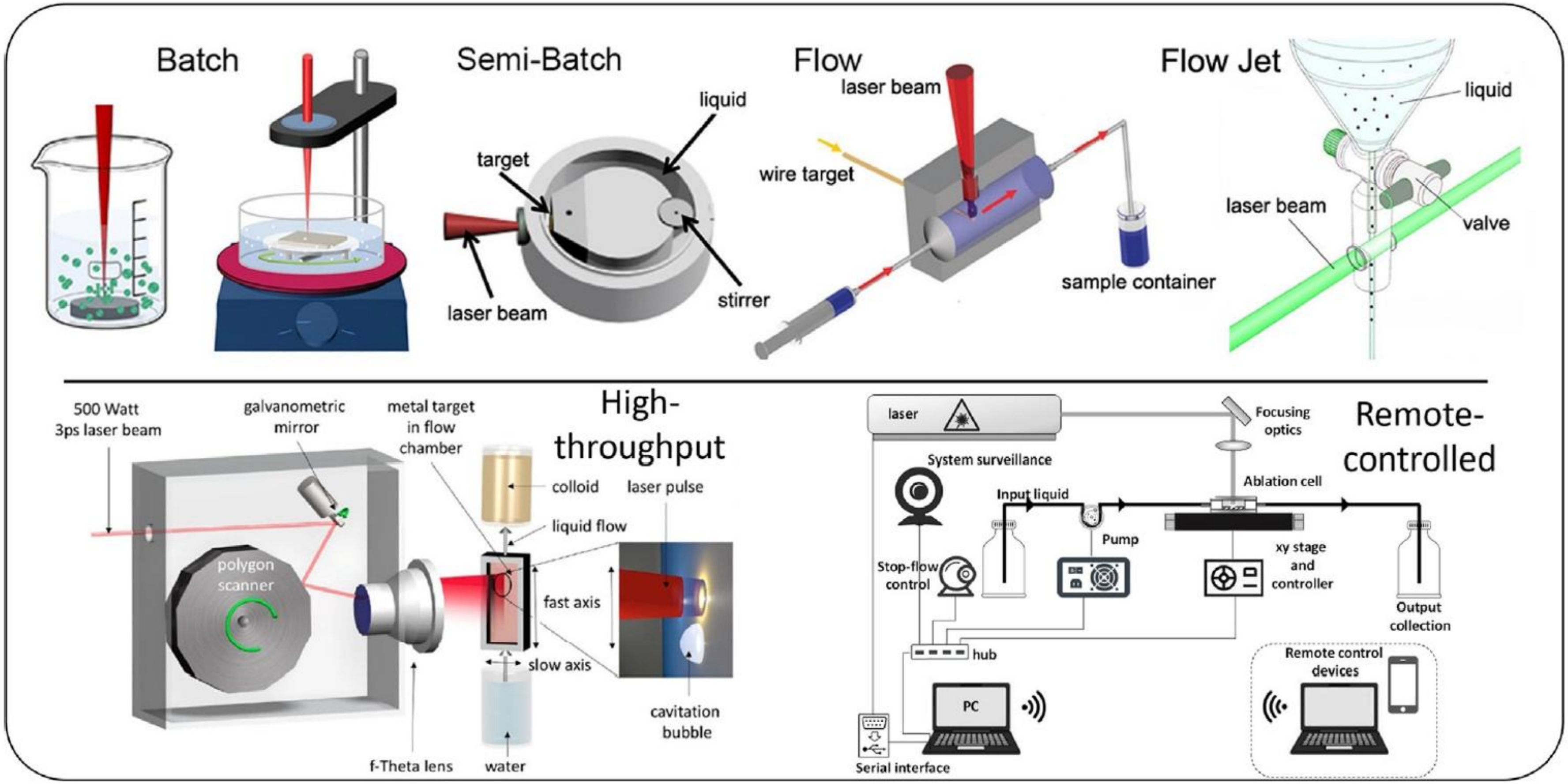
A more complex scheme for LAL …



Multiple phenomena occuring is a very shot period of time

(Shaheen, 2025)

Variety of ablation cells

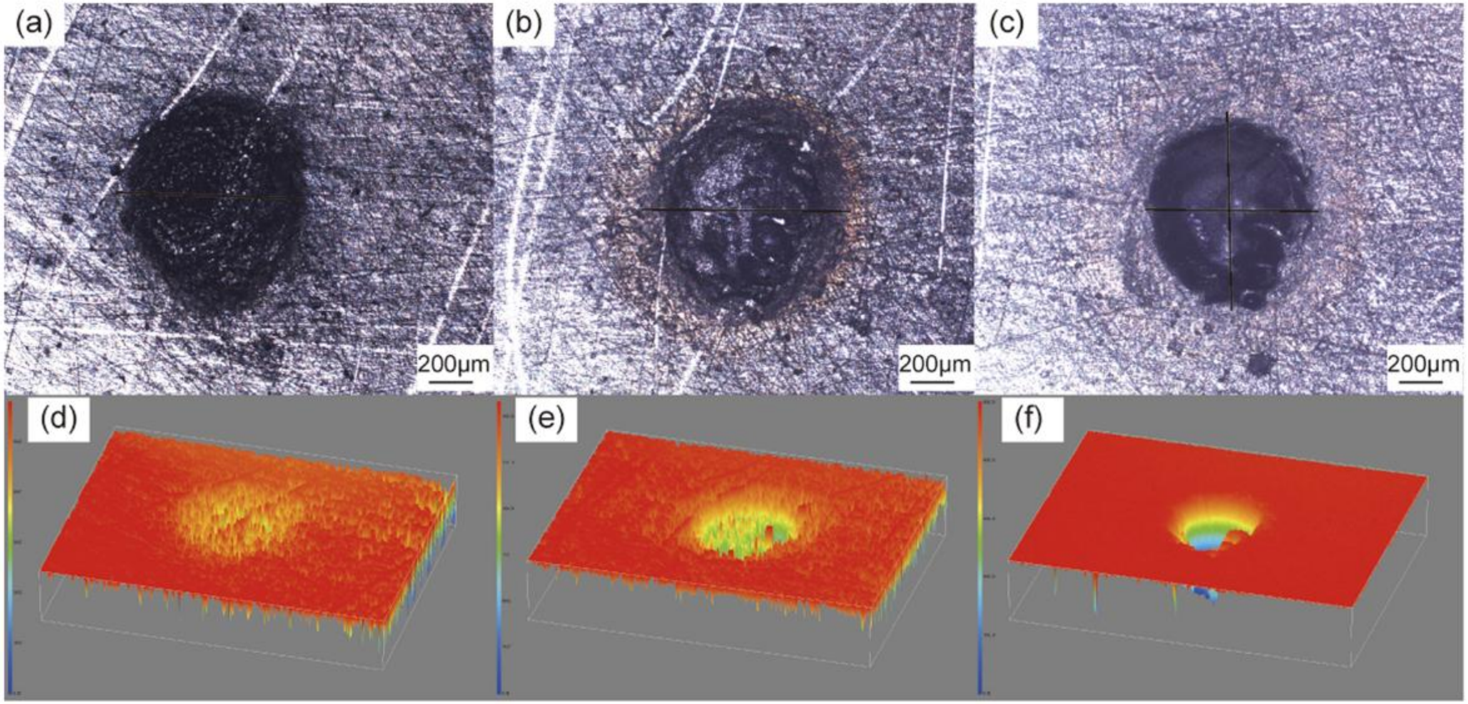


Target morphology after multiple LASER impacts

(Huang, 2019)

Optical microscopy (white light)

Confocal microscopy



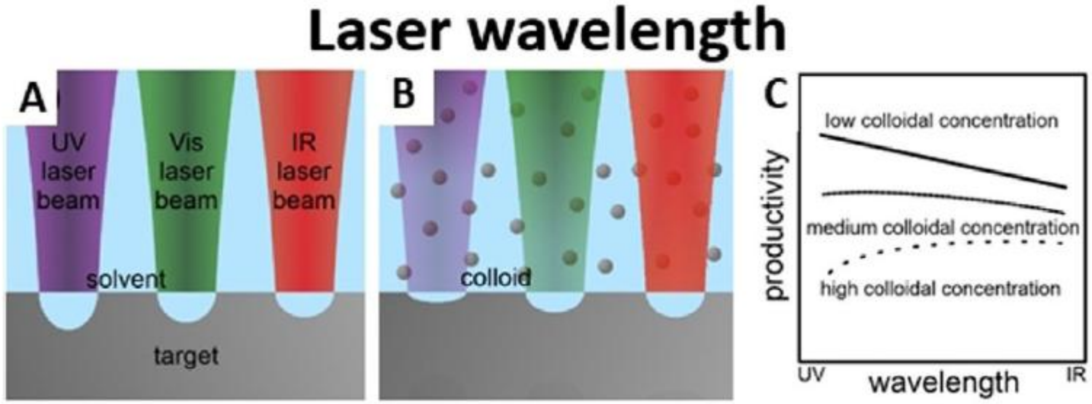
10 pulses
13 µm

1000 pulses
60 µm

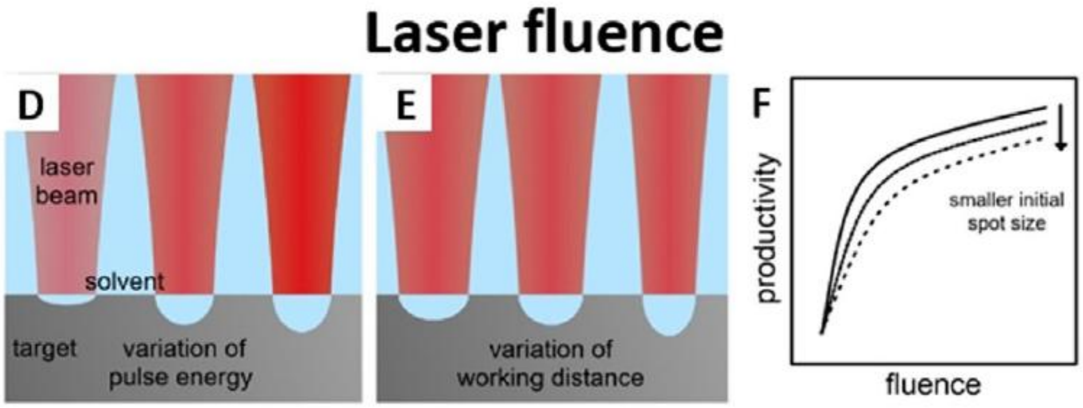
5000 pulses
500 µm

Progressive evolution to cone shape

Some factors controlling the productivity



- The ablation rate is higher when using low wavelengths as long as no NPs synthesized by previous pulses are present

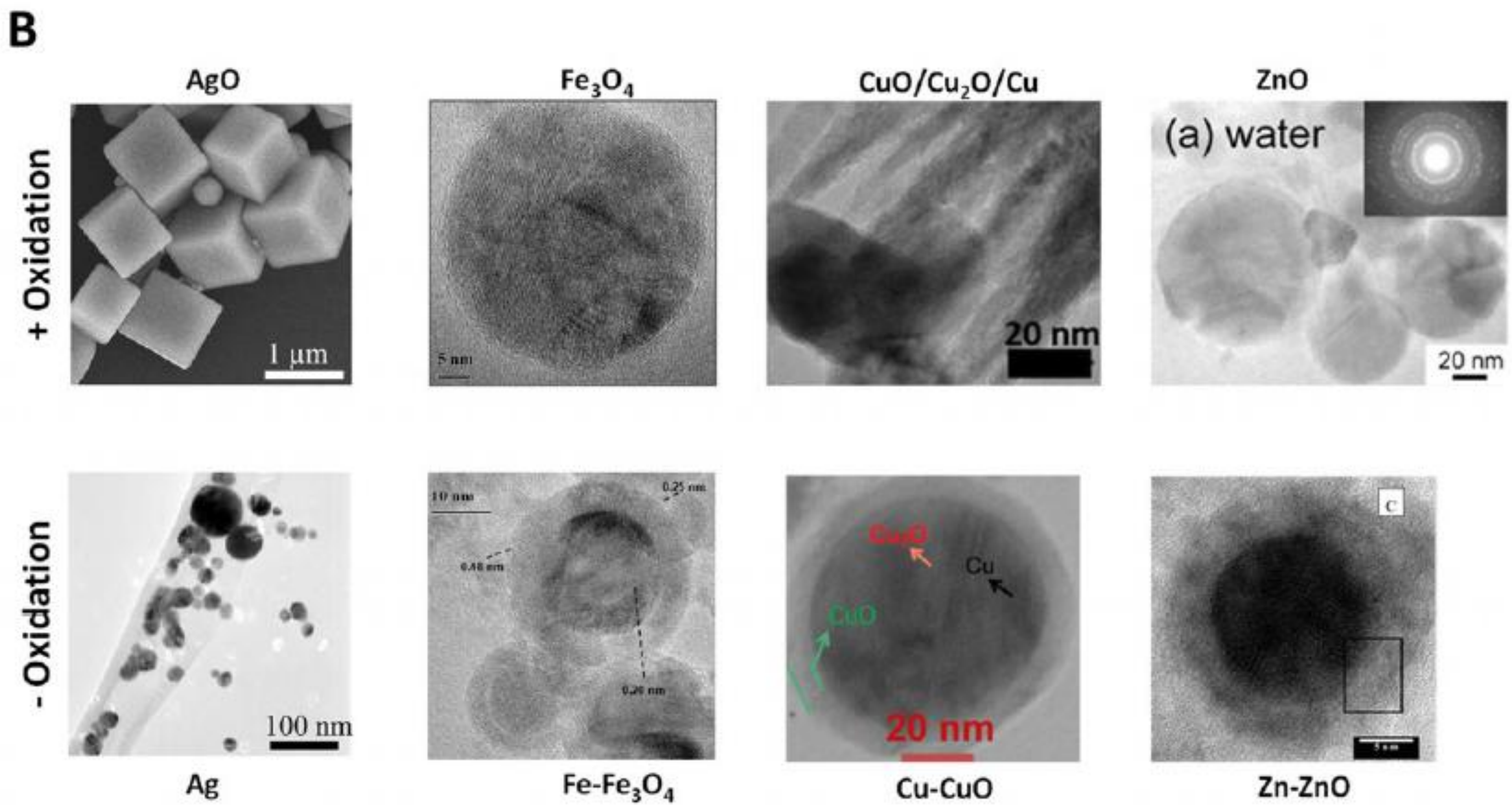


- High laser fluence, short pulse duration and high repetition rate lasers (> kHz, that is, inter-pulse delay of < 1 ms) have shown to be most successful up until now for productivity to gram scale

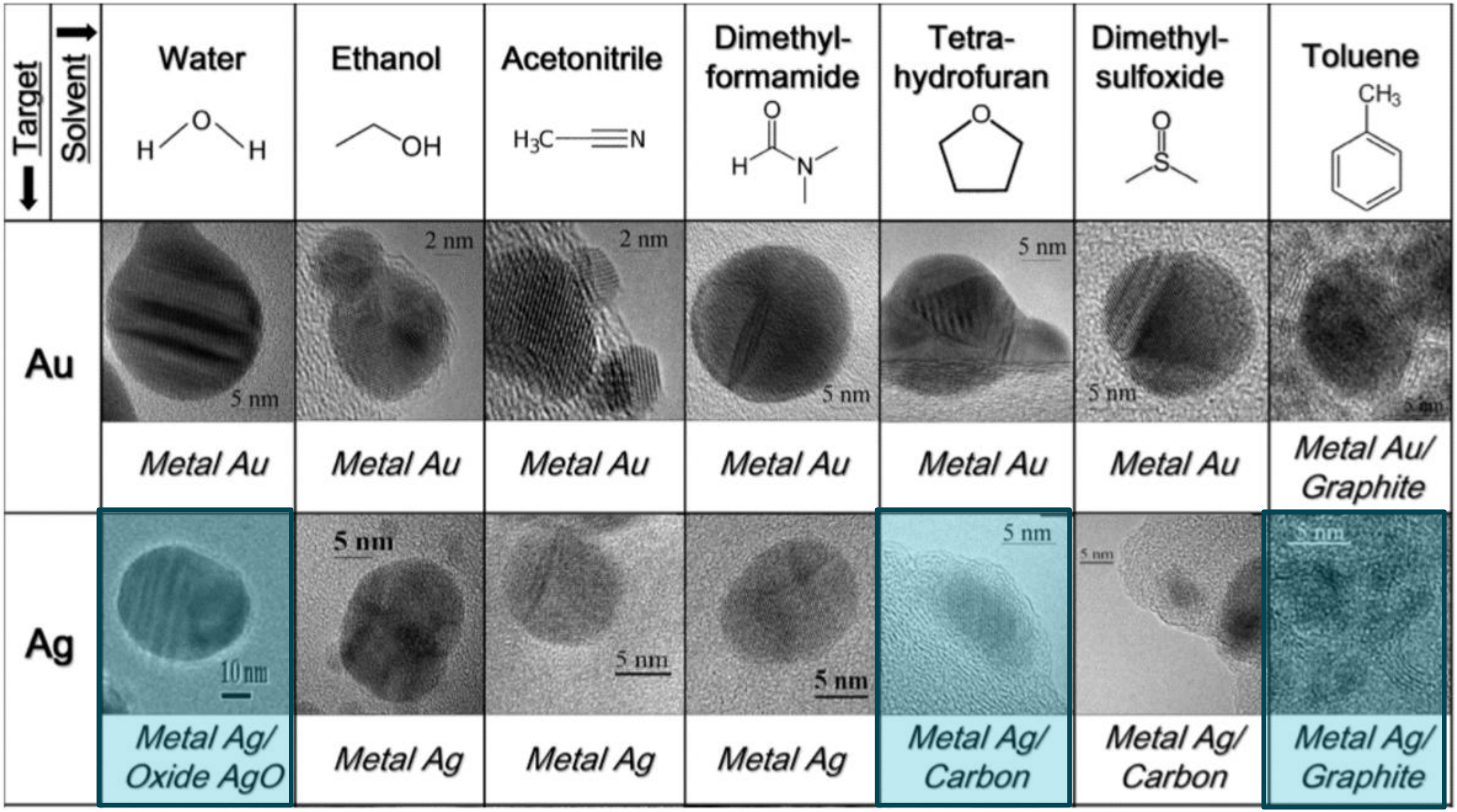
Comparison of LASERs in ablation processes

LASER PULSE DURATION	PROS	CONS
ns	• more and cheaper high-power lasers available (i.e. high productivity) • high power at moderate repetition rates	• heat transfer from target to the liquid • less efficient
ps	• 'gentle ablation' • insignificant heat transfer to liquid • compromise between efficiency and productivity/costs • high power systems available	• optical breakdown at high pulse energies • high power at high repetition rates (bubble shielding) • high power more costly than ns
fs	• 'gentle ablation' • very efficient ablation per pulse • insignificant heat transfer to liquid	• high power at high repetition rates (bubble shielding) • optical breakdown • high power more costly

Complexity of the products : shape, chemistry



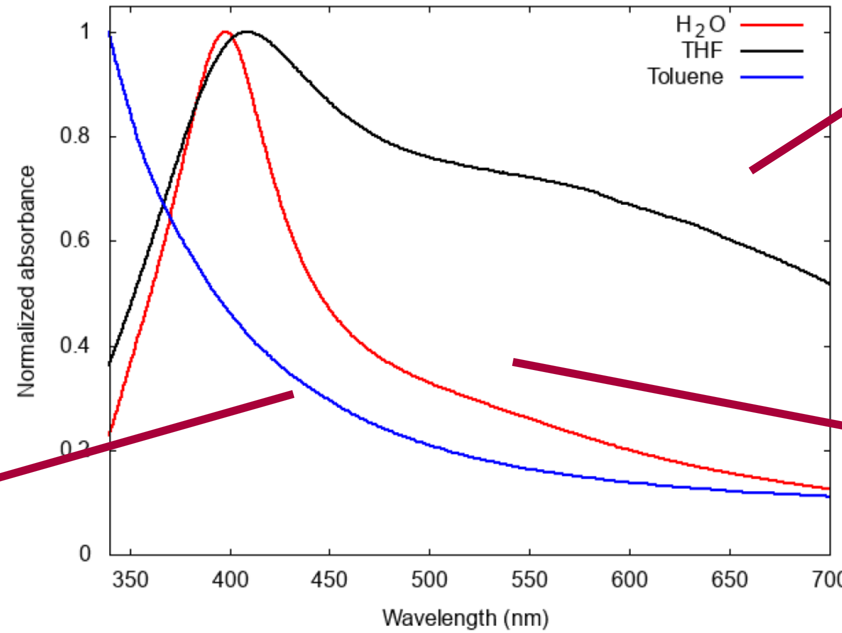
Role of the solvent

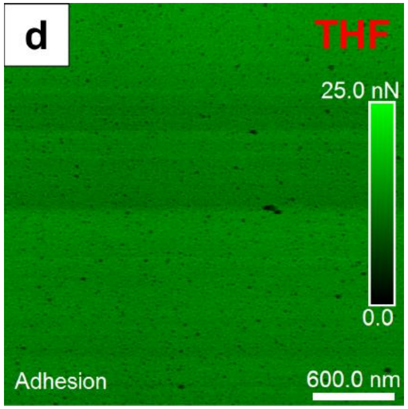


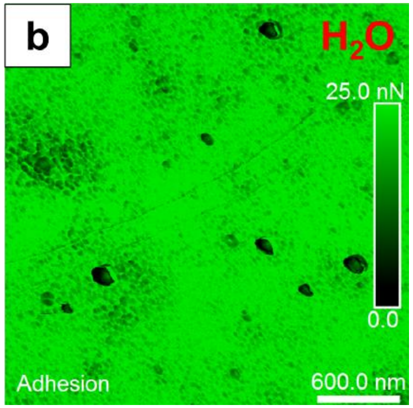
Amendola and Menengetti, 2013

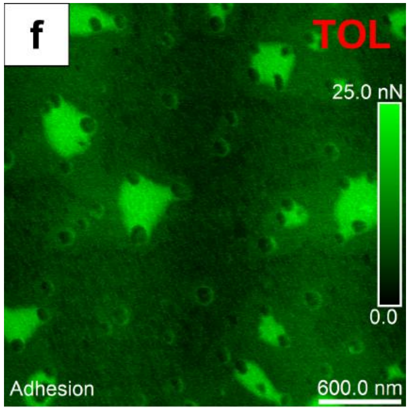
Influence of the solvent on the SPR

- Adhesion from AFM measurements in PS casted films
- SPR in solvents
- Silver target – 6.5 mJ/pulse NdYAG / Fluence: 6.5 10^3 J/cm²
- λ = 1064 nm





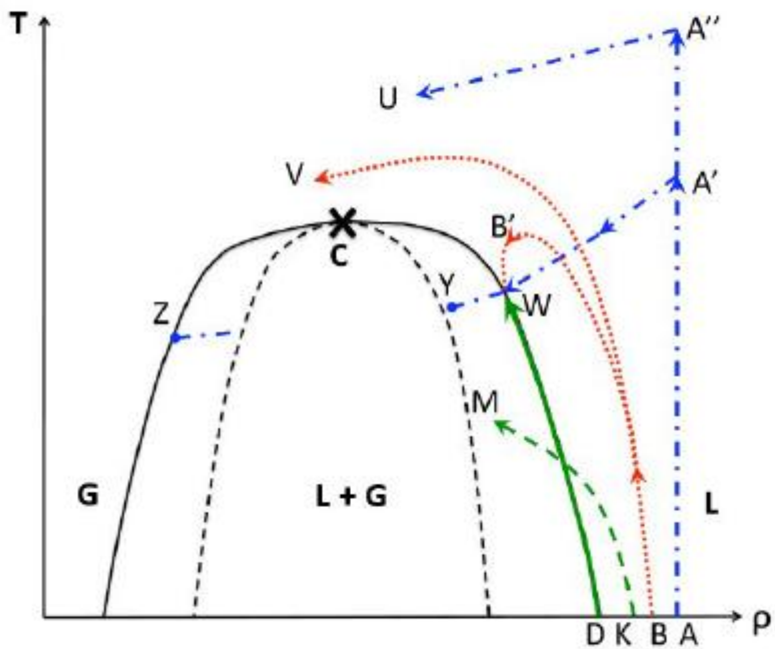




Quenching of the SPR in TOL
Carbonaceous shell

De Muijlder, Voué and Leclère, 2023

Phase diagram



Phase diagram density/temperature

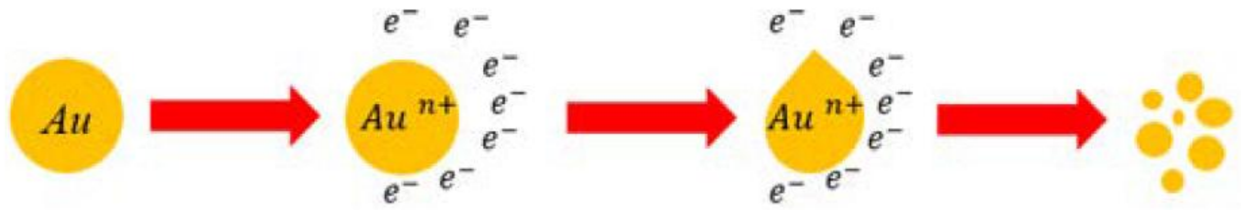
- Path D -> W : quasi steady-state regime(ms, ns) -> binodal curve (equilibrium LV)
- In ns regime : temperature increase induces a rapid expansion (beyond binodal curve (K -> M path)
- Metastable states between binodal and spinodal curves

Mansour, 2020

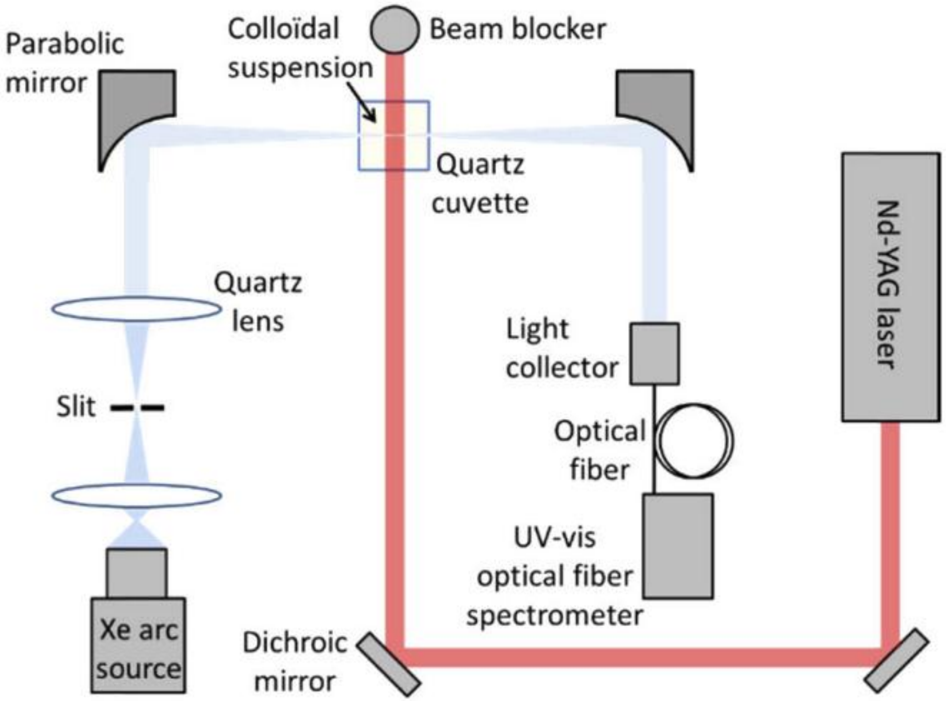
Models for fragmentation

Takami's model : thermal model based on phase transitions

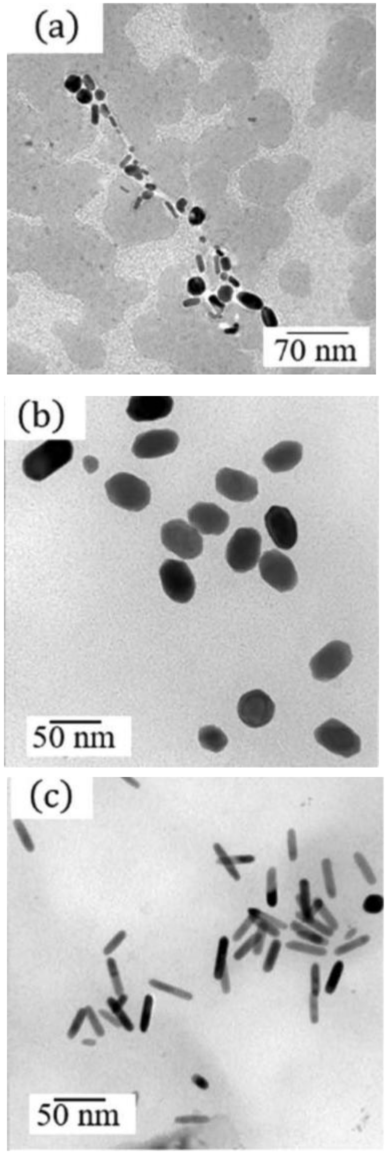
Kamat's model : Coulombian interactions induces NP explosion



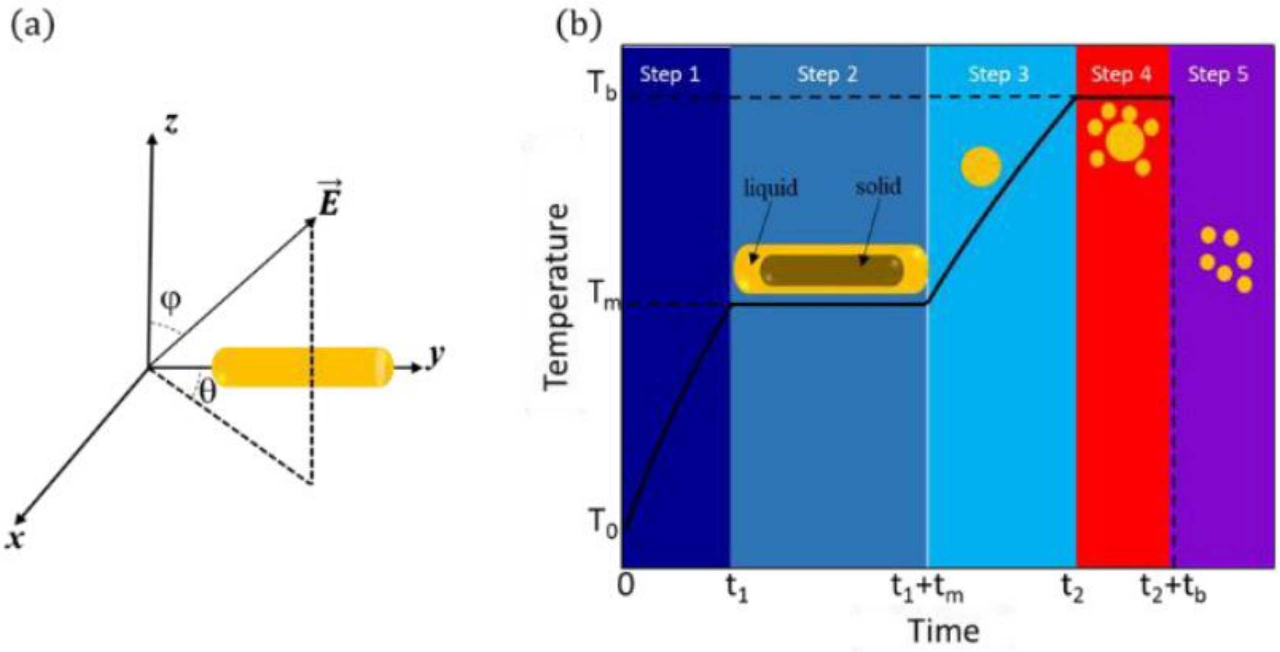
Realtime monitoring the aspect ratio distribution



(Mansour et al, 2020)



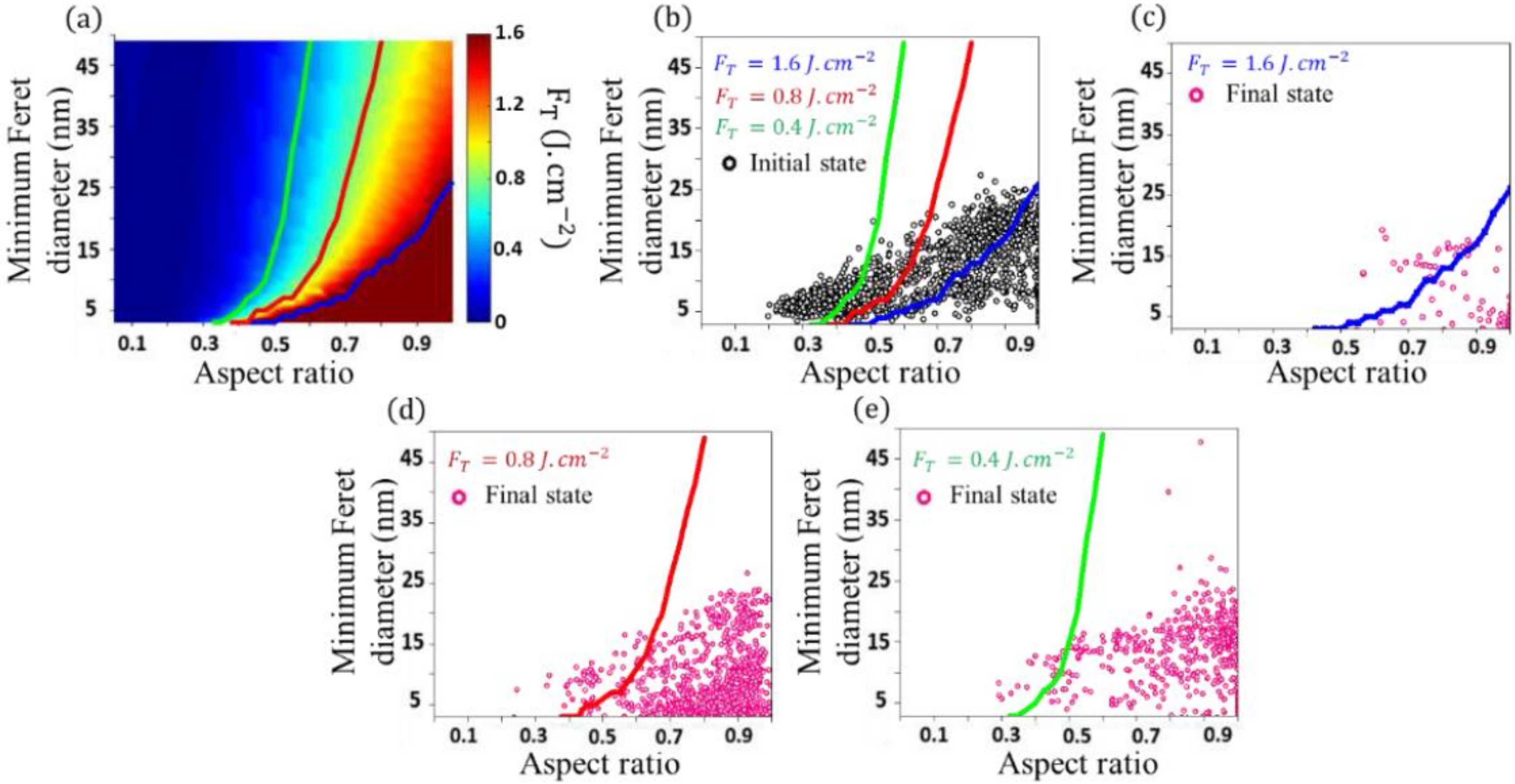
Mansour's model (2020)



This model takes into account the **orientation of the NRs**, **radiative and convective losses**, and **phase transitions** of the NRs.

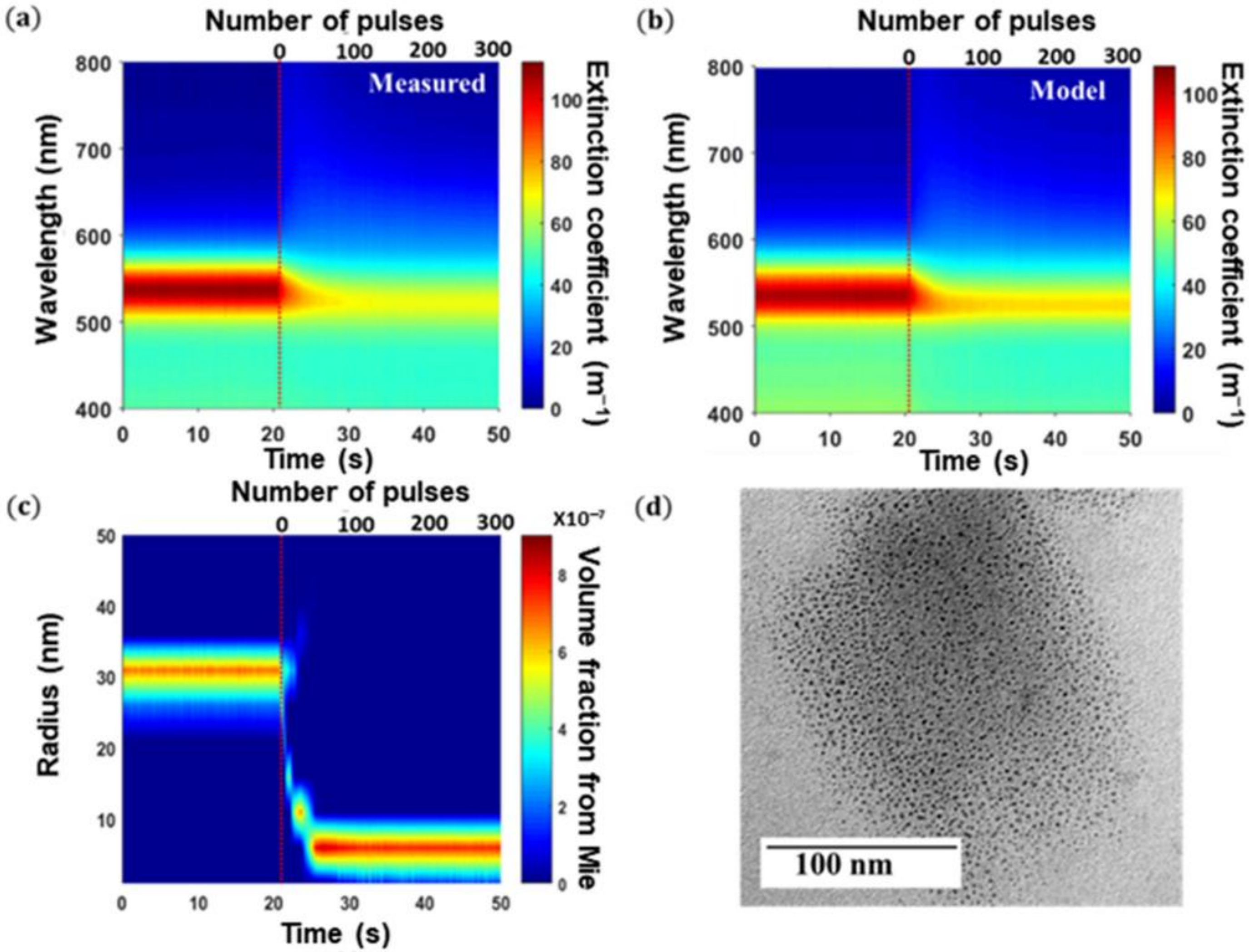
Evolution of temperature and the transformations in shape and size of the NRs during laser exposure.

(Mansour et al, 2019)



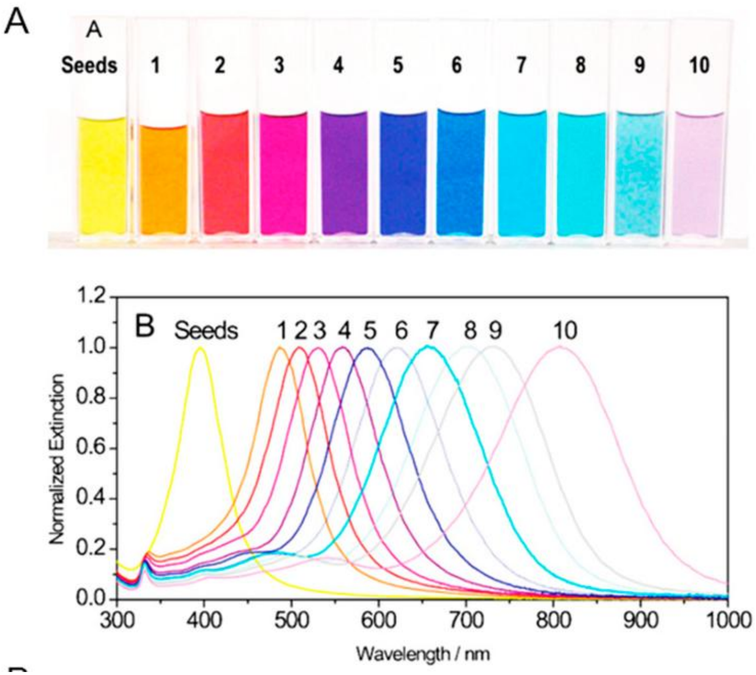
(Mansour et al, 2019)

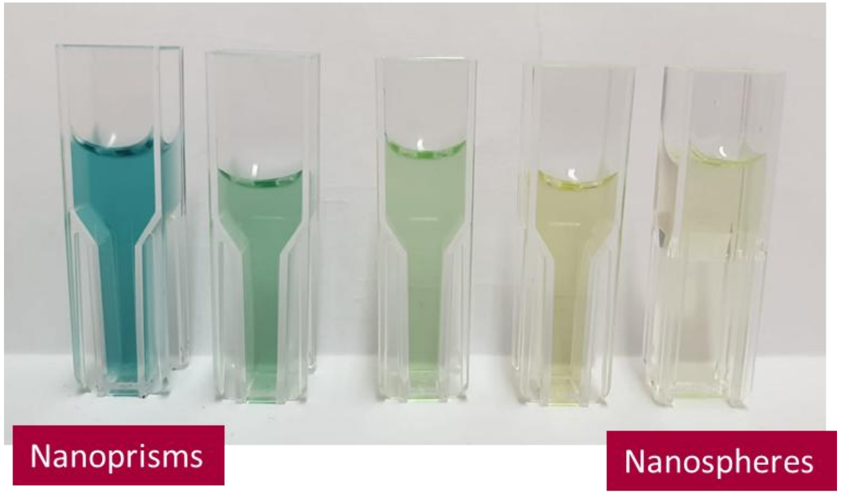
Reshaping of Au colloids



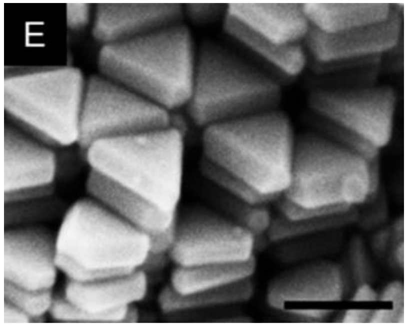
(Mansour et al, 2021)

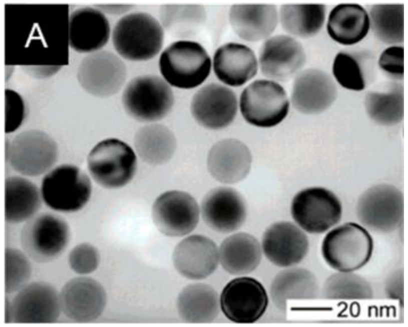
Application to reshaping of silver triangular nanoprisms





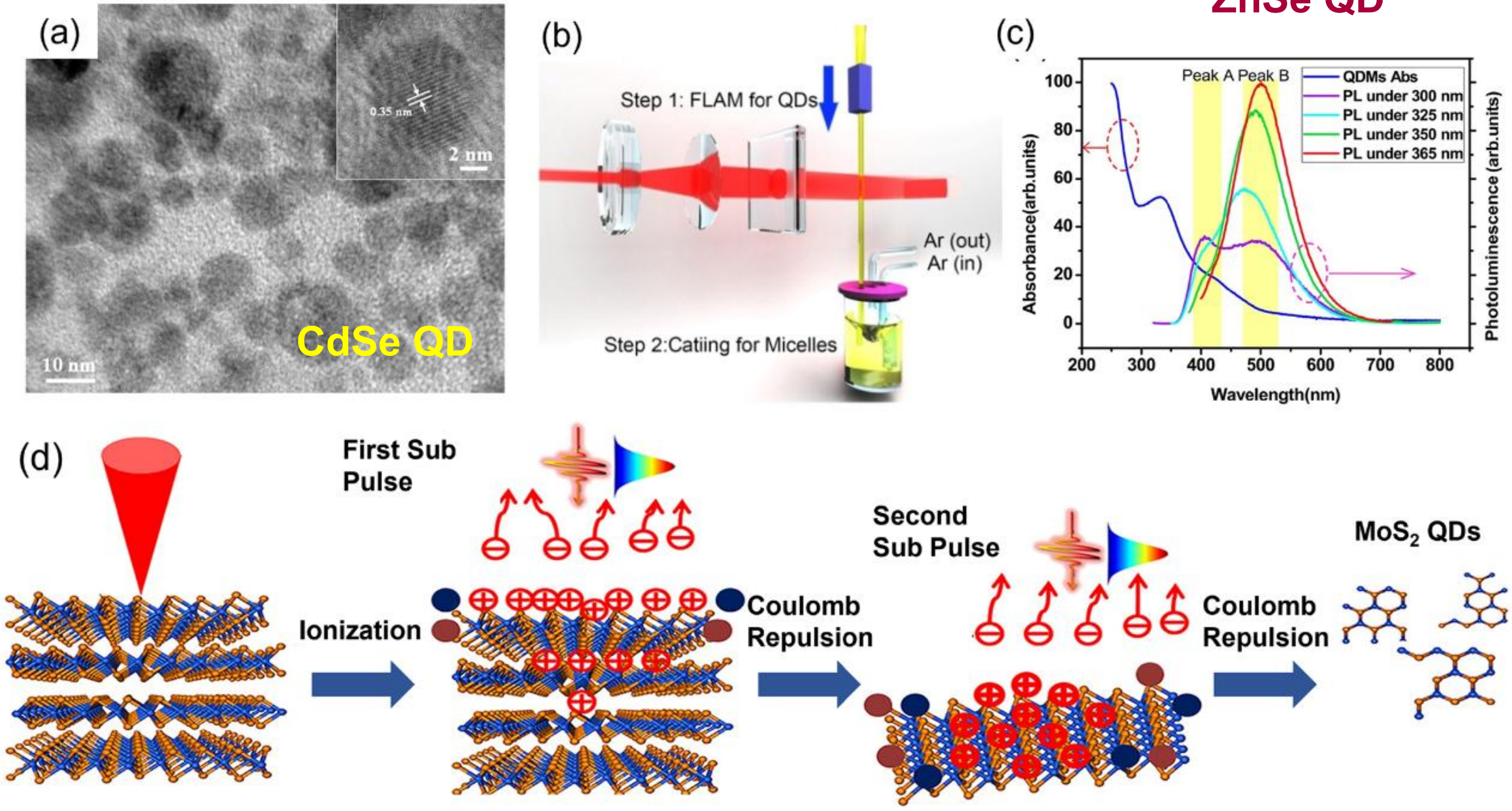
Number of pulses





Synthesis of quantum dots

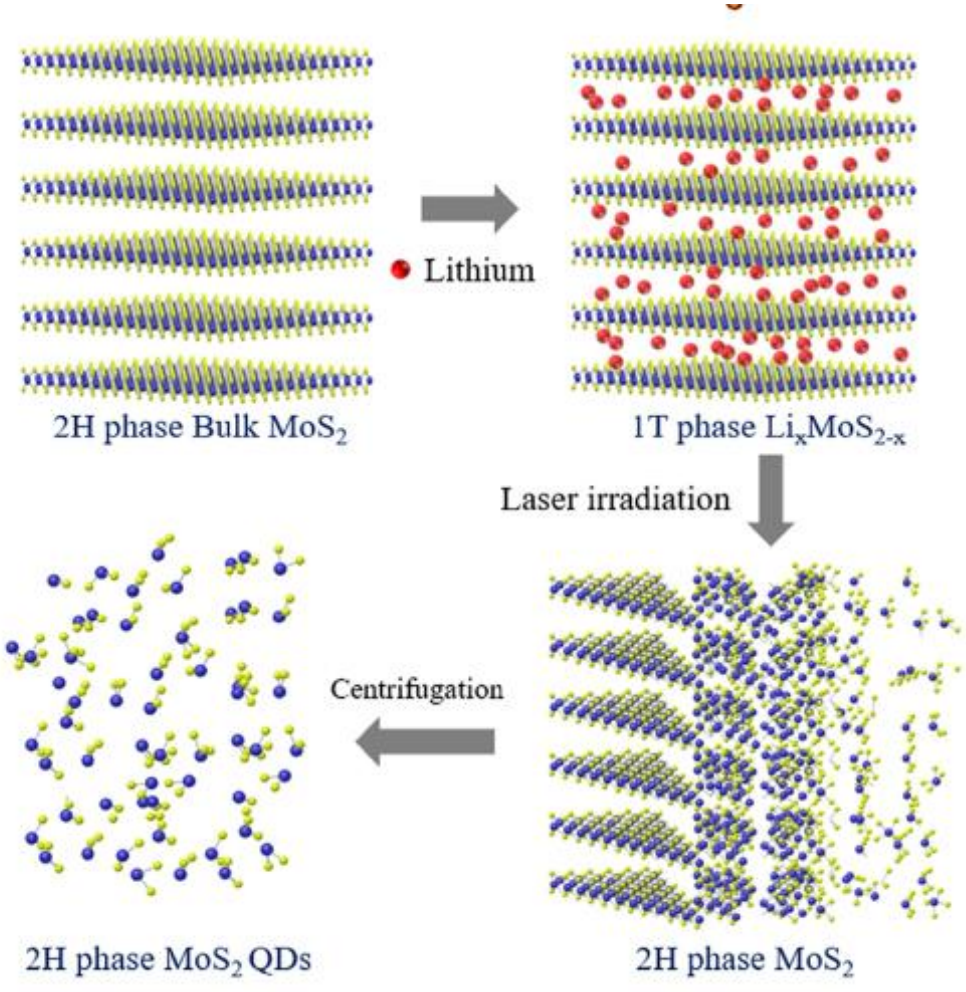
ZnSe QD



MoS2 QD

Horoz et al, 2012

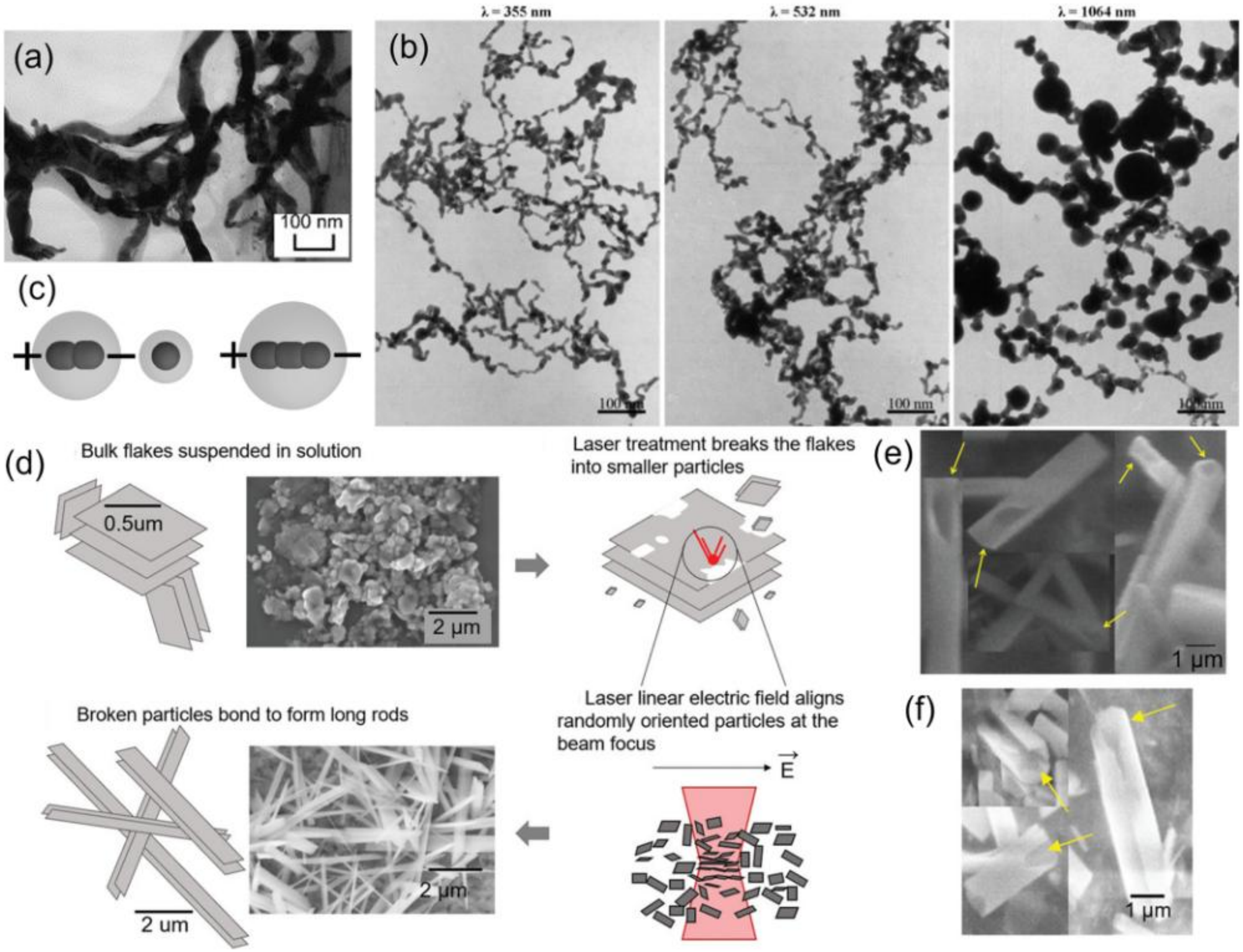
Ablation of Li-intercalated MoS2



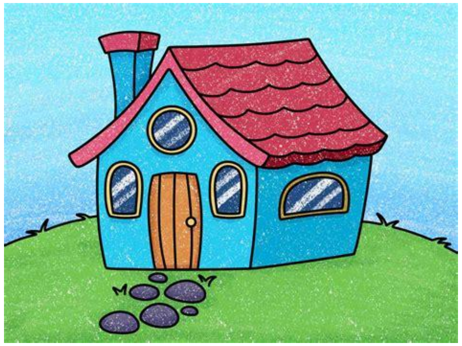
- Direct gap semiconductor
- Pseudo 2D material
- Applications in electronics and optoelectronics
- Different from graphene (2D, metallic behaviour)

Ye, 2024

Synthesis of 1D nanomaterials



Take-Home messages



- LAL is a clean production method of NPs
- Widely applied to a very large range of materials including 2D materials
- Cost effective and upscalable method
- Optical properties of NPs allow to bypass the TEM/SEM analysis
- Thermodynamics of low dimensionality systems

Globally : **an interesting playground** ☺