The 7th International Conference on Advanced Nanoparticle Generation and Excitation by Lasers in Liquids (ANGEL)
Charlottesville, Virginia, USA, May 26-30, 2024

ANGEL 2024 - TUTORIAL

Unique nanoparticle properties and functionalities accessible by laser synthesis and processing of colloids

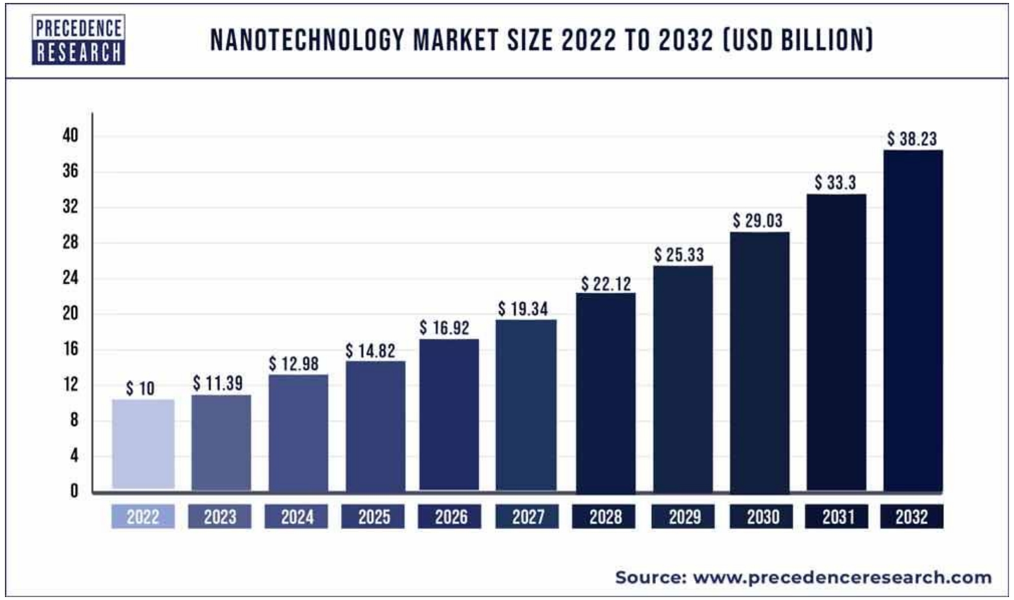
Vincenzo Amendola
University of Padova

CONTEXT

- **25 years** since the beginning of the **National Nanotechnology Initiative** and its Implementation Plan (2000)
  https://www.nano.gov/strategicplans

- **The global Nanotechnology Market** size was estimated at US$ 10 billion in 2022
  and it is expected to hit over US$ 38.23 billion by 2032
  with a registered CAGR* of 14.40% from 2023 to 2032
  https://www.precedenceresearch.com/nanotechnology-market

* The compound annual growth rate (CAGR) is the annualized average rate of revenue growth between two given years



Top Factors empowering the Nanotechnology Market's Growth

- *Medicine and Healthcare Diagnosis*
- *Environment*
- *Energy*
- *ICT*
- *Nano-EHS (Nano Environmental Health and Safety)*

Top Types of Nanotechnology on the Market

- *Nanomaterials*
- *Nanotools*
- *Nanodevices*

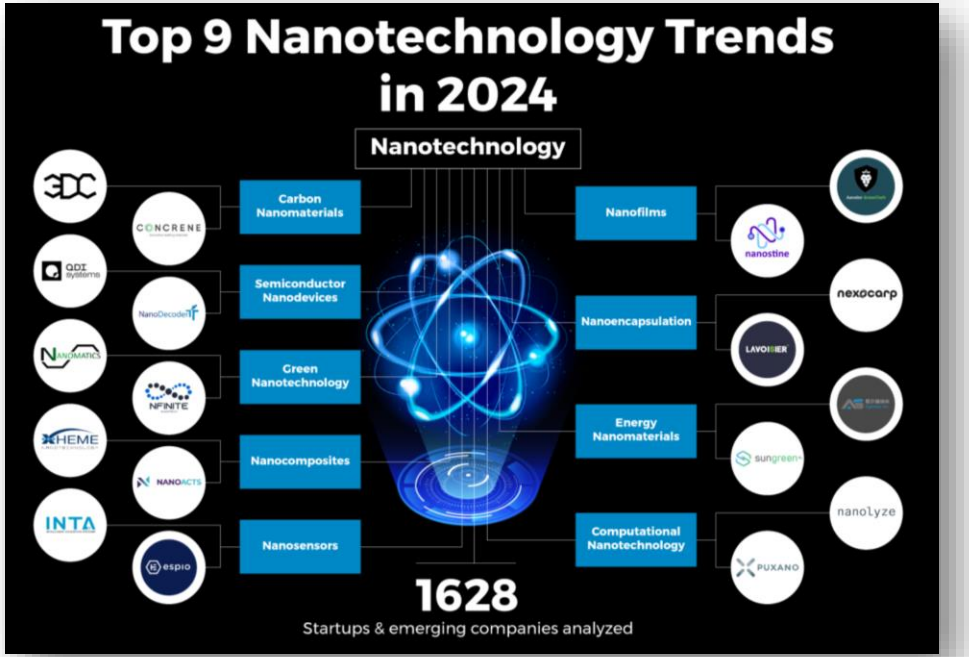
https://www.linkedin.com/pulse/nanotechnology-market-size-share-growth-h4wuc/

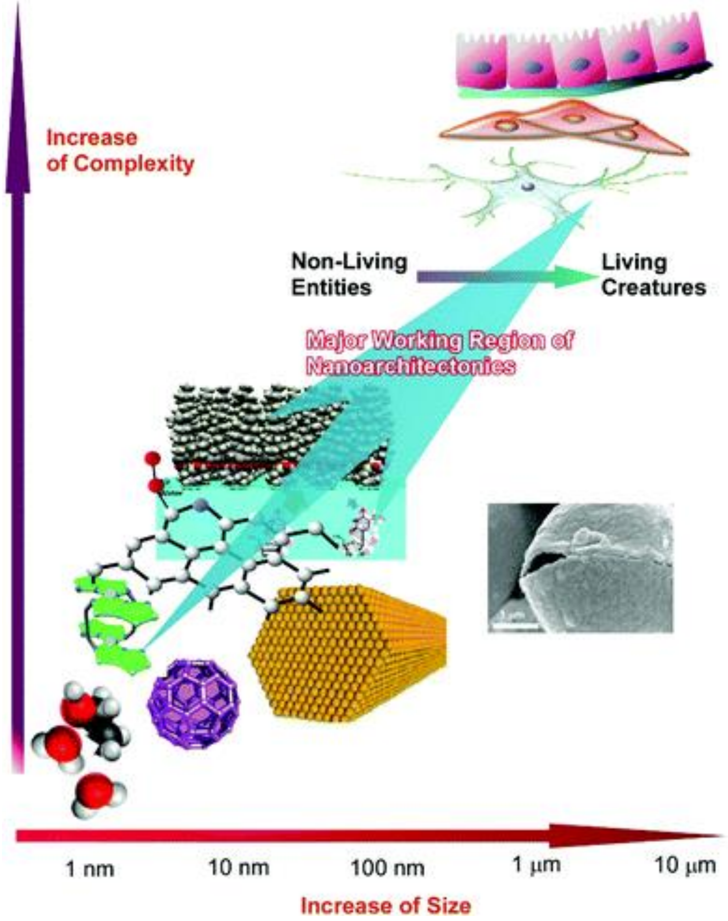
V. Amendola
University of Padova

Top 9 Trends in Nanotechnology

- Carbon Nanomaterials
- Semiconductor Nanodevices
- Green Nanotechnology
- Nanocomposites
- Nanosensors
- Nanofilms
- Nanoencapsulation
- Energy Nanomaterials
- Computational Nanotechnology

https://www.startus-insights.com/innovators-guide/nanotechnology-trends/

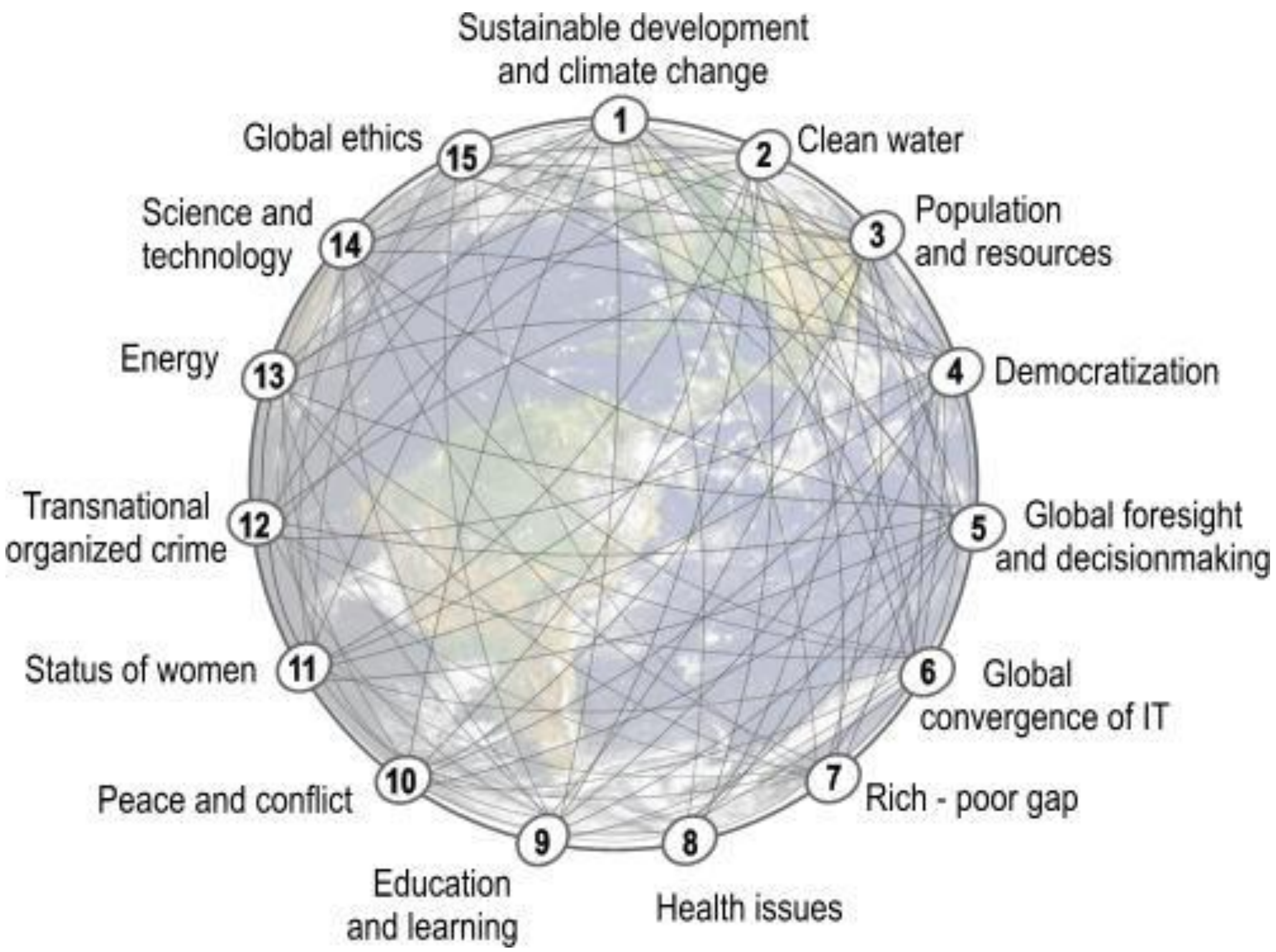


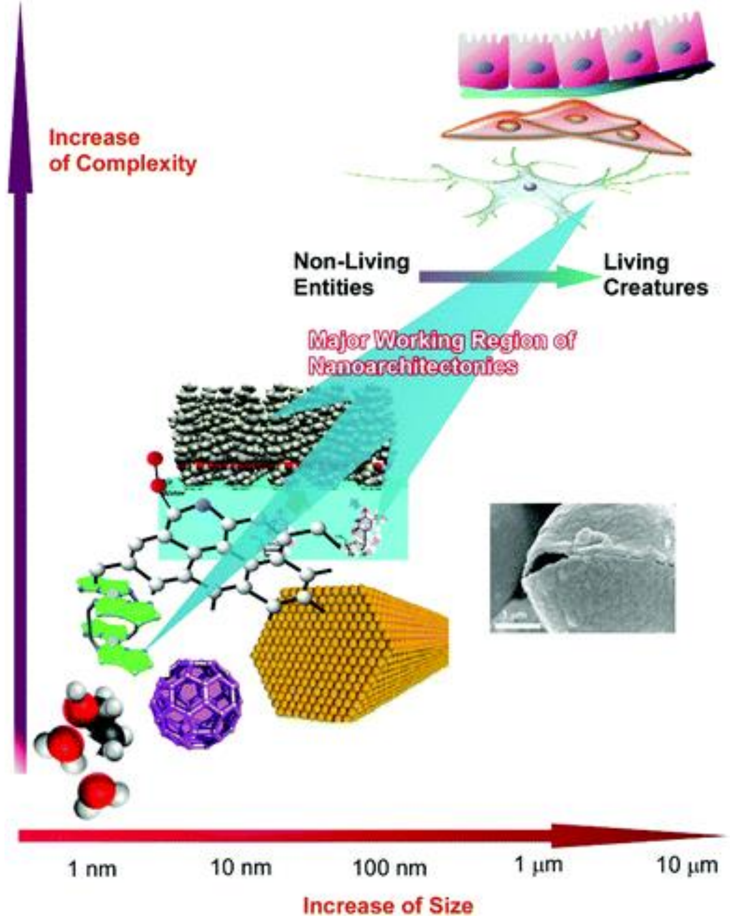


We are moving
from «Nanomaterials» to «Nanoarchitectonics»
which is the architecting of functional materials using nanoscale units based on the principles of nanotechnology
https://doi.org/10.1039/D0NH00680G

CONTEXT

https://www.millennium-project.org/15-global-challenges/

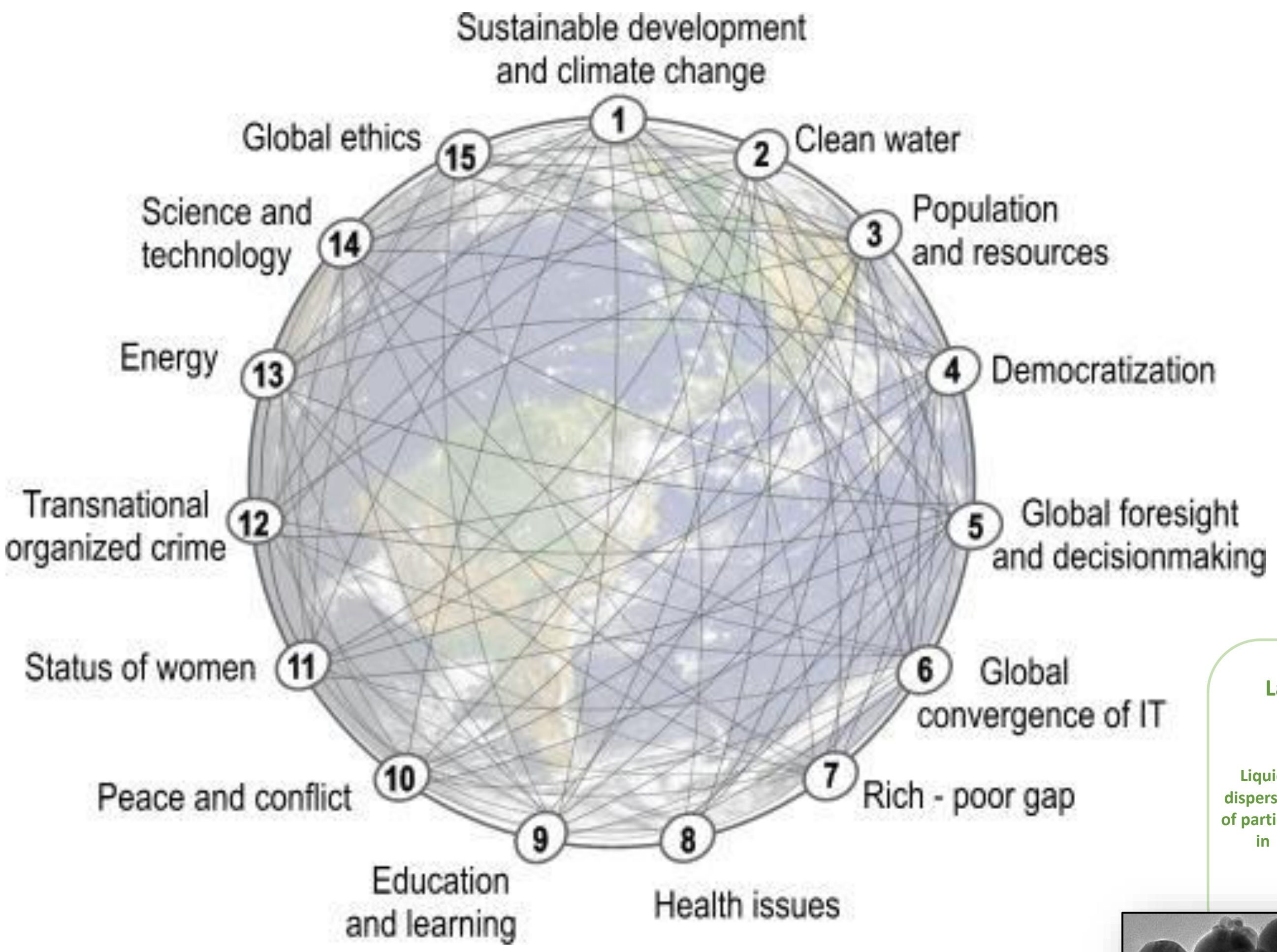


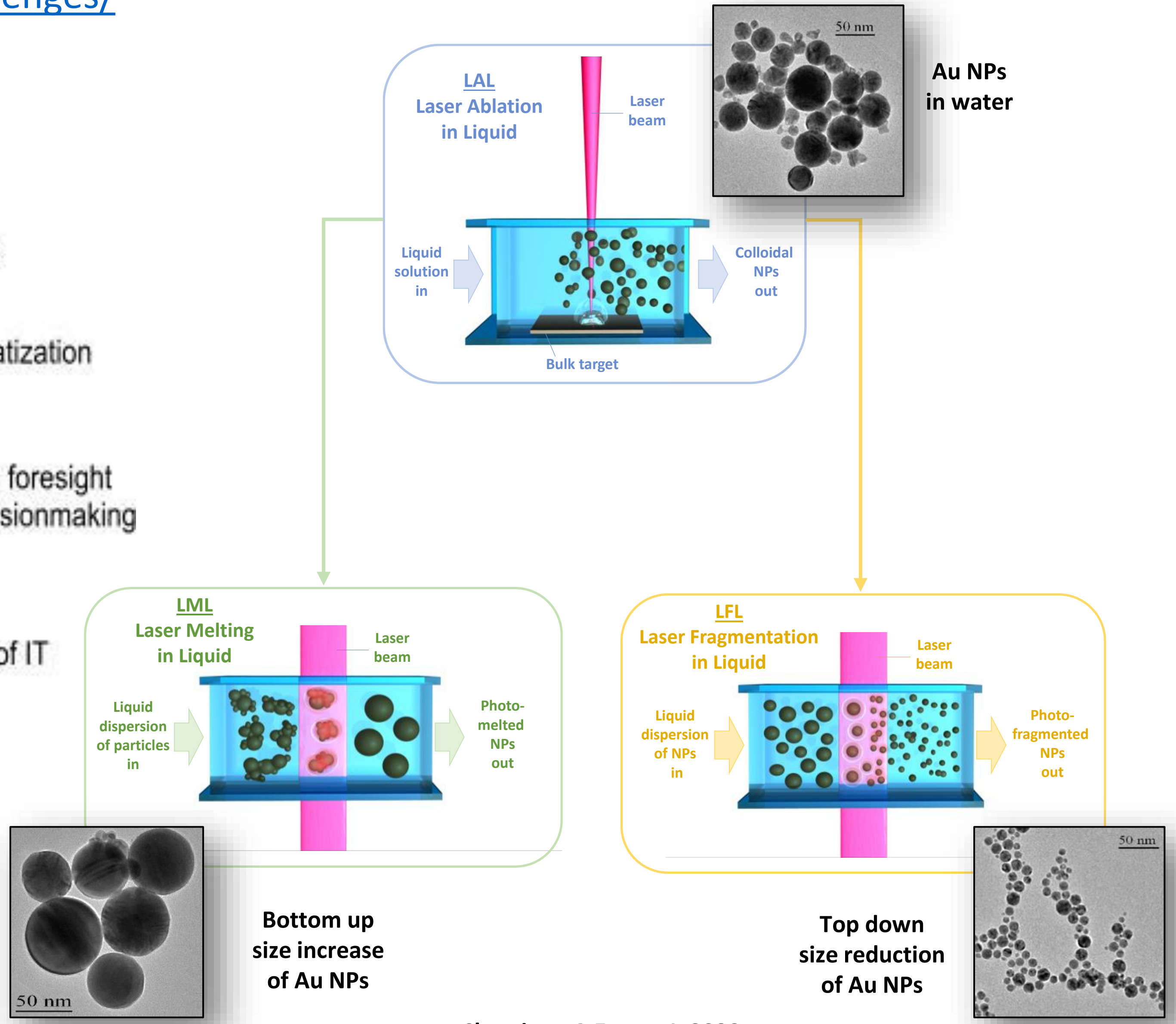


We are moving
from «Nanomaterials» to «Nanoarchitectonics»
which is the architecting of functional materials using nanoscale units based on the principles of nanotechnology
https://doi.org/10.1039/D0NH00680G

P.S.: Beware of the retard between new technologies and social consciousness about their negative effects
This retard is of decades up to centuries

https://www.millennium-project.org/15-global-challenges/





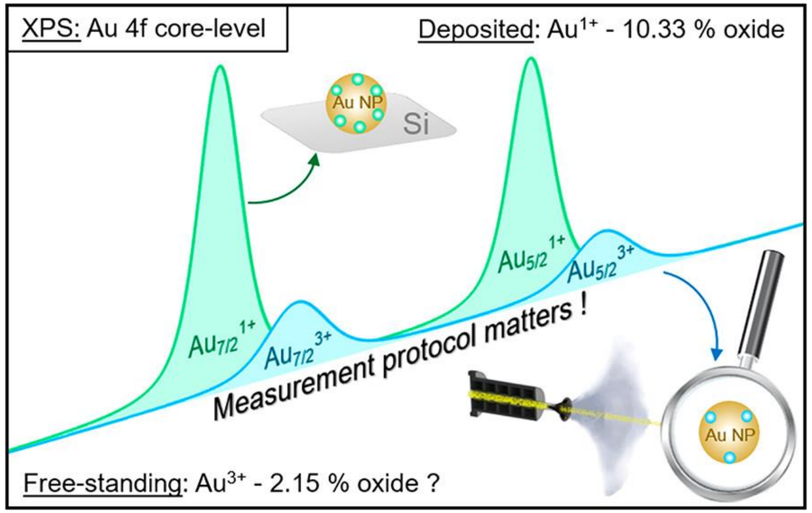
Chemistry A Europ. J. 2020

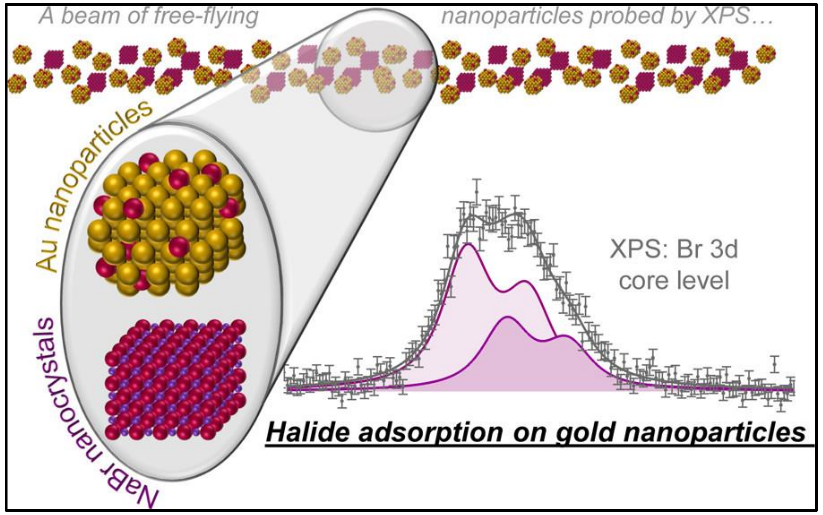
Size Manipulation of surface clean Au NPs: J. Mater. Chem. 2007

PURITY AND STERILITY

LSPC is renowned for the possibility of obtaining colloids starting just **from a bulk material and a pure solvent**

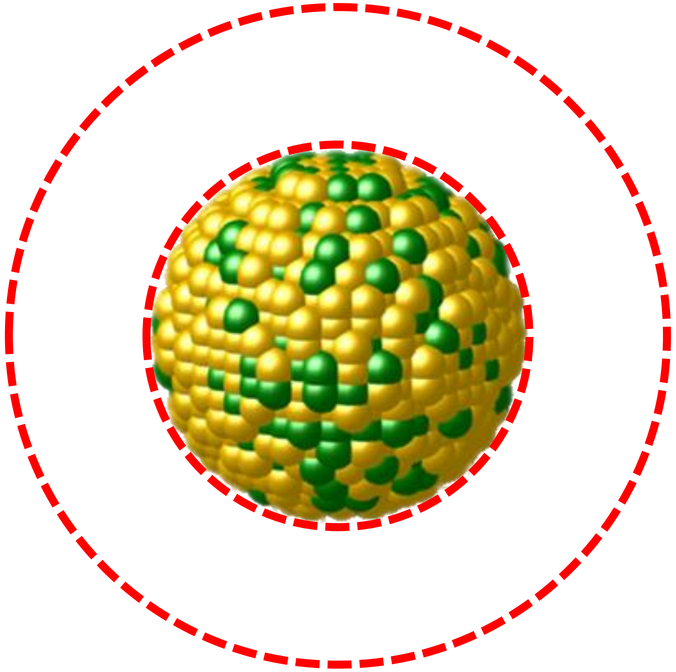
Au NPs are the most investigated example:





- **Halogen ions adsorption** on Au NPs from LAL in electrolyte solutions has been identified by several experiments, included XPS in a free jet of colloids

https://doi.org/10.1021/acs.langmuir.9b02159
https://doi.org/10.1021/acs.langmuir.1c00092

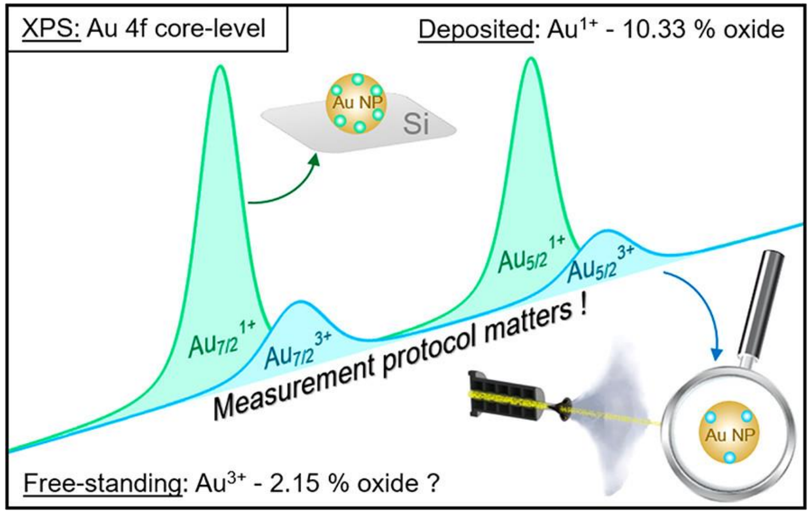


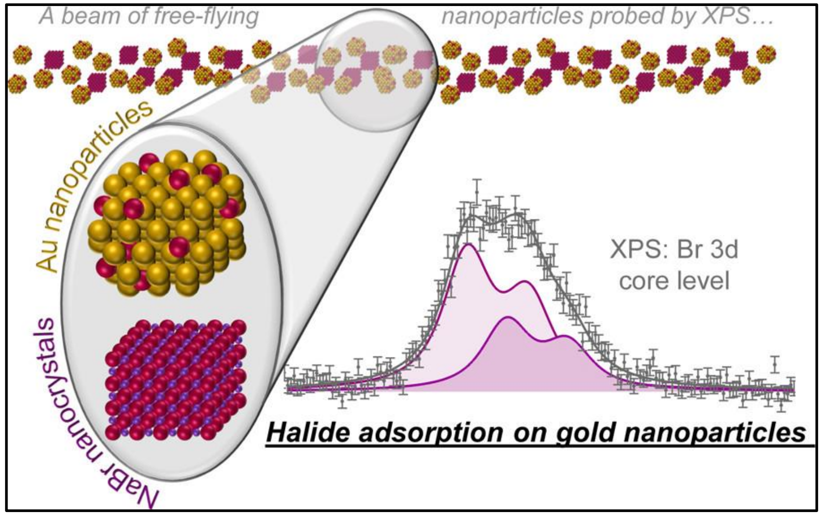
PURITY AND STERILITY

V. Amendola
University of Padova

LSPC is renowned for the possibility of obtaining colloids starting just **from a bulk material and a pure solvent**

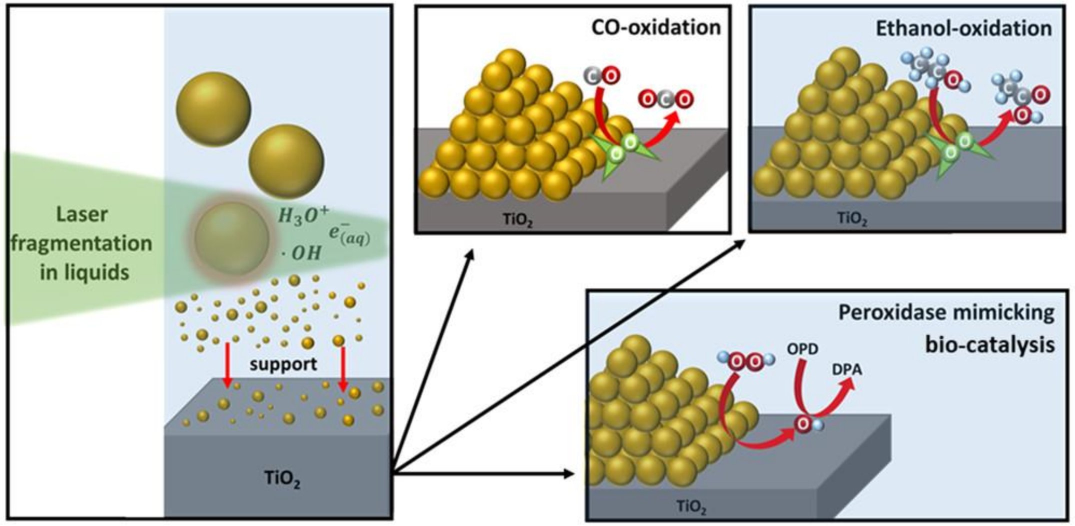
Au NPs are the most investigated example:





- **Halogen ions adsorption** on Au NPs from LAL in electrolyte solutions has been identified by several experiments, included XPS in a free jet of colloids

https://doi.org/10.1021/acs.langmuir.9b02159
https://doi.org/10.1021/acs.langmuir.1c00092



- The formation of **radical oxygen species** was observed also **during LFL of Au NPs in aqueous solution**, which initiates oxidative processes
- Lower surface charge density resulted beneficial for the catalytic activity in CO and ethanol oxidation, while their peroxidase-like activity was affected less

https://doi.org/10.1021/acs.jpcc.0c06257

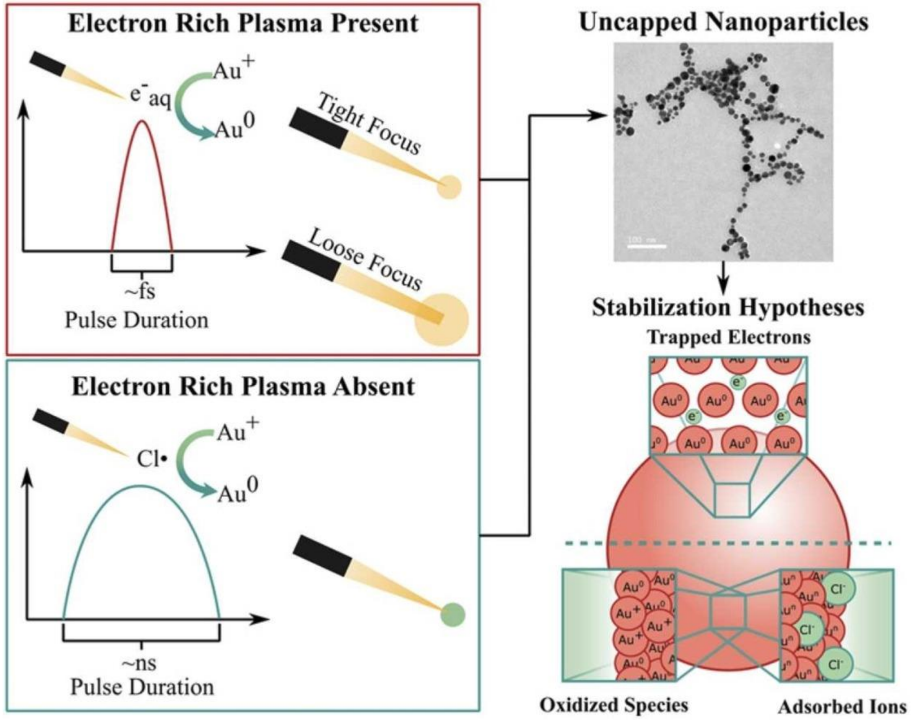
V. Amendola
University of Padova

PURITY AND STERILITY

LSPC is renowned for the possibility of obtaining colloids starting just **from a bulk material and a pure solvent**

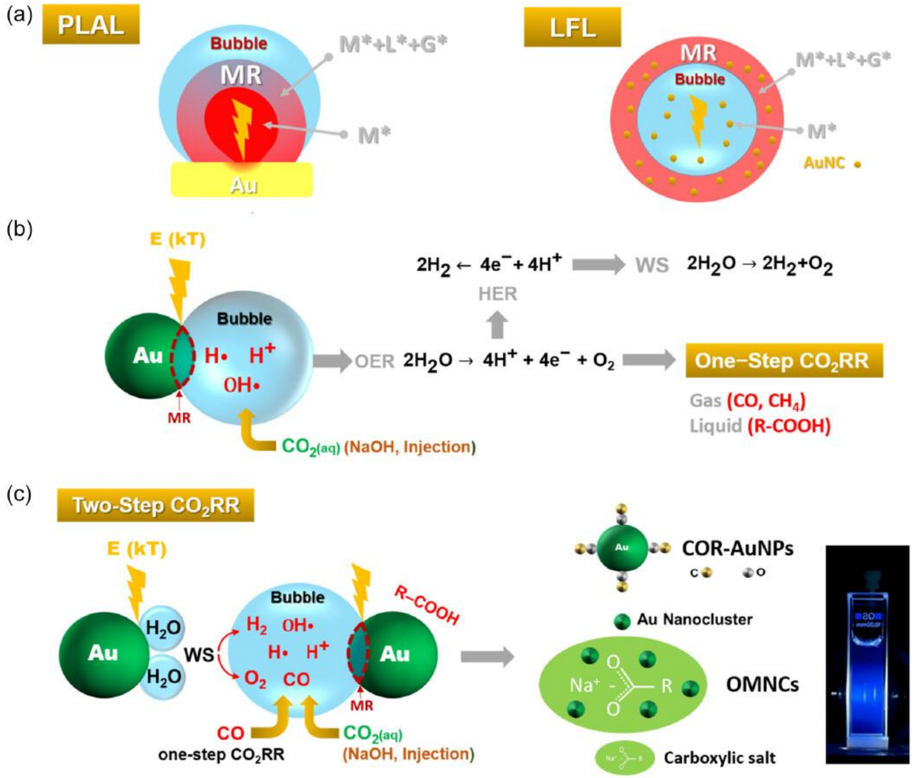
- **Electrostatic repulsion** is crucial for the stability of uncapped Au NPs and of any NPs in general
- Laser Reduction in Liquid (LRL) also produces stable uncapped NPs
- **oxidized species at the particle surface**, **adsorbed anions at the particle surface**, or **trapped electrons within the particle** are thought to contribute to it

https://doi.org/10.1016/j.colsurfa.2022.129860



- **CO_2 fixation** into Au NPs by laser synthesis and processing is observed
- **carbon monoxide-rich Au NPs** are observed after synthesis in deionized water
- carboxylic acids-rich Au NPs are observed in alkaline water

https://doi.org/10.1002/smsc.202300328



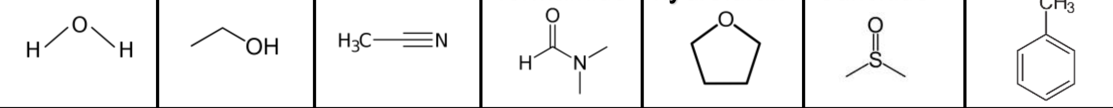
PURITY AND STERILITY

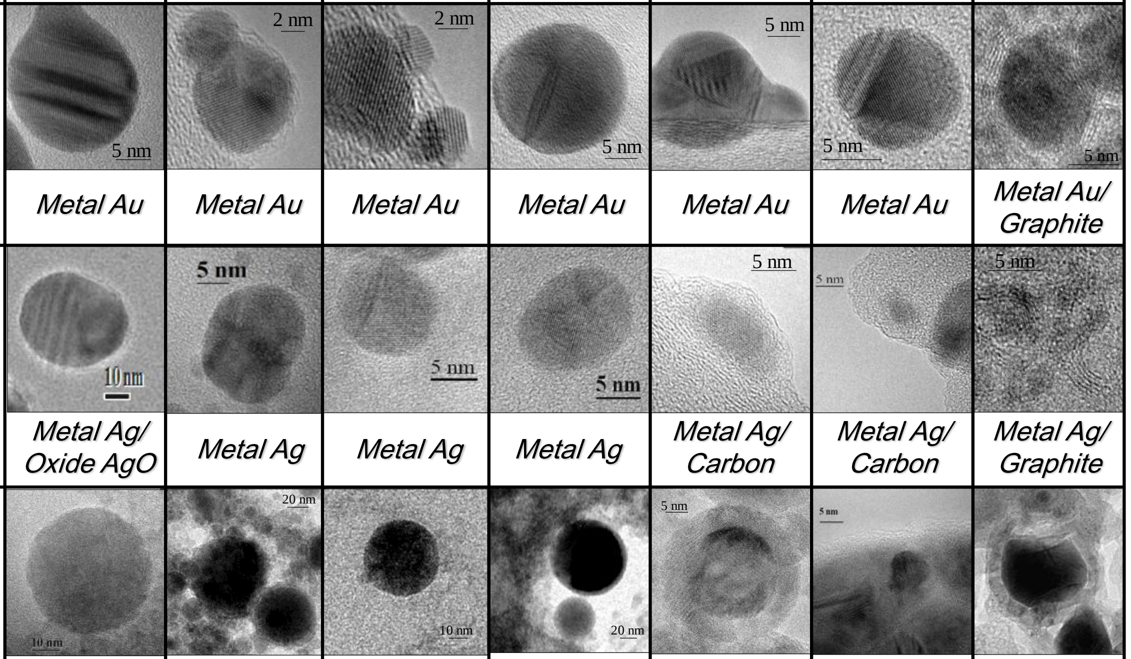
V. Amendola
University of Padova
DiSC

LSPC is renowned for the possibility of obtaining colloids starting just **from a bulk material and a pure solvent**

- **Solvent pyrolysis** is a well known effect
- A **matrix** around the NPs may form in several cases

https://doi.org/10.1016/j.colsurfa.2022.129860

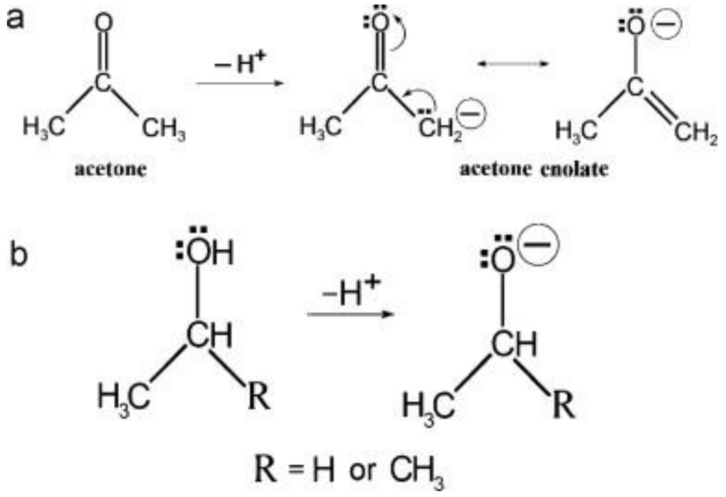




	Water	Ethanol	Acetonitrile	Dimethyl-formamide	Tetra-hydrofuran	Dimethyl-sulfoxide	Toluene
Au	*Metal Au*	*Metal Au*	*Metal Au*	*Metal Au*	*Metal Au*	*Metal Au*	*Metal Au/ Graphite*
Ag	*Metal Ag/ Oxide AgO*	*Metal Ag*	*Metal Ag*	*Metal Ag*	*Metal Ag/ Carbon*	*Metal Ag/ Carbon*	*Metal Ag/ Graphite*
Fe	*Fe_3O_4, Fe_2O_3, $Fe(OOH)_2$*	*Fe_3O_4, FeC_3*	*Fe_3O_4, Carbon*	*Fe_3O_4, Carbon*	*Metal Fe/ Fe_3O_4*	*Metal Fe/ Carbon*	*Fe-Carbide/ Graphite*

- **Solvent pyrolysis** byproducts such as enolates and alcholates are adsorbed on NPs and are involved in NPs **stability and final composition**
- For instance, ethanol molecules act as a reducing agent during LSPC, being converted in acetaldehyde, acetic acid or carbon oxide (CO), hydrogen (H_2), or methane (CH_4)

https://doi.org/10.1016/j.apsusc.2011.11.084
https://doi.org/10.1002/cphc.201601185



$$Pt + FeO_x/CoO_x/NiO_x + CH_3CH_2OH \rightarrow Pt - Fe/Co/Ni + C_xH_yO_z$$

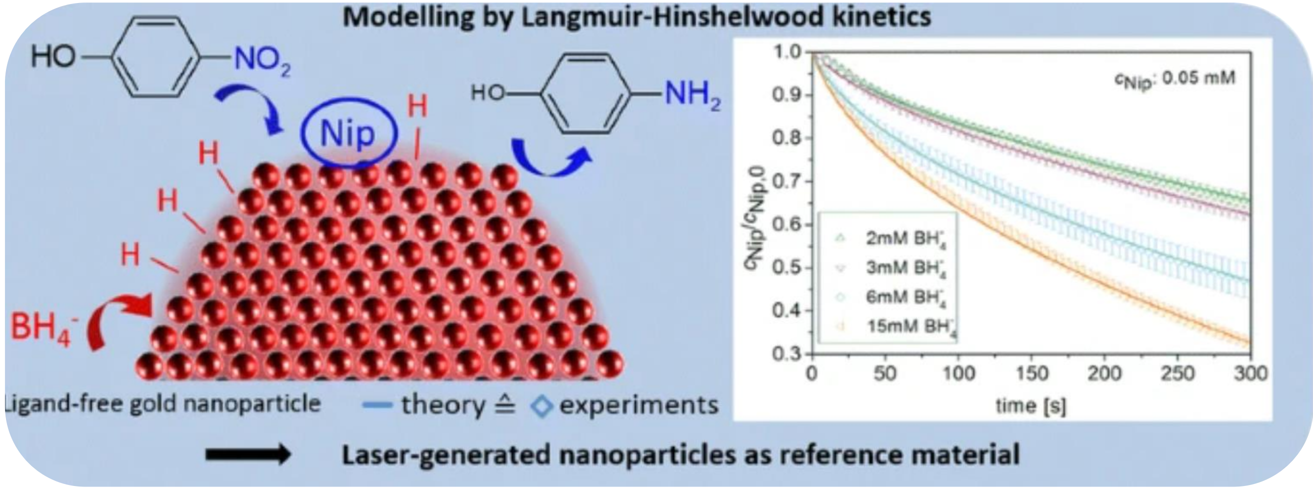
V. Amendola
University of Padova
DiSC

Nonetheless multiple examples on the advantages of uncapped NPs from LSPC exist:

Catalysis

- Au NPs from LAL were used as **reference material** for the reduction of 4-nitrophenol by sodium borohydride accordin to the **Langmuir–Hinshelwood model**
- Excellent agreement between theory and experiment is found
- Instead, ligand-coverage of metal nanoparticles impedes the merging of theory and experiment

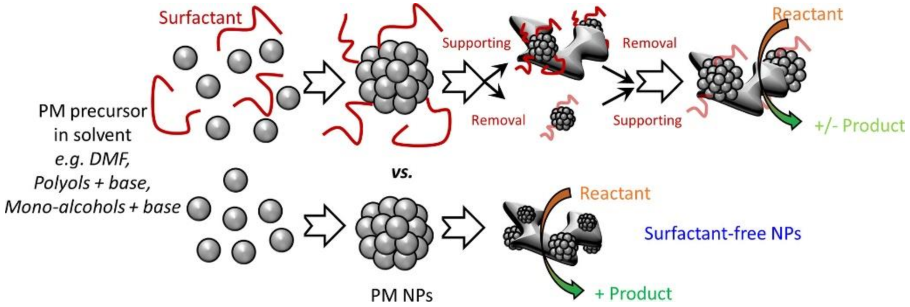
https://doi.org/10.1007/s10562-015-1514-7

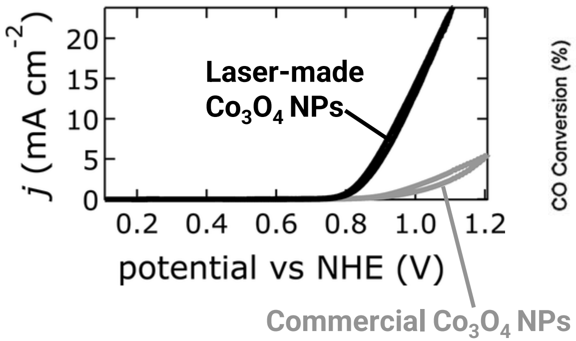


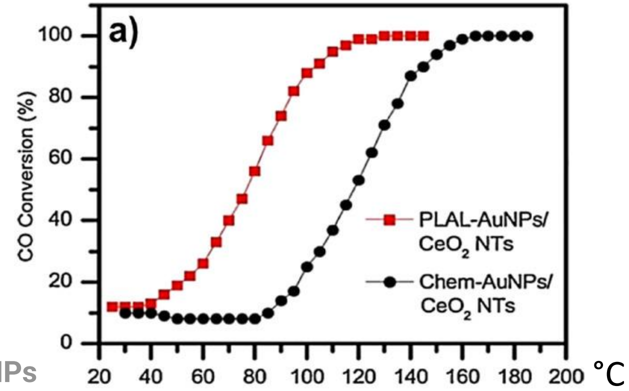
- **Many reviews** highlighted the advantages of surfactant free NPs from LSPC for catalysis

Some of them are

https://doi.org/10.1021/acs.chemrev.0c01069
https://doi.org/10.1002/cctc.201900666
https://doi.org/10.1021/acscatal.2c05998







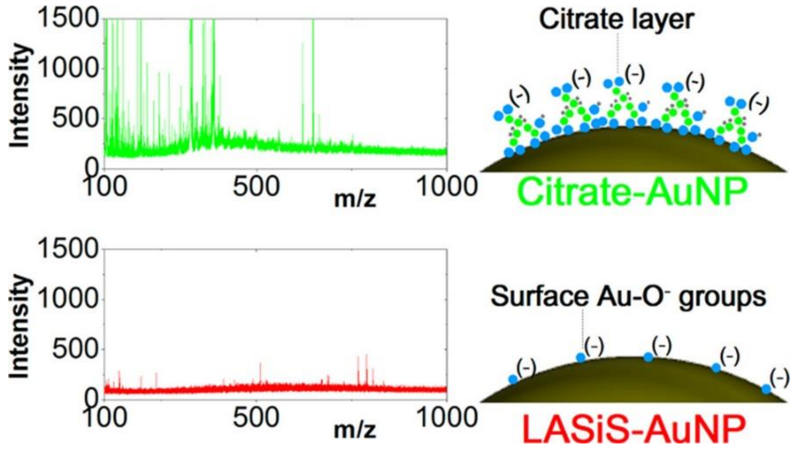
V. Amendola
University of Padova

Nonetheless multiple examples on the advantages of uncapped NPs from LSPC exist:

Surface clean apps

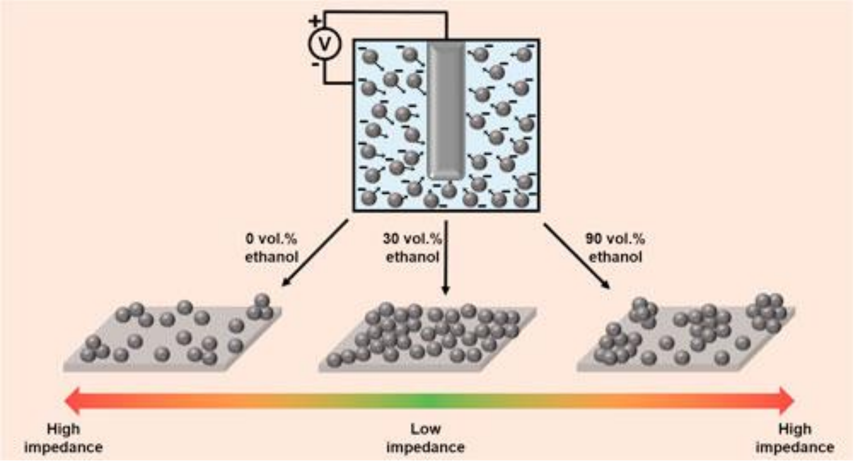
- **Laser Desorption Ionization mass spectrometry (LDI-MS)** Assisted by Chemical-Free Gold NPs from LAL allows Enhanced Sensitivity and Reduced Background in the Low-Mass Region, contrary to chemically synthesized NPs

https://doi.org/10.1021/ac401662r



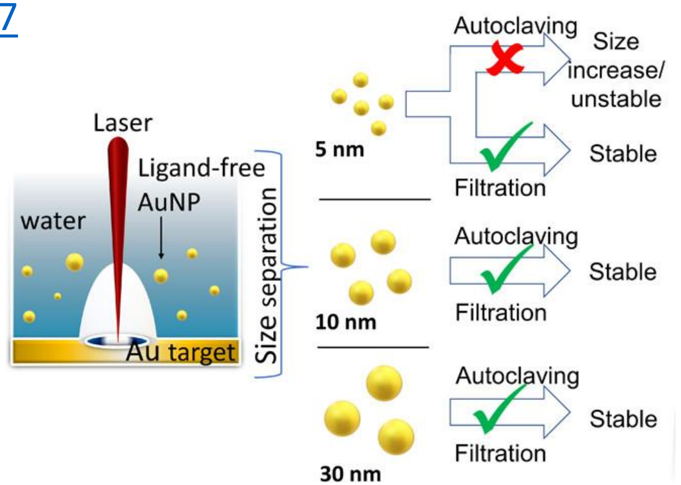
- Electrophoretic Deposition of laser generated Pt NPs for Reduced **Neural Electrode** Impedance, preventing unwanted contamination of the surfaces and allowing for well-controlled deposition since deposition rates scale linearly with time

https://doi.org/10.1149/1945-7111/ac51f8



- **Sterilization** is a major prerequisite for the utilization of nanoparticle colloids in biomedicine
- Following autoclaving, NPs growth attributed to cluster ripening occurs in ~5 nm AuNPs, while ~10 and ~30 nm NPs remain stable
- Sterile filtration has no impact on the colloidal stability of AuNPs, regardless of particle size, despite a mass loss of 5–10%

https://doi.org/10.1021/acs.langmuir.2c01557



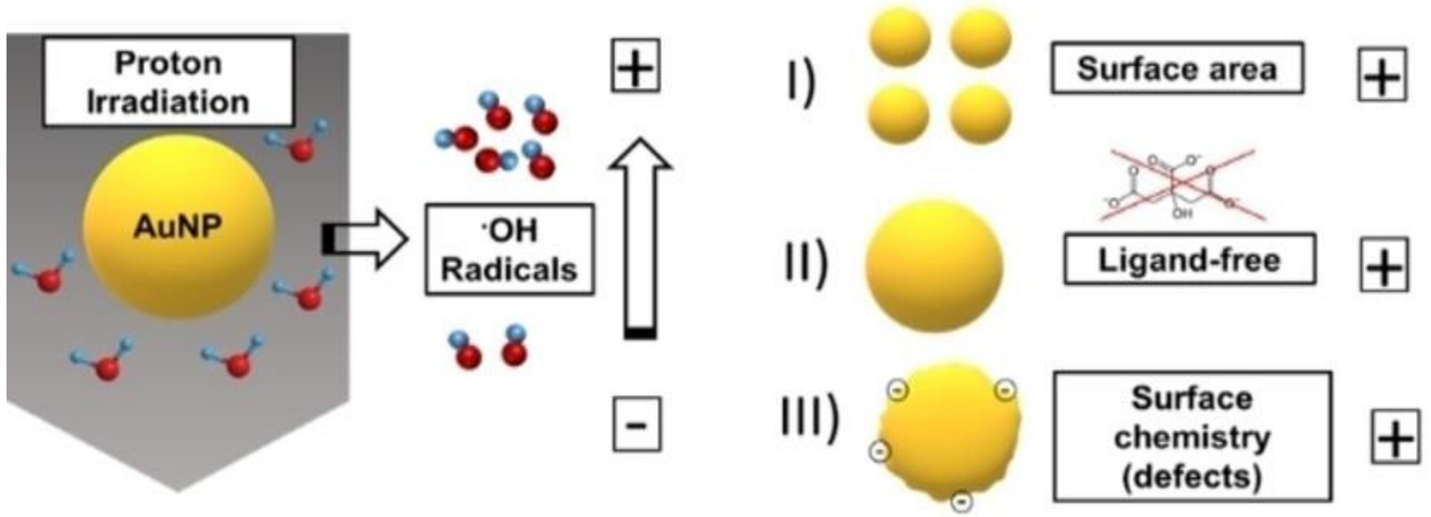
Nonetheless multiple examples on the advantages of uncapped NPs from LSPC exist:

Surface clean apps

- Gold nanoparticles (AuNPs) are currently the most studied radiosensitizers **in proton therapy** (PT) applicable for the treatment of solid tumors, where they amplify production of reactive oxygen species (ROS)
- Enhancement of ROS production driven by

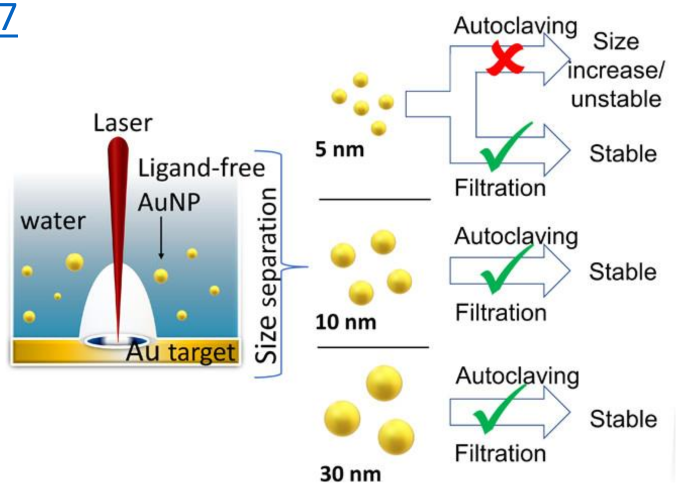
1. total particle surface area
2. utilization of ligand-free AuNPs avoiding sodium citrate as a radical quencher ligands
3. higher density of structural defects generated by LFL synthesis, indicated by surface charge density

https://doi.org/10.1002/chem.202301260



- **Sterilization** is a major prerequisite for the utilization of nanoparticle colloids in biomedicine
- Following autoclaving, NPs growth attributed to cluster ripening occurs in ~5 nm AuNPs, while ~10 and ~30 nm NPs remain stable
- Sterile filtration has no impact on the colloidal stability of AuNPs, regardless of particle size, despite a mass loss of 5–10%

https://doi.org/10.1021/acs.langmuir.2c01557

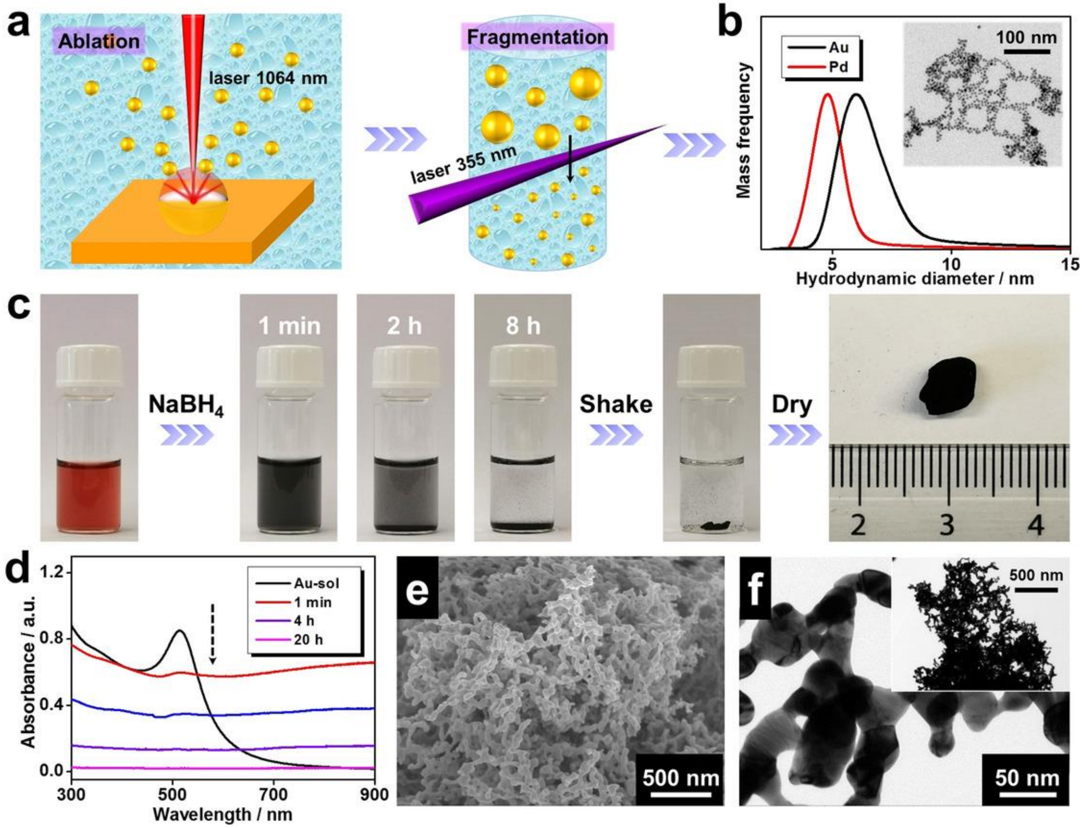


Nonetheless multiple examples on the advantages of uncapped NPs from LSPC exist:

Aerogels

- **Noble metal aerogels** (NMAs) are porous materials displaying unprecedented performance in diverse electrocatalytic processes
- Impurities, particularly organic ligands, are often involved in the synthesis and remain in the corresponding products, hindering the investigation of the intrinsic electrocatalytic properties of NMAs
- Starting from laser-generated **inorganic-salt-stabilized metal nanoparticles**, various impurity-free NMAs (Au, Pd, and Au-Pd aerogels) were fabricated

https://doi.org/10.1002/ange.201913079

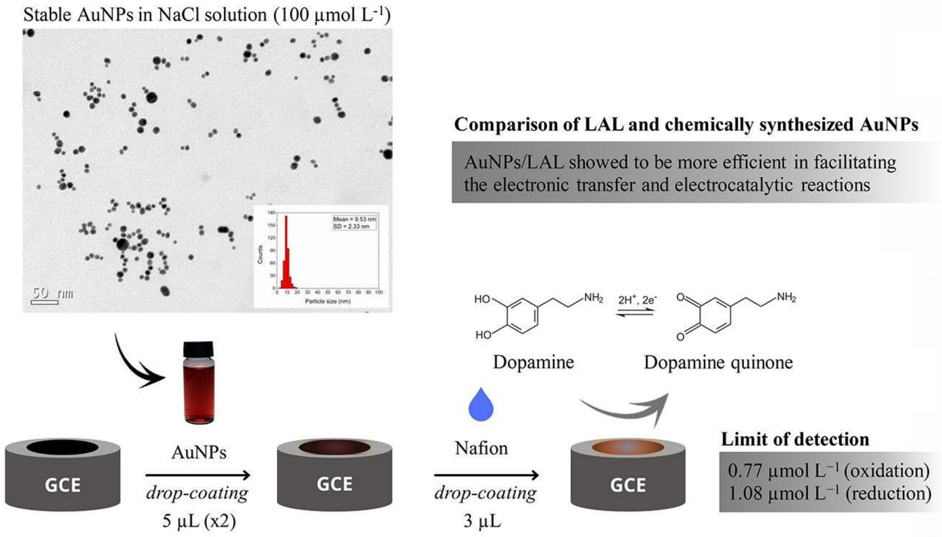


Nonetheless multiple examples on the advantages of uncapped NPs from LSPC exist:

Surface clean apps

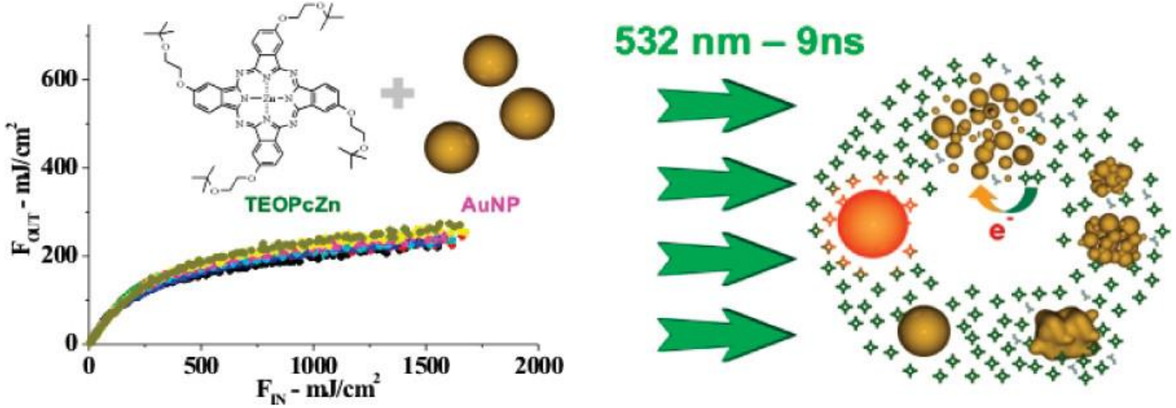
- Stable and ligand-free gold nanoparticles were produced by laser ablation
- NaCl helps to obtain smaller and more stable and monodisperse AuNPs by LAL
- AuNPs produced by LAL are more efficient for **electrochemical sensing** of Dopamine than chemically synthesized NPs
- Laser ablation is promising to produce AuNPs ideal for electrochemical applications

https://doi.org/10.1016/j.jelechem.2023.117744



- A solution of surface clean AuNPs shows very good **nonlinear absorption properties** in the nanosecond time regime at 532 nm, also at high fluences
- The enhanced nonlinear response is due to **the self-healing of Au NPs** in the presence of organic chromophores, which do not undergo the fast photoinduced fragmentation usually observed during irradiation with intense laser pulses
- This happens through a charge transfer process between the organic chromophores and the free surface of AuNPs in solution during laser irradiation

https://doi.org/10.1021/jp810921w

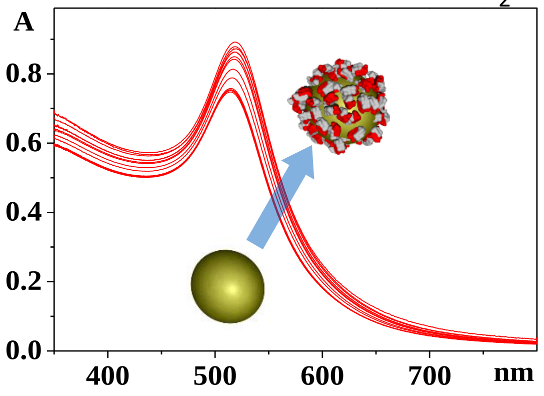


V. Amendola
University of Padova

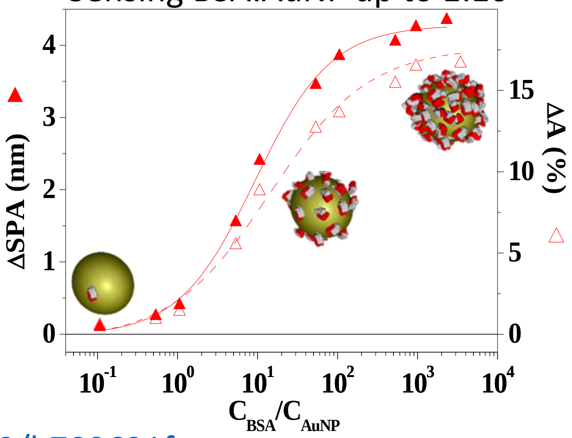
Nonetheless multiple examples on the advantages of uncapped NPs from LSPC exist:

Surface functionalization and multifunctionality

Addition of BSA to AuNP in H_2O

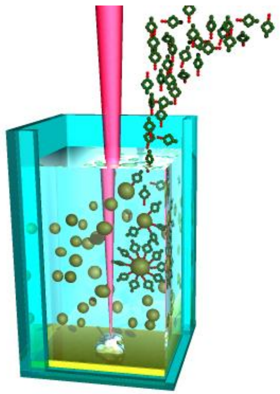


Sensing BSA:AuNP up to 1:10

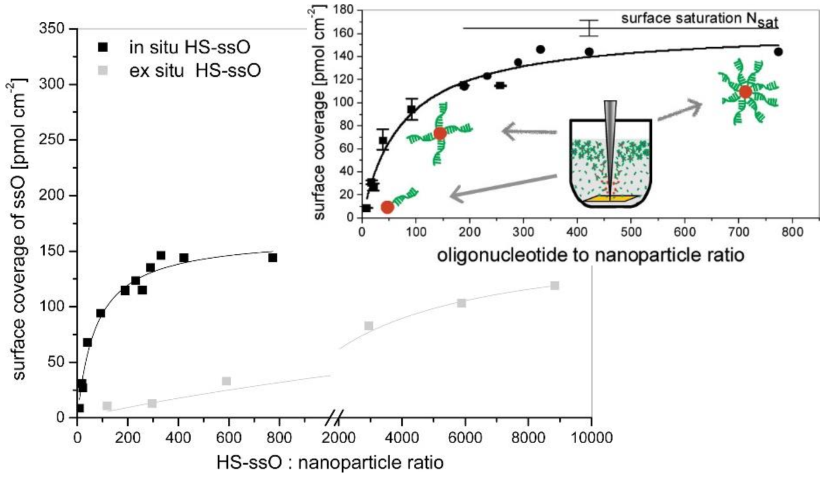


https://doi.org/10.1039/b709621f

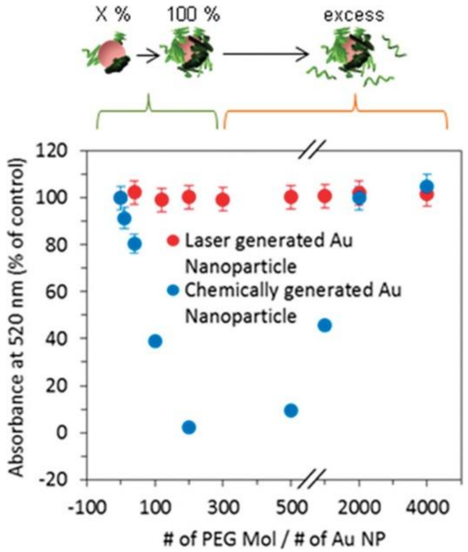
- **Real time monitoring of surface coverage** possible with Au NPs
- **Surface coverage tunable** to be any percent value between 0 and 100%
- **In situ conjugation** possible with **higher efficiency** but size quenching
- **Ex situ conjugation** possible to achieve **same NPs with different coatings**
- **Higher stability** reported in several cases **compared to citrate stabilized Au NPs**



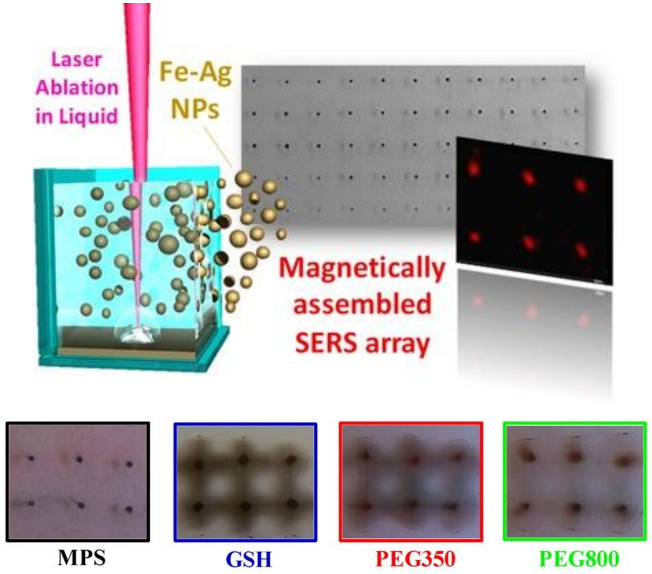
https://doi.org/10.1039/b900654k



https://doi.org/10.1021/jp905962f



https://doi.org/10.1021/jp2079567



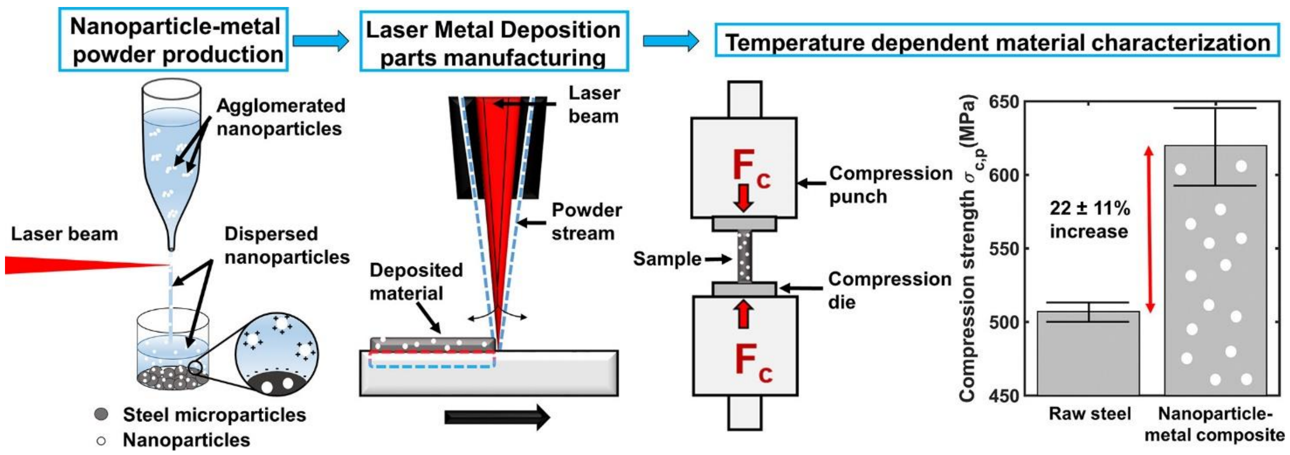
https://doi.org/10.1002/cphc.201600651

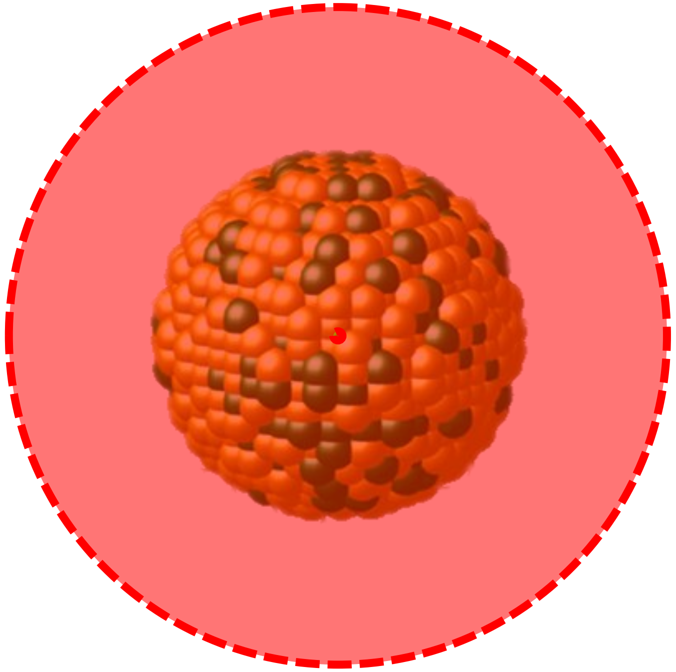
Laser generated colloids have inherent advatanges for their inclusion in a multitude of matrixes and mixtures

Additive Manufacturing and inks

- NPs-metal **composite powders for laser additive manufacturing** of oxide-dispersion strengthened alloys are formed with laser-generated Y_2O_3 and yttrium iron garnet (YIG) NPs
- The mechanical properties are attributed to the dispersed and deagglomerated nature of the laser-generated NPs that were used during the powder-preparation step

https://doi.org/10.1016/j.jelechem.2023.117744





Laser generated colloids have inherent advatanges for their inclusion in a multitude of matrixes and mixtures

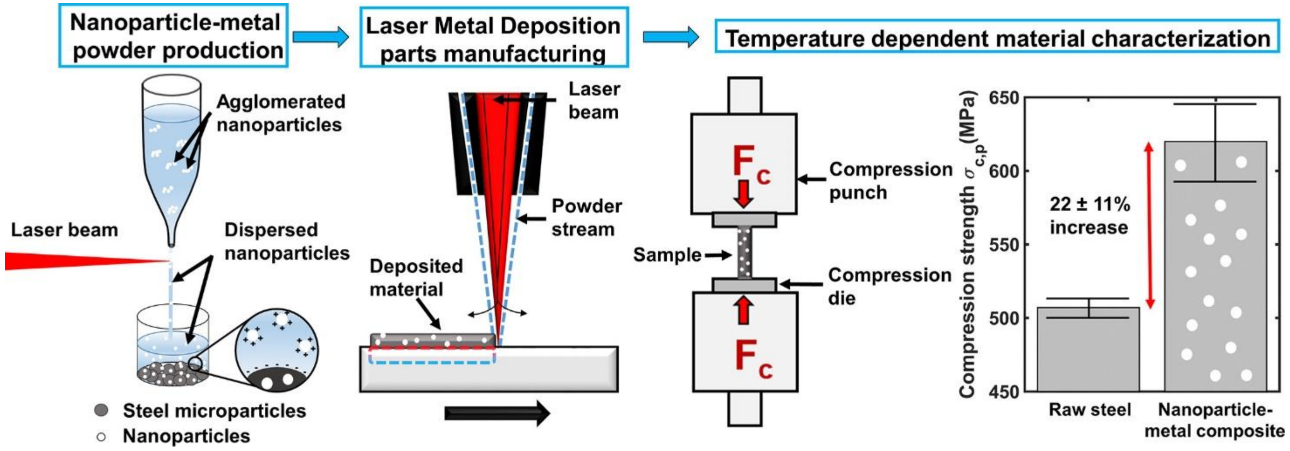
Additive Manufacturing and inks

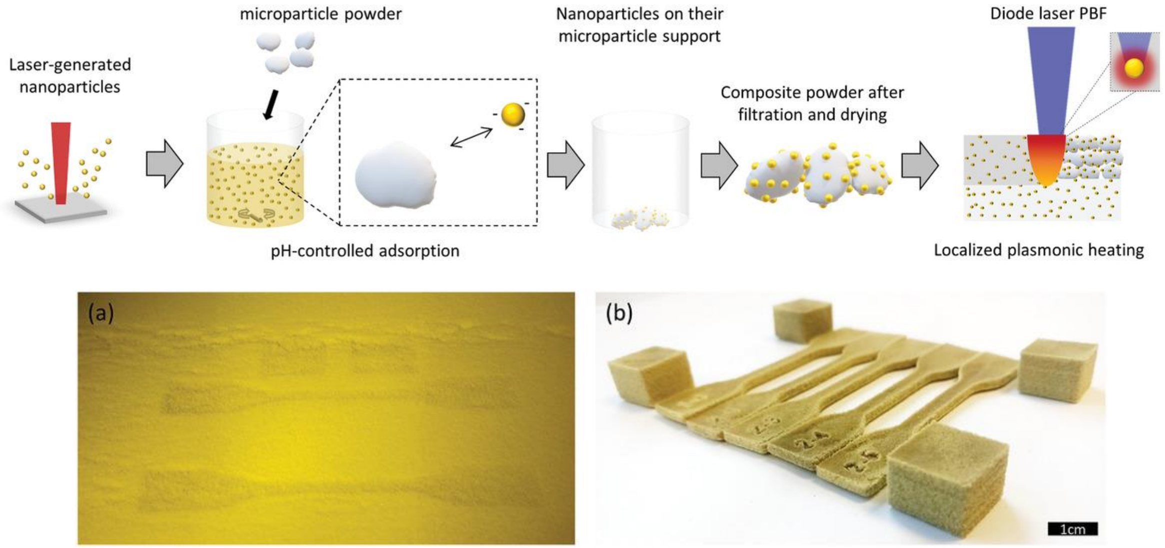
- NPs-metal **composite powders for laser additive manufacturing** of oxide-dispersion strengthened alloys are formed with laser-generated Y_2O_3 and yttrium iron garnet (YIG) NPs
- The mechanical properties are attributed to the dispersed and deagglomerated nature of the laser-generated NPs that were used during the powder-preparation step

https://doi.org/10.1016/j.jelechem.2023.117744

- **3D printing of polymers by laser powder bed fusion (PBF-LB)** with desktop 3D printers still is limited to a few polymer powder materials
- Tuning the absorption properties of thermoplastic polyurethane polymers and incorporating color into printed objects by using minute amounts (i.e., 0.01 vol%) of highly dispersed laser generated plasmonic silver nanoparticles was demonstrated

https://doi.org/10.1002/adom.202000473



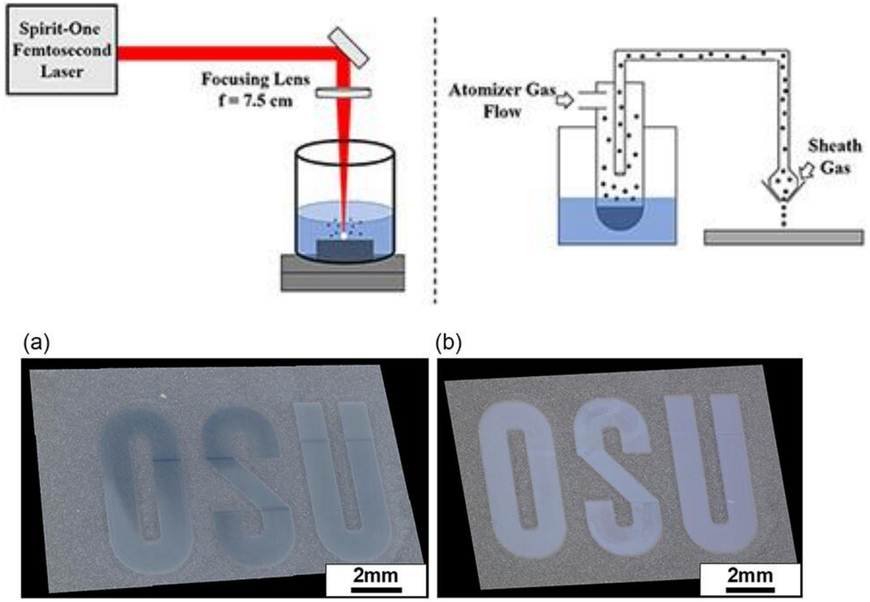


Laser generated colloids have inherent advatanges for their inclusion in a multitude of matrixes and mixtures

Additive Manufacturing and inks

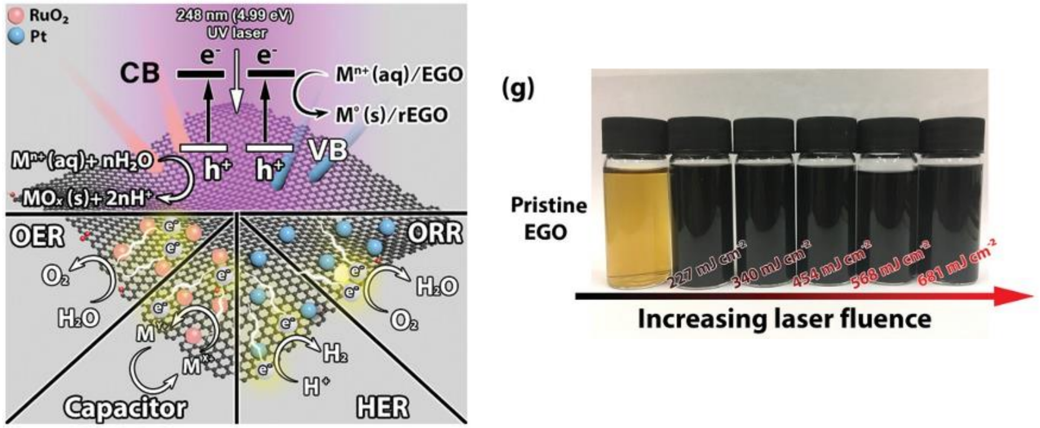
- Flexible and printed electronics have become increasingly popular as they make possible the production of flexible, low-cost, multifunction devices that are unachievable through traditional manufacturing methods
- High-quality **titanium dioxide (TiO_2) nanoparticle ink** compatible with aerosol jet printing using laser ablation synthesis in solution (LASiS)are produced without the need for any post processing

https://doi.org/10.1002/adem.202400721



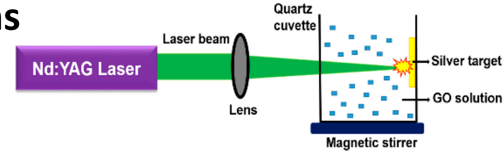
- UV laser assisted method based on photoinduced redox processes for **continuous solution reduction and modification of electrochemical graphene oxide (EGO) with functional nanoparticles**
- Various types of ultrafine metal and metal oxide nanoparticles (Au, Pt, PtPd, RuO_2, MnO_x) have been uniformly deposited on the rEGO support simply by using different metal salts precursor solutions

https://doi.org/10.1002/adfm.202001756
https://doi.org/10.1039/D0CP02953J



- **LAL of metals directly in GO solutions** is also effective (for ex. Ag NPs/GO)

https://doi.org/10.3390/nano11040880



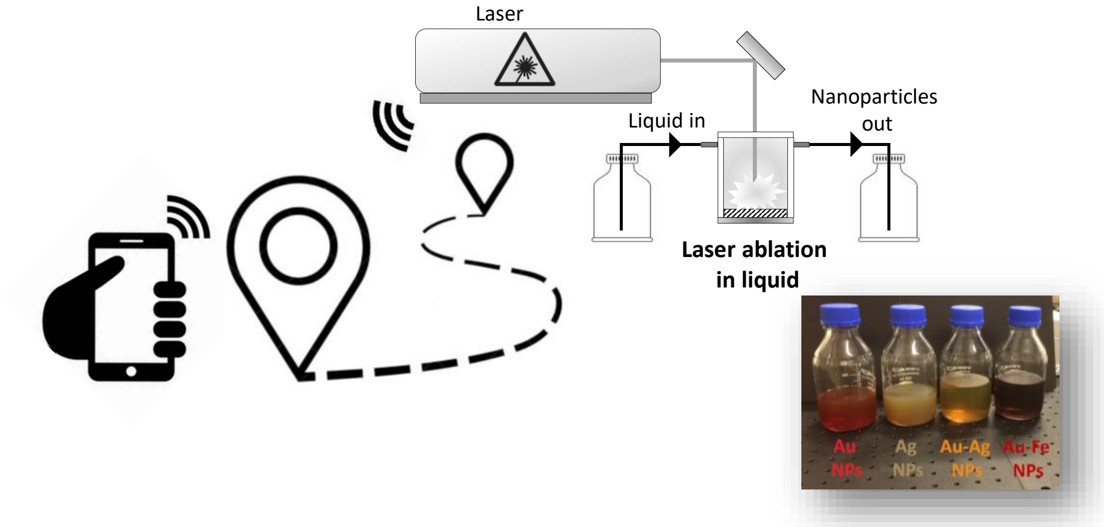
AUTHOMATIC AND SCALABLE SYNTHESIS

V. Amendola
University of Padova
DiSC

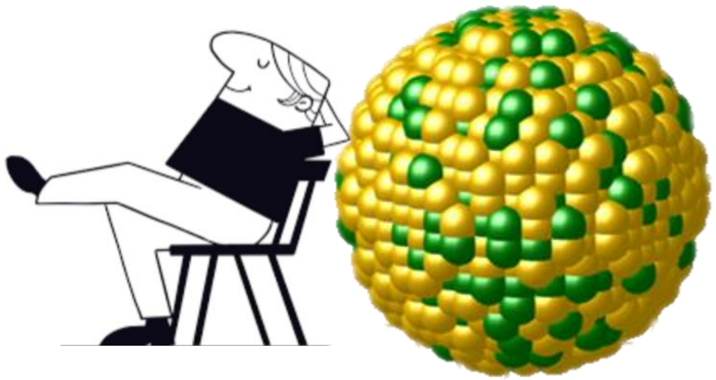
LSPC is amenable to remote, automatic and scalable processes with limited and easy operation

- the use of high energy and high power laser beams is harmful, especially when coupled with flammable or toxic liquids or other compunds
- a system for the production of nanoparticles by laser ablation synthesis in liquid solution (LASiS), which is **remotely controllable with a personal computer or a smartphone** is easily implementable in any LAL lab with commercial components
- Laser energy and solution flux are selectable, and the synthesis status can be monitored and managed at any time off site

https://doi.org/10.1063/1.5083811



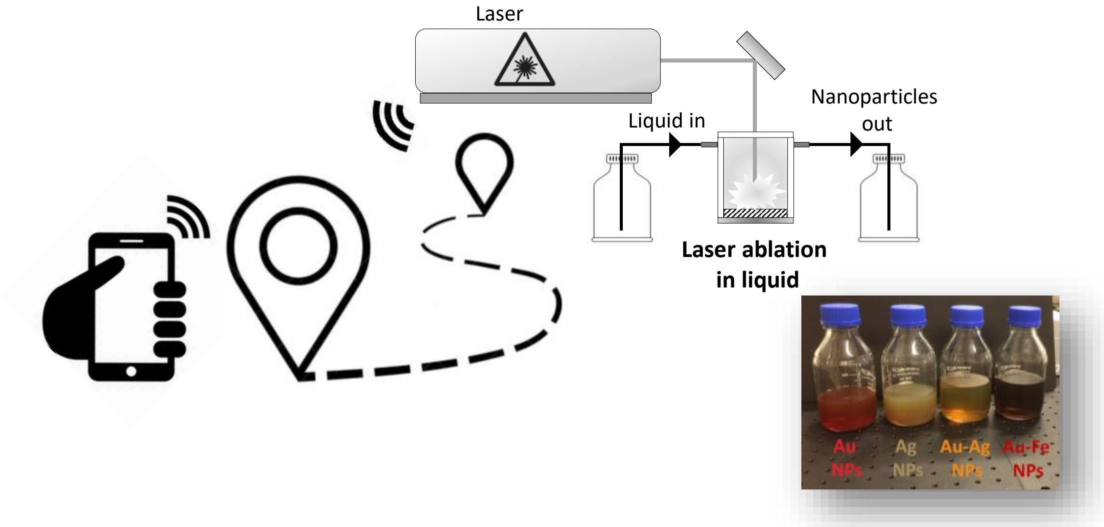
14:45: *Practical course and demonstration of automated laser synthesis* (Waag)



LSPC is amenable to remote, automatic and scalable processes with limited and easy operation

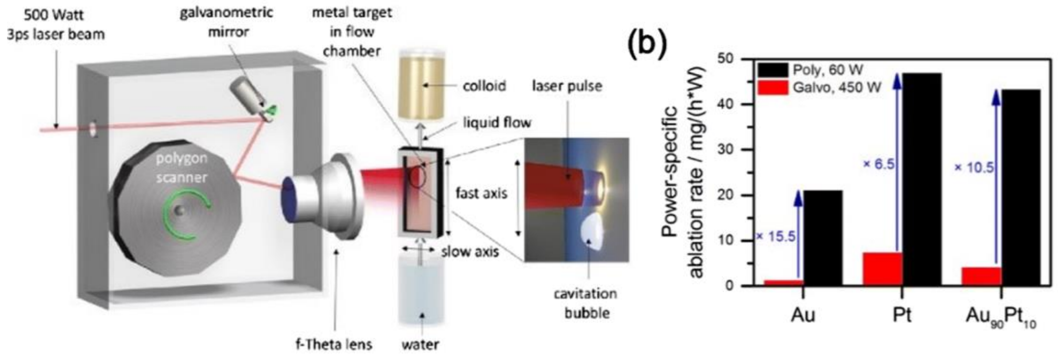
- the use of high energy and high-power laser beams is harmful, especially when coupled with flammable or toxic liquids or other compounds
- a system for the production of nanoparticles by laser ablation synthesis in liquid solution (LASiS), which is **remotely controllable with a personal computer or a smartphone** is easily implementable in any LAL lab with commercial components
- Laser energy and solution flux are selectable, and the synthesis status can be monitored and managed at any time off site

https://doi.org/10.1063/1.5083811



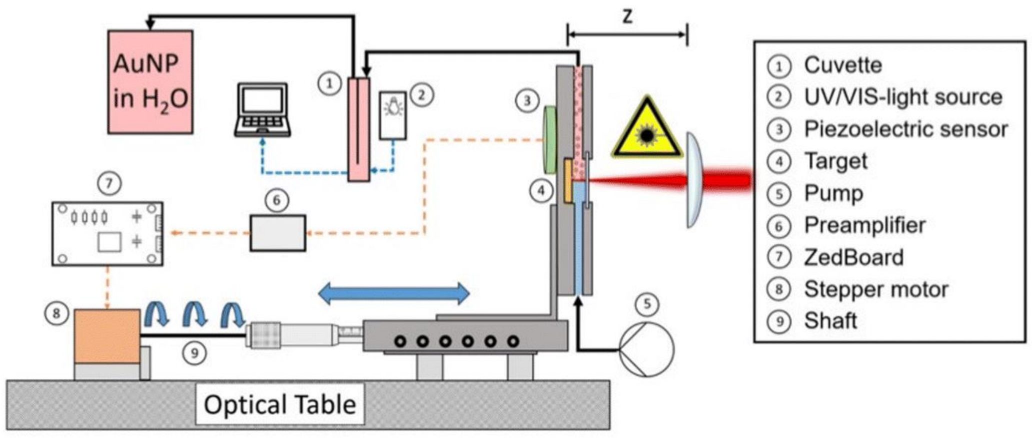
The fast scanning speed of polygon scanners allows the bypass of the cavitation bubble, reaching **productivities as high as 4 g h^{-1} for PLAL of Pt**

https://doi.org/10.1039/D3CP01214J



Set-up for **automatic focus adjustment**

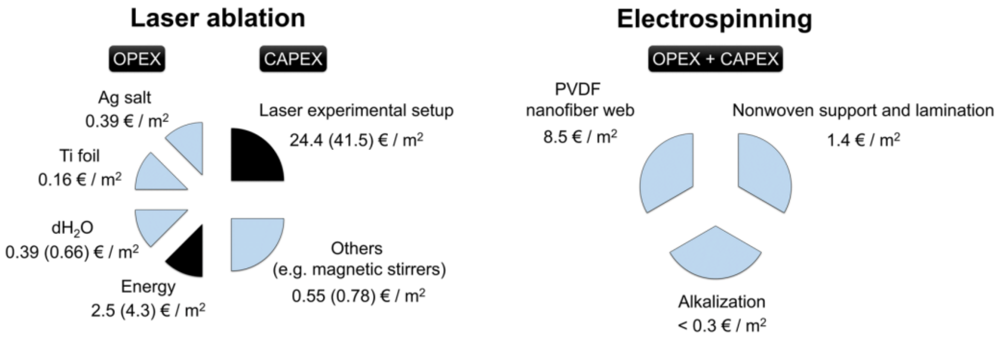
https://doi.org/10.1016/j.apsusc.2019.02.080

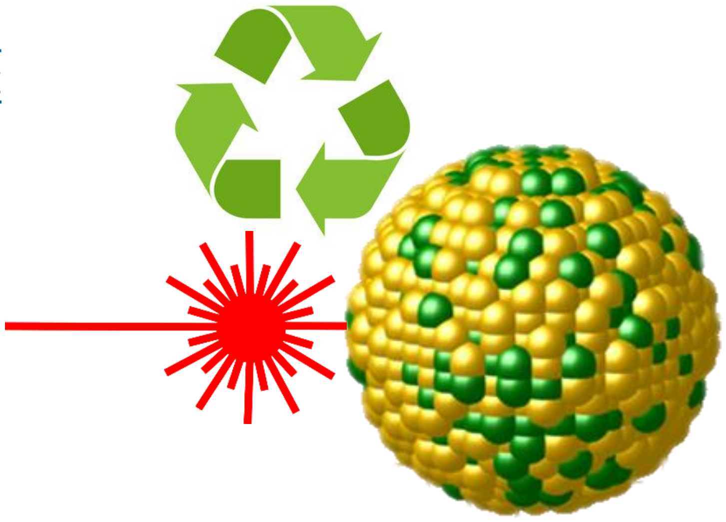


V. Amendola
University of Padova

Laser-generated colloids are often compatible with the **12 principles of green chemistry**

Analysis of the economic sustainability footprint (**operational expenditures (OPEX), capital expenditure (CAPEX)**) of Reactive LAL and electrospinning points to the sustainable and scalable development of PVDF-OH Ag/TiOx nanocomposites with laser generated NPs for simultaneous oil/water separation and pollutant degradation
https://doi.org/10.1039/D3EN00335C





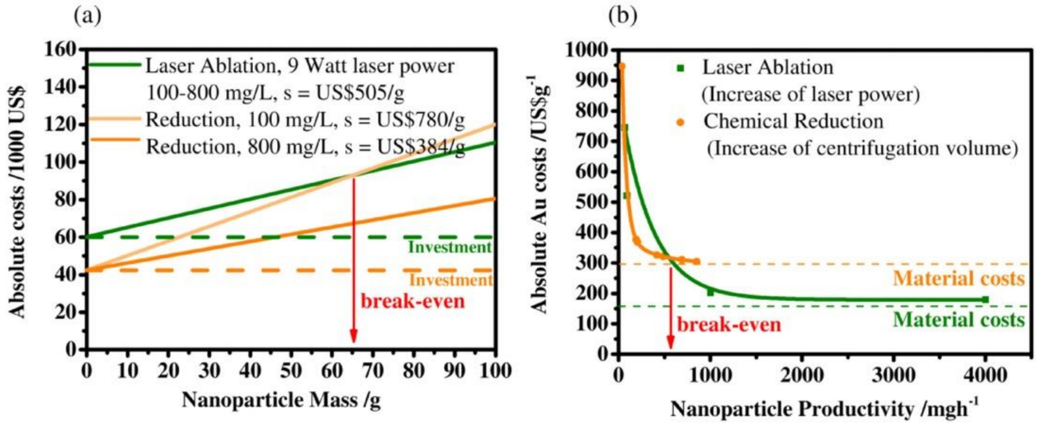
https://www.acs.org/greenchemistry/principles/12-principles-of-green-chemistry.html

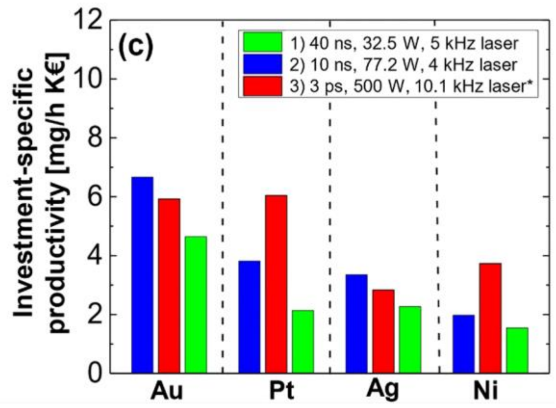
Laser-generated colloids are often selected because cost-competitive with chemically synthesized analogues

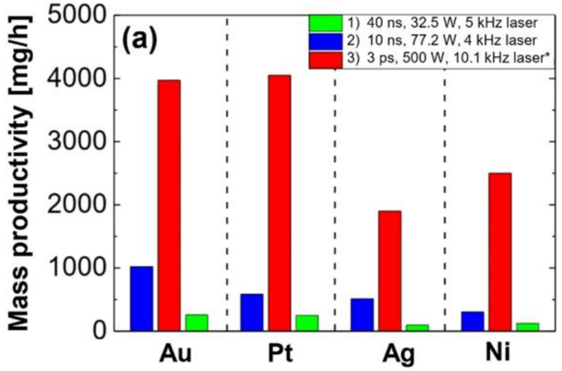
The investment-specific productivity, which defines the mass of generated NPs divided by time and investment cost (c), showed that the 10 ns-laser performed better than the 3 ps-laser for gold and silver NP production by 11% and 15% in every 1000 € investment, respectively
https://doi.org/10.1039/D3CP01214J

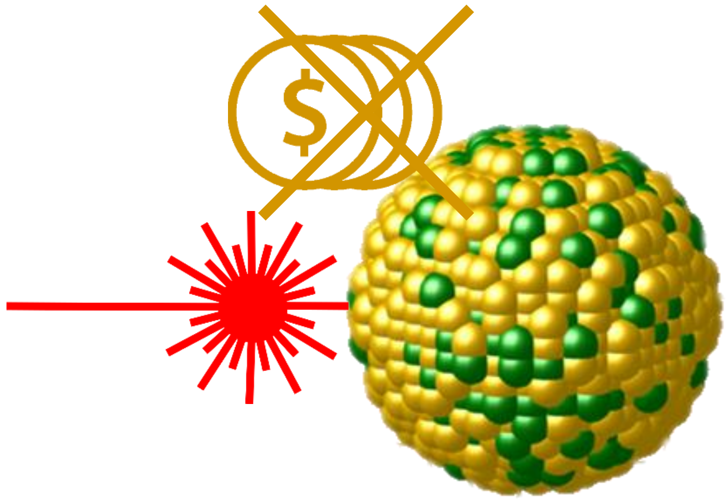
- As a rule of thumb, the LAL **productivity scales with the material density**, makingthe lighter oxides less productive than, for example, the noble metals
- For AuNPs, it has been calculated that the break-even point where laser synthesis beats chemical synthesis in the costs versus the mass of produced NPs plot already happens at tens of grams

https://doi.org/10.1002/cphc.201601139
https://doi.org/10.1002/chem.202000686









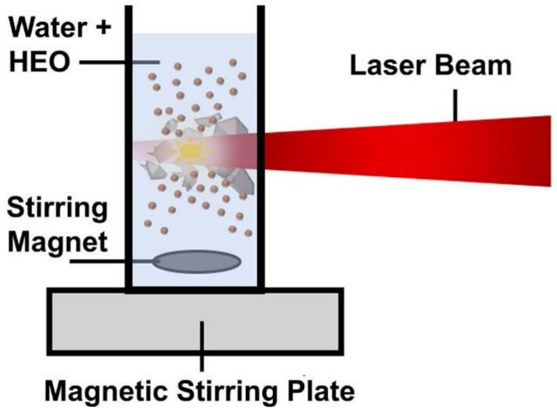
SIZE TUNEABLE WITH LASER PULSES

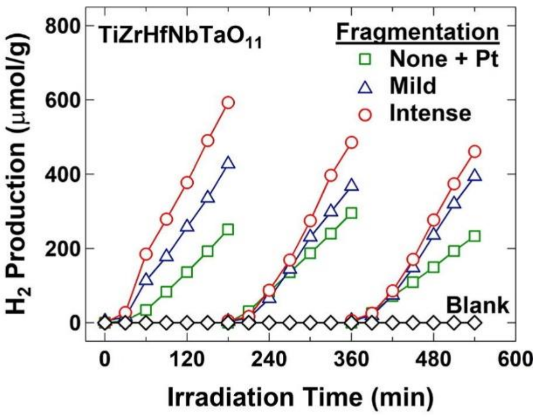
Size distribution in laser-generated colloids usually is a pitfall, but sometimes can be an opportunity

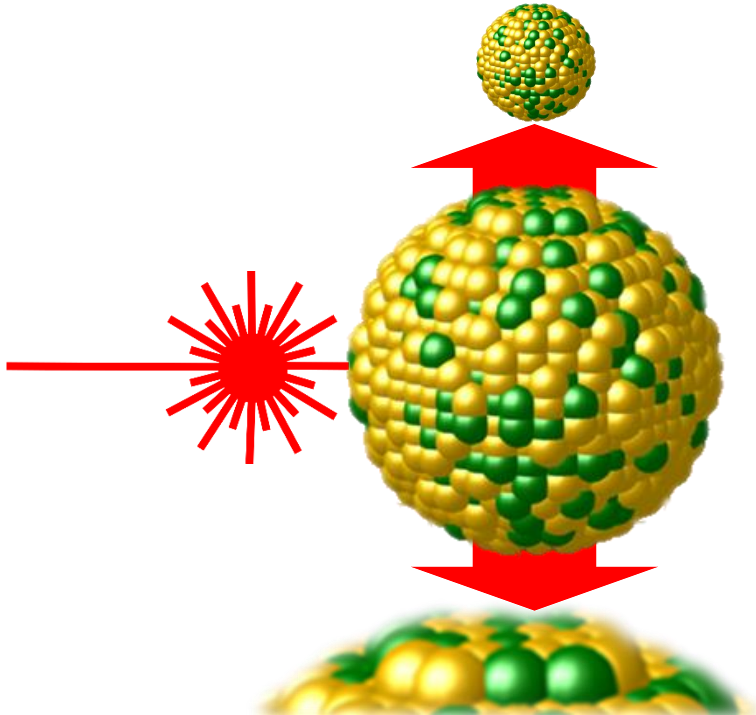
Catalysis

- Pulsed laser processing was used to **enhance the activity of a high-entropy photocatalyst**
- $TiZrNbHfTaO_{11}$ high-entropy oxide fragmented from micropowders to nanopowders
- CO_2 conversion and H_2 production rates were enhanced by one order of magnitude
- The laser-treated oxide showed photocatalytic activity **without the need for a co-catalyst**
- Laser treatment appears an effective method for producing active photocatalysts

https://doi.org/10.1016/j.apt.2024.104448







SIZE TUNEABLE WITH LASER PULSES

V. Amendola
University of Padova

Size distribution in laser-generated colloids usually is a pitfall, but sometimes can be an opportunity

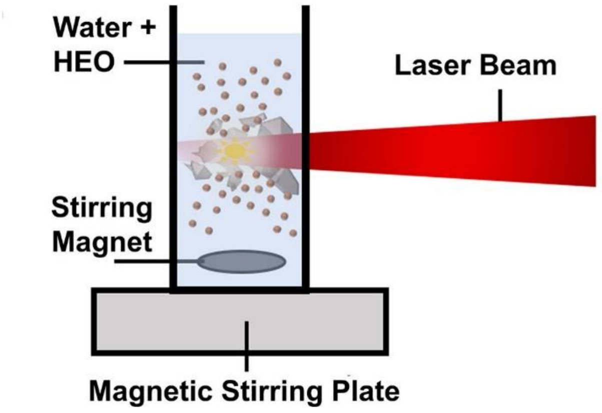
Catalysis

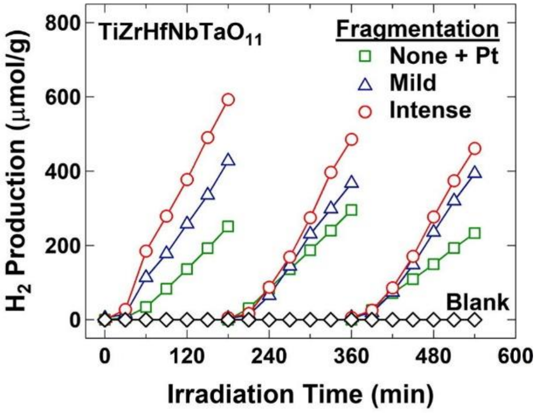
- Pulsed laser processing was used to enhance the activity of a high-entropy photocatalyst
- $TiZrNbHfTaO_{11}$ high-entropy oxide fragmented from micropowders to nanopowders
- CO_2 conversion and H_2 production rates were enhanced by one order of magnitude
- The laser-treated oxide showed photocatalytic activity without the need for a co-catalyst
- Laser treatment appears an effective method for producing active photocatalysts

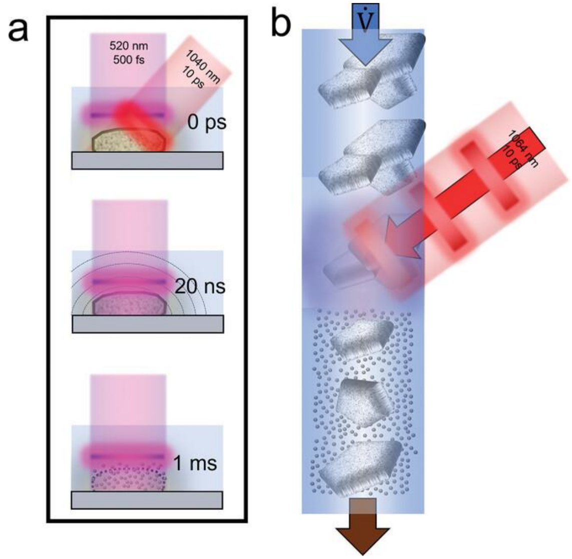
https://doi.org/10.1016/j.apt.2024.104448

- Single-pulse, multiparticle **laser fragmentation of IrO_2 microparticles (MPs)** in liquid is performed in a **continuously** operated liquid jet, giving 2 nm-sized nanoclusters (NCs) accompanied by larger fragments
- The NCs exhibit high catalytic activity and stability in oxygen evolution reactions
- An efficiency of up to 18 µg J^{-1} is reached, one order of magnitude larger than values reported for high-power LAL
- Compared with LAL, MPs enables a fully continuous, single-step synthesis of colloidal NPs

https://doi.org/10.1002/smll.202206485



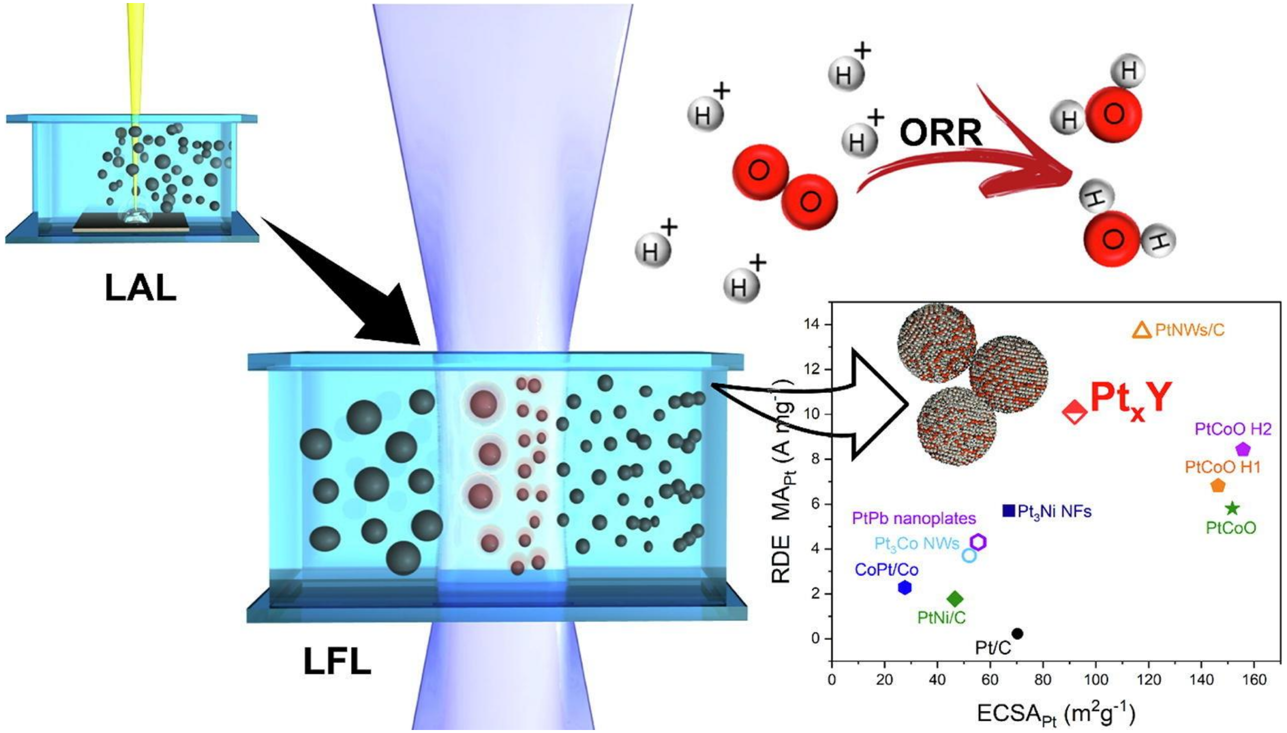




Size distribution in laser-generated colloids usually is a pitfall, but sometimes can be an opportunity

Catalysis

- The development of **active yet stable catalysts for oxygen reduction reaction (ORR)** is still a major issue for the extensive permeation of fuel cells into everyday technology
- While nanostructured Pt catalysts are to date the best available systems in terms of activity, the same is not true for stability, particularly under operating conditions.
- **Pt_xY alloy nanoparticles** are synthesized by LAL and further **optimized by laser fragmentation in liquid**
- The integrated laser-assisted methodology succeeded in producing Pt-Y nanoparticles with the ideal size (<10 nm) of commercial Pt catalysts, yet resulting remarkably more active with $E_{1/2}$ = 0.943 V vs. RHE, specific activity = 1095 µA cm^{-2} and mass activity > 1000 A g^{-1}
- At the same time, the nanoalloys are embedded in a fine Pt oxide matrix, which allows a **greater stability of the catalyst than the commercial Pt reference**, as directly verified on a gas diffusion electrode



https://doi.org/10.1016/j.jechem.2023.12.031

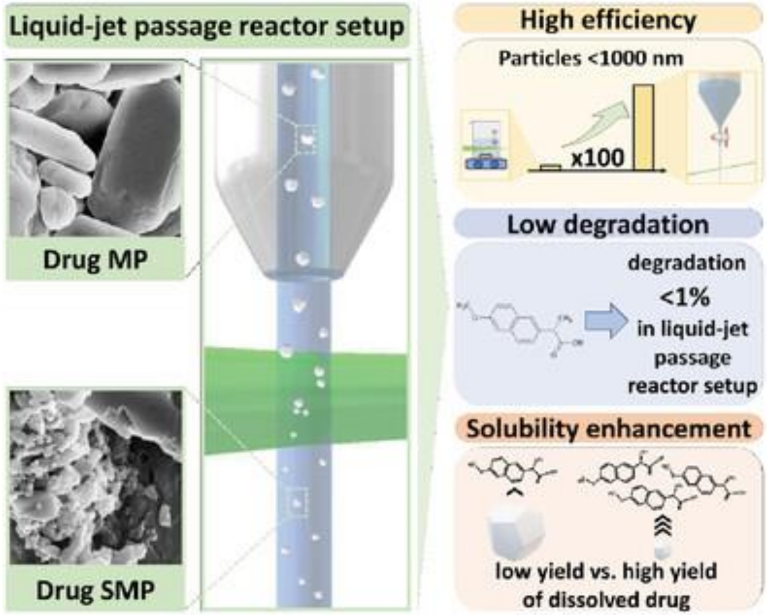
SIZE TUNEABLE WITH LASER PULSES

Size distribution in laser-generated colloids usually is a pitfall, but sometimes can be an opportunity

Nanomedicine

- The increasing prevalence of water insoluble or poorly soluble drugs calls for the development of new formulation methods
- State-of-the-art techniques like cryo-milling suffer from degradation and contamination of the drugs
- Superior fragmentation efficiency by **LFL in liquid-jet reactor enhanced solubility with minimal chemical degradation** (<1%)

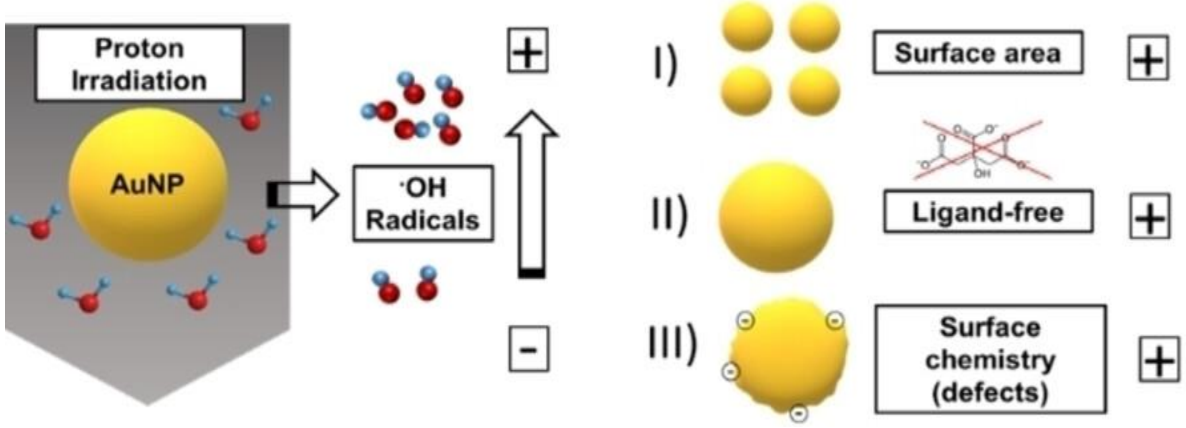
https://doi.org/10.1002/ppsc.202300034
https://doi.org/10.1038/s41598-023-36922-7



- Gold nanoparticles (AuNPs) are currently the most studied radiosensitizers **in proton therapy** (PT) applicable for the treatment of solid tumors, where they amplify production of reactive oxygen species (ROS)
- Enhancement of ROS production driven by

1. total particle surface area
2. utilization of ligand-free AuNPs avoiding sodium citrate as a radical quencher ligands
3. higher density of structural defects generated by LFL synthesis, indicated by surface charge density

https://doi.org/10.1002/chem.202301260

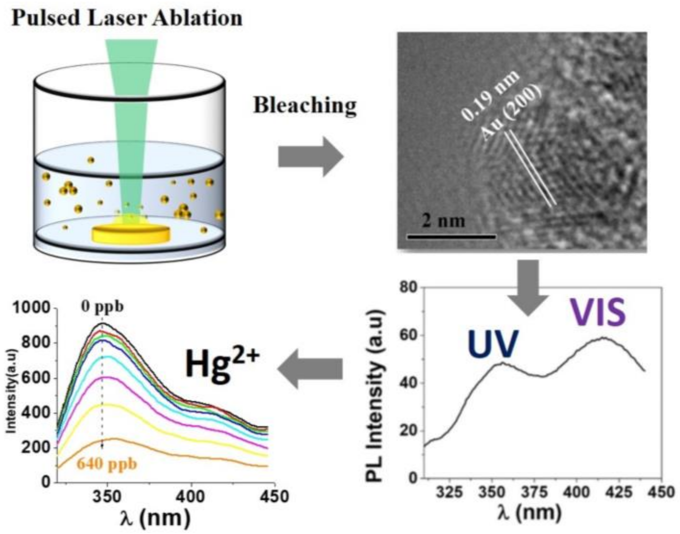


Size distribution in laser-generated colloids usually is a pitfall, but sometimes can be an opportunity

Photonics

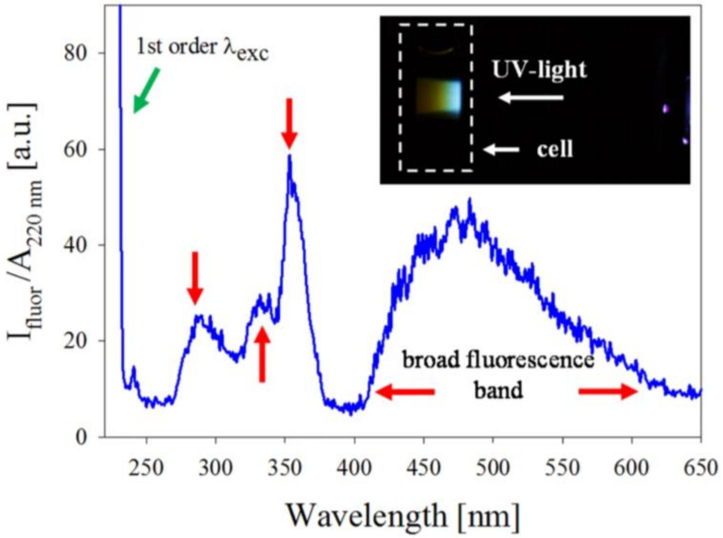
- **Luminescent oxidized AuNCs (ca. 3 nm)** emitting in both ultraviolet (UV) and visible (blue) regions were synthesized by pulsed laser ablation of a gold target in NaOH aqueous solution
- Photoluminescence is bleached in the presence of Cd^{2+}, Pb^{2+}, Hg^{2+} and CH_3Hg^{+} ions

https://doi.org/10.3390/chemosensors11020118



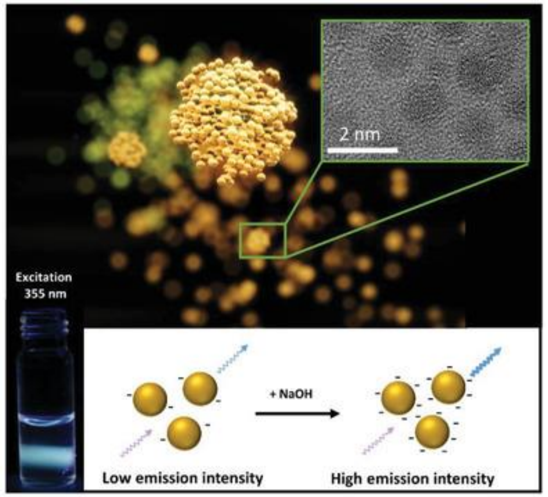
- **Luminescent Ag NCs** were obtained by fs laser ablation of Ag in water
- HRTEM measurements confirmed the presence of few atoms Ag NCs together with ther Ag NPs in different formation stages

https://doi.org/10.1038/s41598-020-64773-z



- **Fully inorganic**, colloidal gold nanoclusters (NCs) constitute a new class of nanomaterials that are clearly distinguishable from their commonly studied metal–organic ligand-capped counterparts
- LFL of Au NPs in water gives **luminiescent AuNCs** (2.5 – 1 nm) with up to 2 % of quantum yield (QY)
- QY strongly dependent on the surface charge and adsorbed ions

https://doi.org/10.1002/adma.202101549

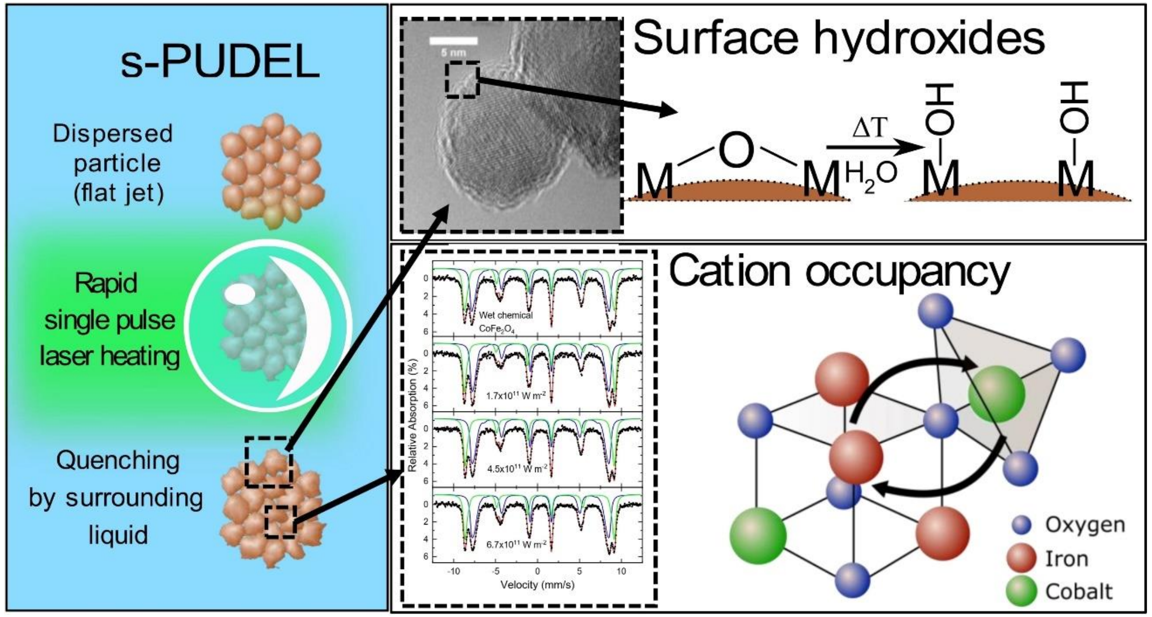


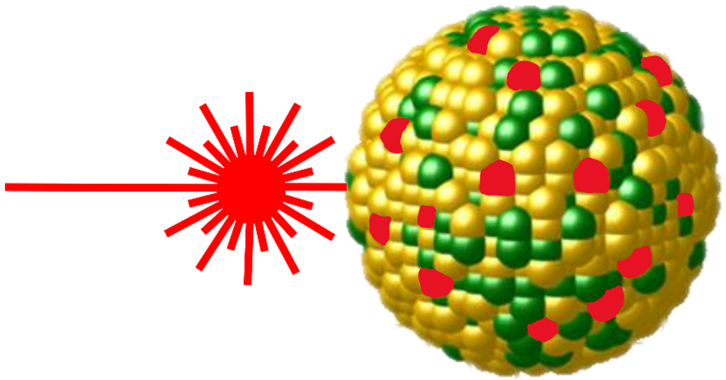
Entering «inside» the laser-generated nanomaterials, defects are one relevant feature exploited so far

Catalysis

- Pulsed laser defect engineering of $CoFe_2O_4$ nanoparticles in water was employed
- **The catalyst surface and the cation occupancy of octahedral and tetrahedral sites was gradually altered with single laser pulses**
- The laser-induced randomization of the cation occupancy was verified by Mössbauer spectroscopy and linearly correlated with the conversion of cinnamyl alcohol solidifying the importance of octahedral Co^{3+}-sites in oxidation catalysis

https://doi.org/10.1002/cctc.202101785





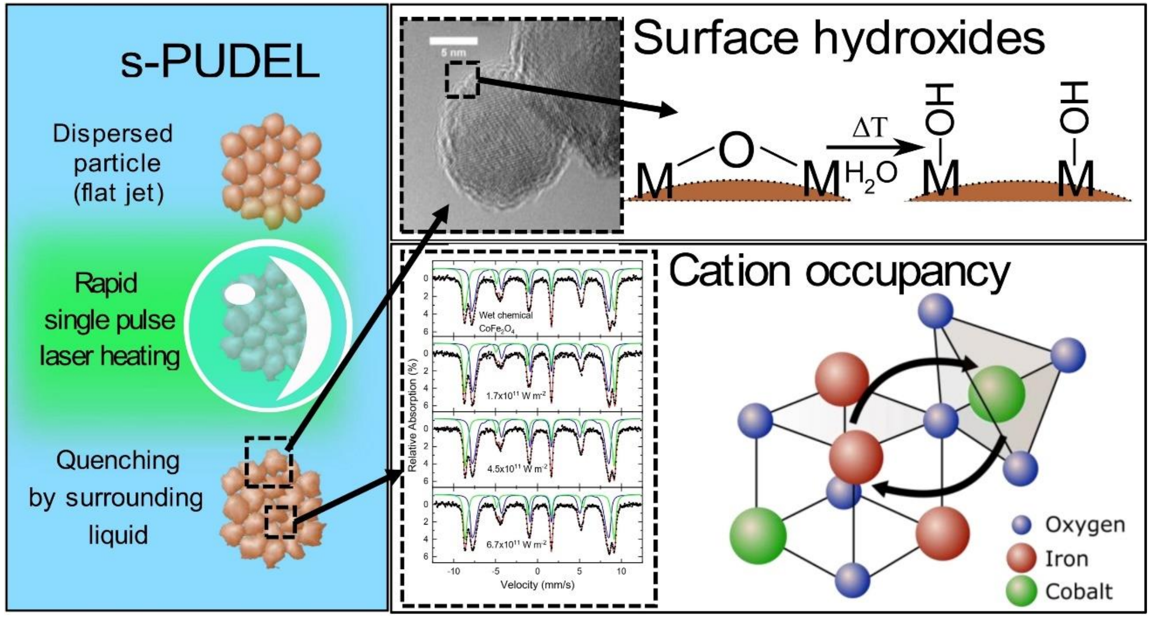
V. Amendola
University of Padova

Entering «inside» the laser-generated nanomaterials, defects are one relevant feature exploited so far

Catalysis

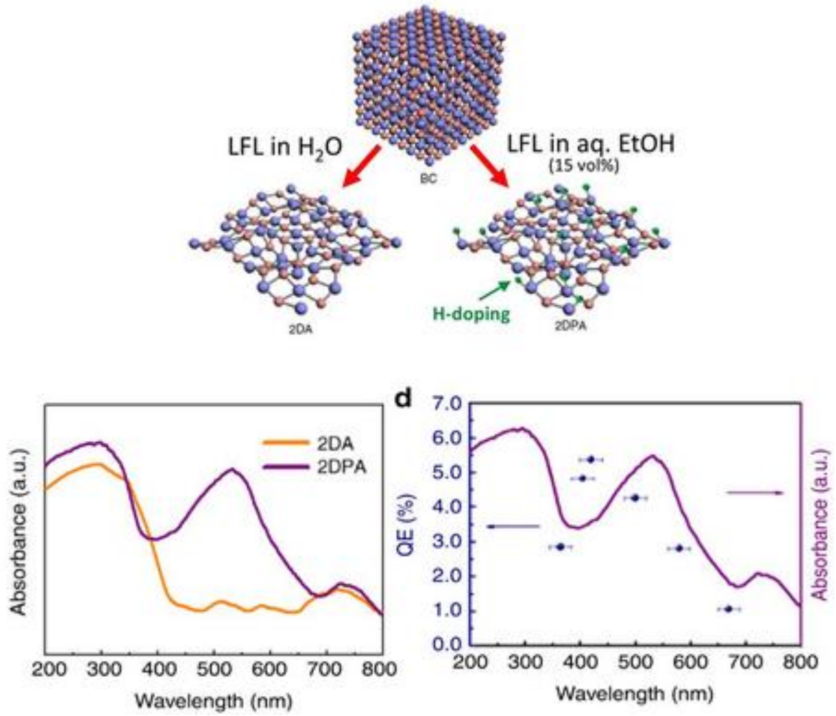
- Pulsed laser defect engineering of $CoFe_2O_4$ nanoparticles in water was employed
- **The catalyst surface and the cation occupancy of octahedral and tetrahedral sites was gradually altered with single laser pulses**
- The laser-induced randomization of the cation occupancy was verified by Mössbauer spectroscopy and linearly correlated with the conversion of cinnamyl alcohol solidifying the importance of octahedral Co^{3+}-sites in oxidation catalysis

https://doi.org/10.1002/cctc.202101785



- **2D amorphous NiO nanostructure prepared by laser ablating bulk crystalline NiO powders** in water or alcohol solution
- NiO can act as an efficient and robust photocatalyst for solar H_2 evolution without any cocatalysts
- The **surface plasmon resonance was introduced by increasing the electron doping**

https://doi.org/10.1038/s41467-018-06456-y



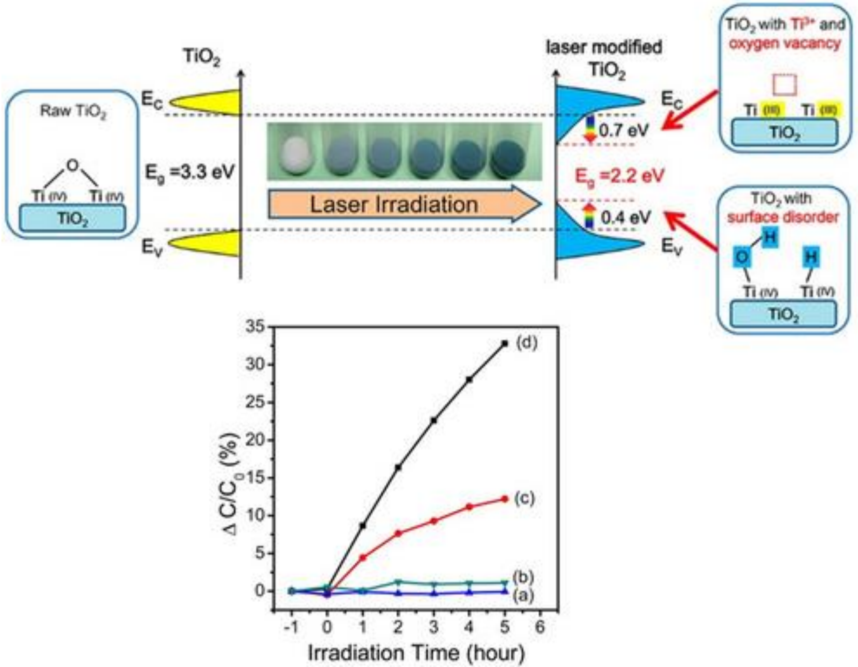
V. Amendola
University of Padova

Entering «inside» the laser-generated nanomaterials, defects are one relevant feature exploited so far

Catalysis

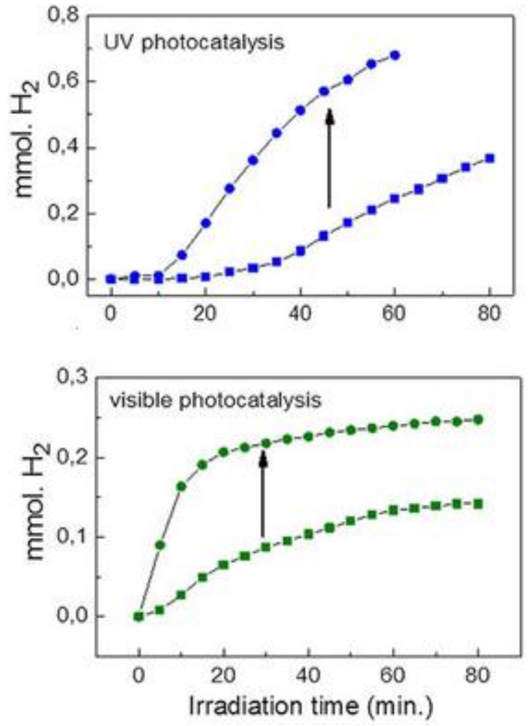
- **Black titanium oxide nanospheres are prepared by pulsed-laser irradiation** of pure titanium oxide in suspended aqueous solution
- High-energy laser irradiation of titanium oxide suspended solution benefited the formation of Ti^{3+} species and surface disorder on the surface of the titanium oxide nanospheres
- The laser-modified black titanium oxide nanospheres **absorb the full spectrum of visible light**, thus exhibiting good photocatalytic performance under visible light.

https://doi.org/10.1021/acsami.5b04568



- High water splitting activity of titania colloids, modified by nanosecond pulsed laser irradiation
- **Laser irradiation increases the hydrogen production efficiency up to a factor of three** for anatase, rutile and P25
- Laser irradiation promotes the formation of disordered surface state and lattice distortion which could be responsible for the observed enhanced photocatalytic activity

https://doi.org/10.1016/j.jcis.2016.08.013

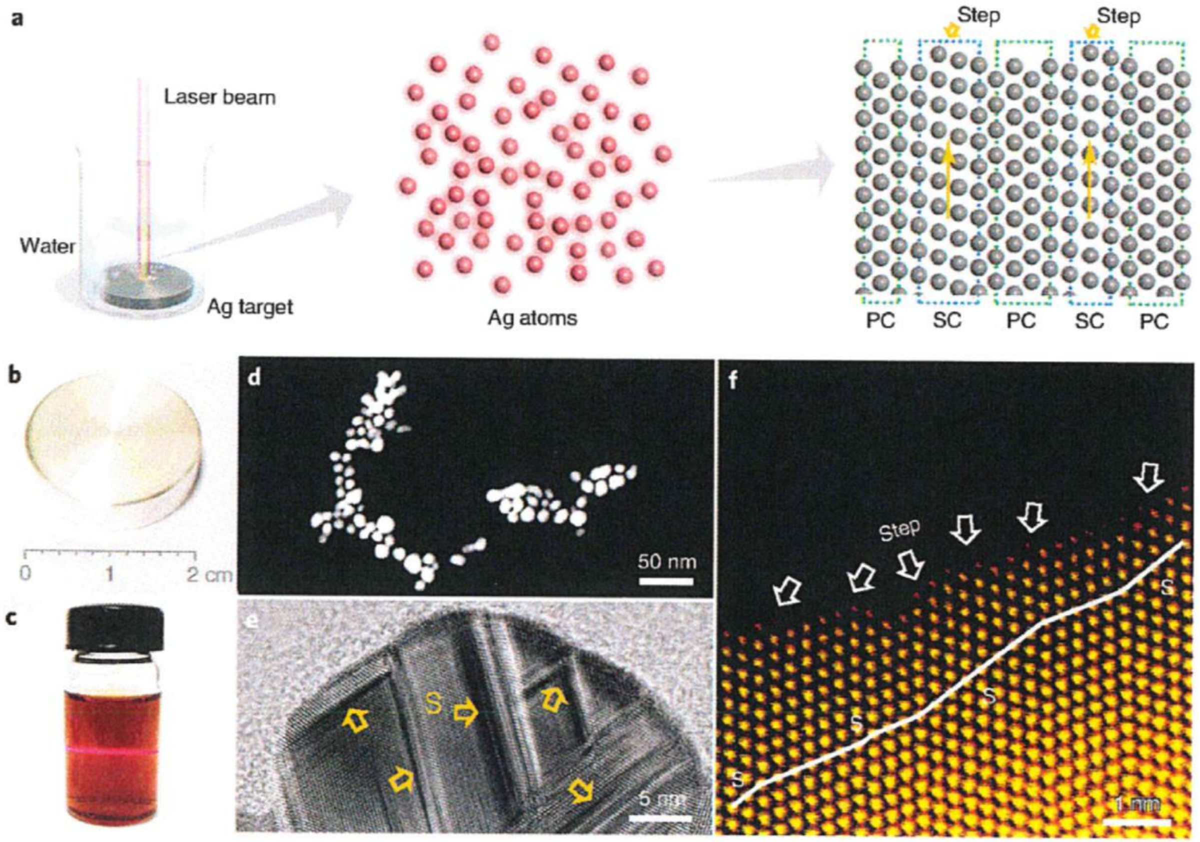


Entering «inside» the laser-generated nanomaterials, defects are one relevant feature exploited so far

Catalysis

- A silver catalyst with superior activity and durability (?) in an acid medium that outperforms commercial platinum on carbon, especially under high applied voltages
- Laser ablation in liquid is adopted to generate a high density of stacking faults in silver nanoparticles
- The **stacking faults can cause a low coordination number and high tensile strain**, which jointly improve the adsorption energy and **transform the non-active silver into a highly active catalyst**

https://doi.org/10.1038/s41929-019-0365-9



V. Amendola
University of Padova

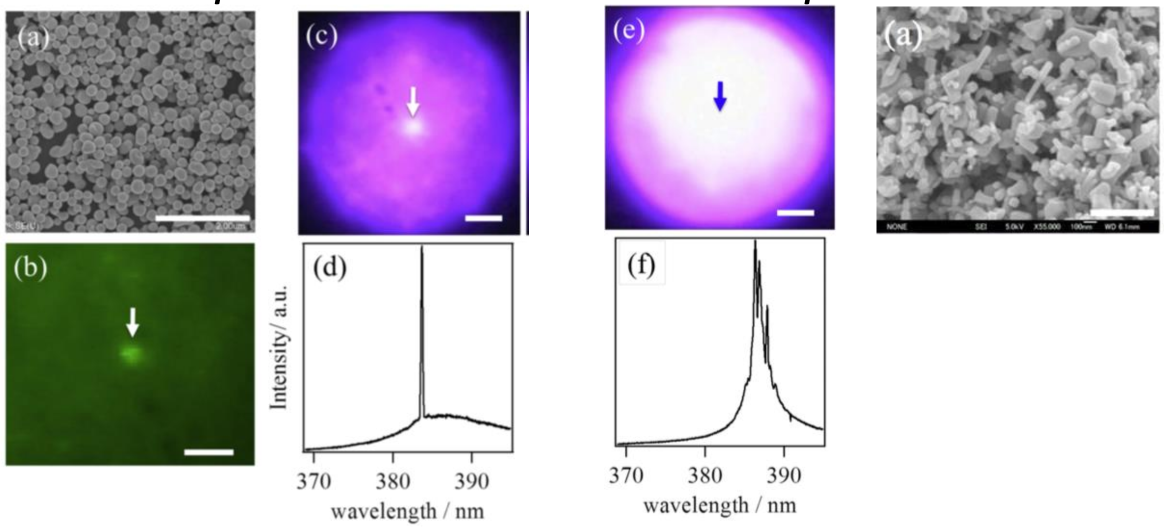
Entering «inside» the laser-generated nanomaterials, defects are one relevant feature exploited so far

Photonics

- An unique random laser exhibiting quasi-single-mode and low lasing threshold was developed by a LML homogenization of submicrometer-sized zinc oxide particle film dispersed with intentionally introduced polymer particles as point defects
- **Random lasing was dominantly initiated at the defect sites**, although multi-mode peaks with a collapsed broad emission spectrum were observed at the defect-free sites as in the conventional random lasers
- The proposed structure is simple and possibly provide the controllability of lasing properties even in random structures

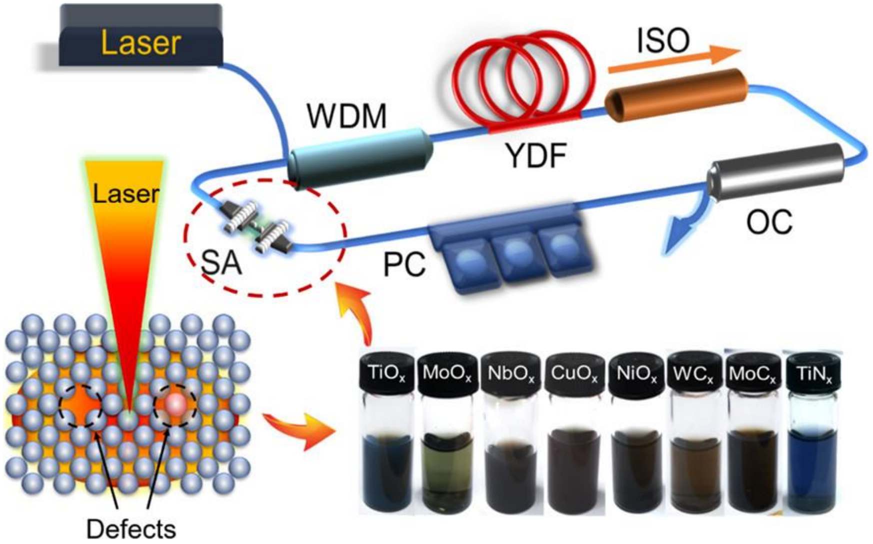
https://doi.org/10.1063/1.4792349
https://doi.org/10.1088/2040-8978/18/3/035202

post LML *pre LML*



- Defect control is a promising technique for the development of ultrafast optical devices because these properties depend largely on the materials defect structure
- **fs laser processing** of a range of colloidal nanocrystals with **abundant defects leading to broadband absorption and enhanced nonlinear optical response** in the near-infrared region
- used to drive an ultrafast optical switch for generation of passively Q-switched laser pulses with a pulse duration of 910 ns at 1.0 μm

https://doi.org/10.1021/acs.chemmater.0c03235

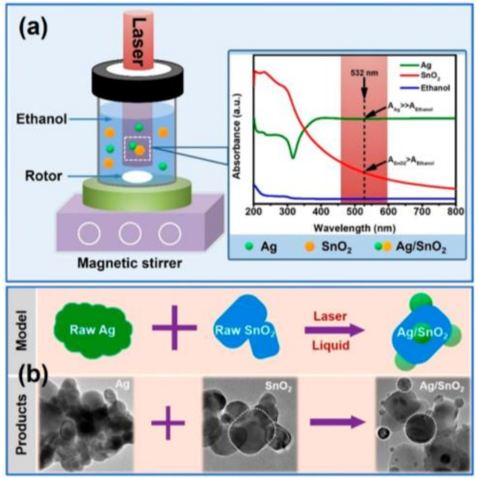


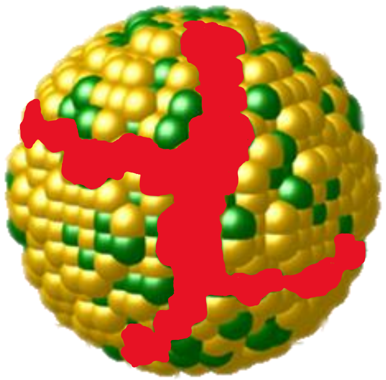
LSPC enables the easy access to a library of uncommon or metastable materials, sometimes otherwise inaccessible

Heterostructures for catalysis

- **Spherical Ag and SnO_2 nanocomposites** were successfully prepared by laser-induced deposition in a liquid medium
- Photocatalytic performance was enhanced 3.1 times than the pure SnO_2 and 13.3 times than the pure Ag
- 99.1% methylene blue can be removed within 60 min under ultraviolet lamp irradiation
- Higher reaction rate constant was achieved and exhibited better performance than previous works in similar conditions
- Spherical Ag anchoring on the surface of SnO_2 promoted the separation of photogenerated electron-hole pairs

https://doi.org/10.1016/j.jallcom.2021.163522
https://doi.org/10.3390/nano13192628



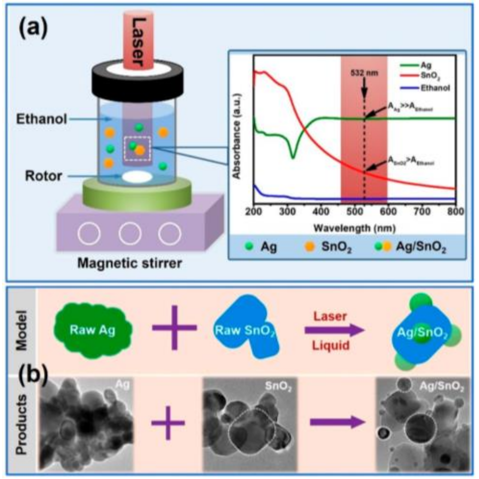


LSPC enables the easy access to a library of uncommon or metastable materials, sometimes otherwise inaccessible

Heterostructures for catalysis

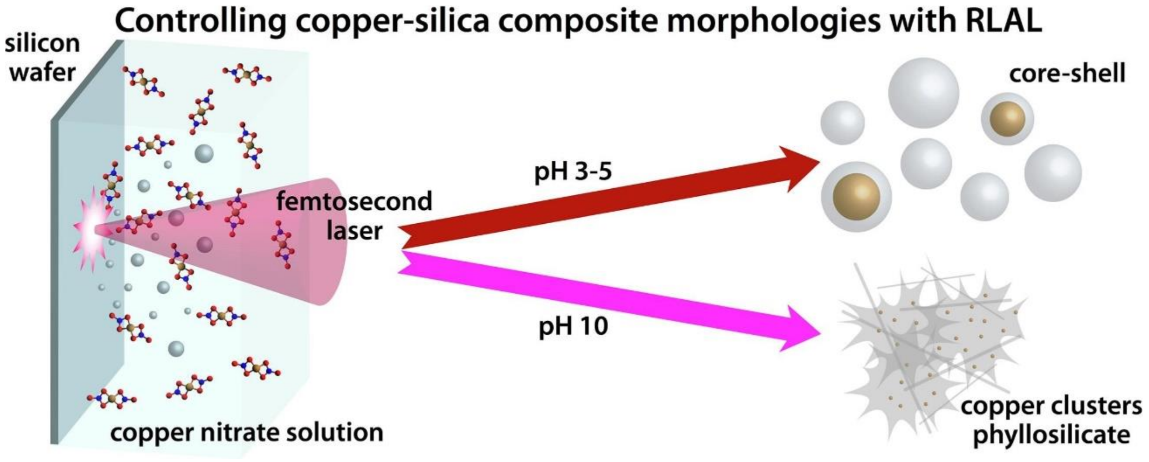
- **Spherical Ag and SnO_2 nanocomposites** were successfully prepared by laser-induced deposition in a liquid medium
- Photocatalytic performance was enhanced 3.1 times than the pure SnO_2 and 13.3 times than the pure Ag
- 99.1% methylene blue can be removed within 60 min under ultraviolet lamp irradiation
- Higher reaction rate constant was achieved and exhibited better performance than previous works in similar conditions
- Spherical Ag anchoring on the surface of SnO_2 promoted the separation of photogenerated electron-hole pairs

https://doi.org/10.1016/j.jallcom.2021.163522
https://doi.org/10.3390/nano13192628



- 31.5 wt.% Cu loading on silica with sub-2 nm CuOx nanoparticles
- **One-step synthesis of sub-2 nm CuOx NPs dispersed in phyllosilicate and silica**
- pH-dependent nanoparticle morphology based on point of zero charge (PZC) of silica
- One-step synthesis of copper-core/silica-shell nanospheres
- pH-dependent catalytic activity toward para-nitrophenol reduction reaction

https://doi.org/10.1016/j.apsusc.2019.145037



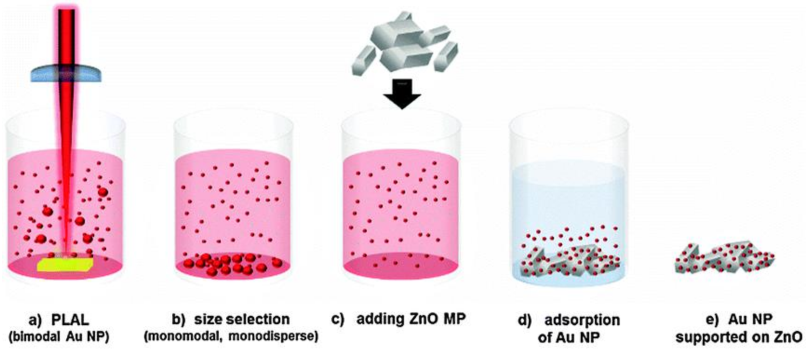
V. Amendola
University of Padova
DiSC

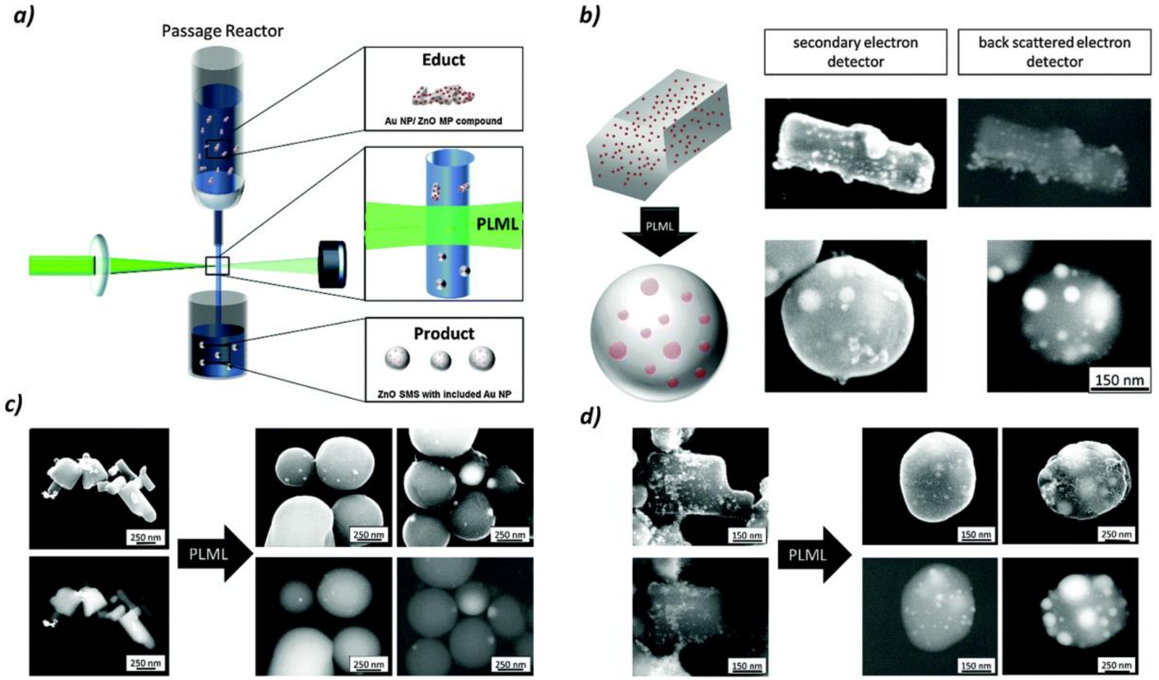
LSPC enables the easy access to a library of uncommon or metastable materials, sometimes otherwise inaccessible

Heterostructures for catalysis

- Supported particles are easily accessible as standard materials used in heterogeneous catalysis and photocatalysis
- The integration of supported nanoparticles into solid support, namely **gold nanoparticles into zinc oxide sub-micrometer spheres, by energy controlled pulsed laser melting in a free liquid jet**
- This one-step, continuous flow-through processing route reverses the educt's structure, converting the ligand-free surface adsorbate into a spherical **subsurface solid inclusion** within its former support
- The results show how a nanoparticulate surface adsorbate can be included in the form of crystalline nanoparticles into the resolidified support matrix, demonstrated by using plasmonic nanoparticles and semiconductor microparticles as reference materials

https://doi.org/10.1039/C5CP04296H





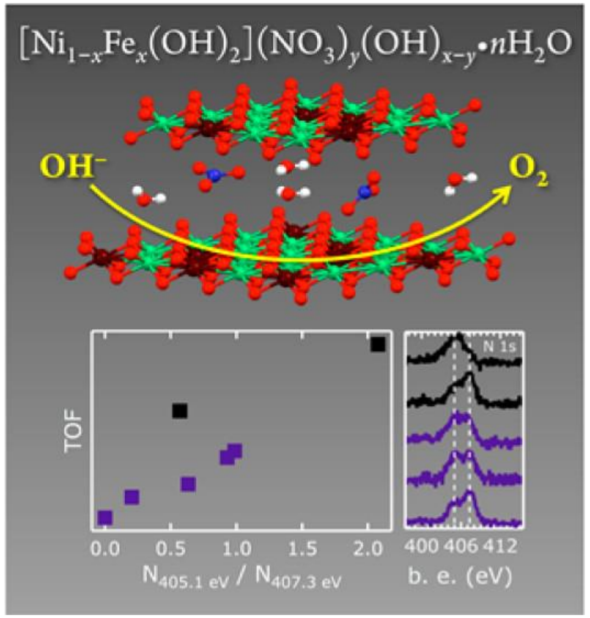
UNCONVENTIONAL AND METASTABLE STRUCTURES

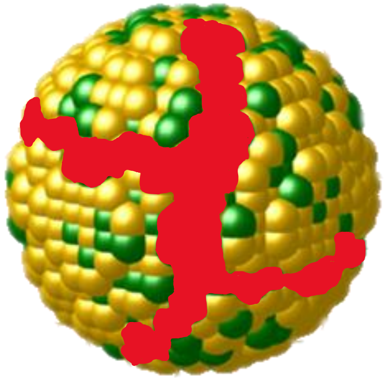
LSPC enables the easy access to a library of uncommon or metastable materials, sometimes otherwise inaccessible

Layered compounds

- **Surfactant-free mixed-metal hydroxide water oxidation nanocatalysts** synthesized by pulsed-laser ablation in liquids
- In a series of [Ni-Fe]-layered double hydroxides with intercalated nitrate and water, $[Ni_{1-x}Fe_x(OH)_2](NO_3)_y(OH)_{x-y}\cdot nH_2O$, higher activity was observed as the amount of Fe decreased to 22%
- Addition of Ti^{4+} and La^{3+} ions further enhanced electrocatalysis, with a lowest overpotential of 260 mV at 10 mA cm^{-2}
- Electrocatalytic water oxidation activity increased with the relative proportion of a 405.1 eV N 1s (XPS binding energy) species in the nanosheets

https://doi.org/10.1021/ja506087h
https://doi.org/10.1039/C6EE00377J
https://doi.org/10.1021/acs.chemrev.6b00398



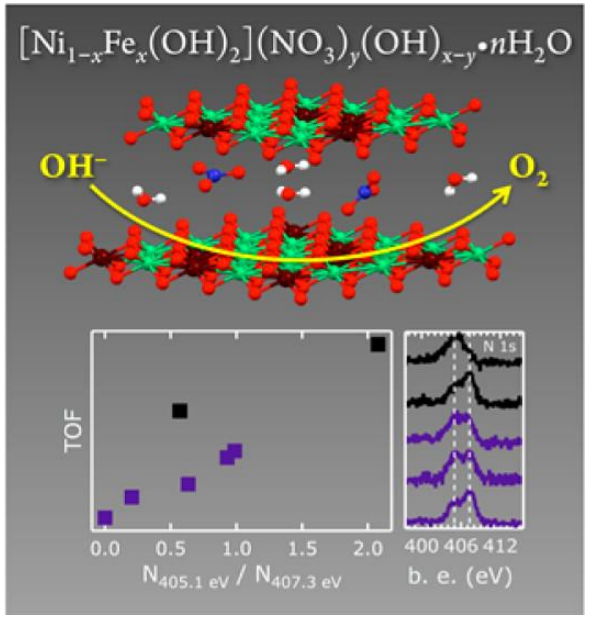


LSPC enables the easy access to a library of uncommon or metastable materials, sometimes otherwise inaccessible

Layered compounds

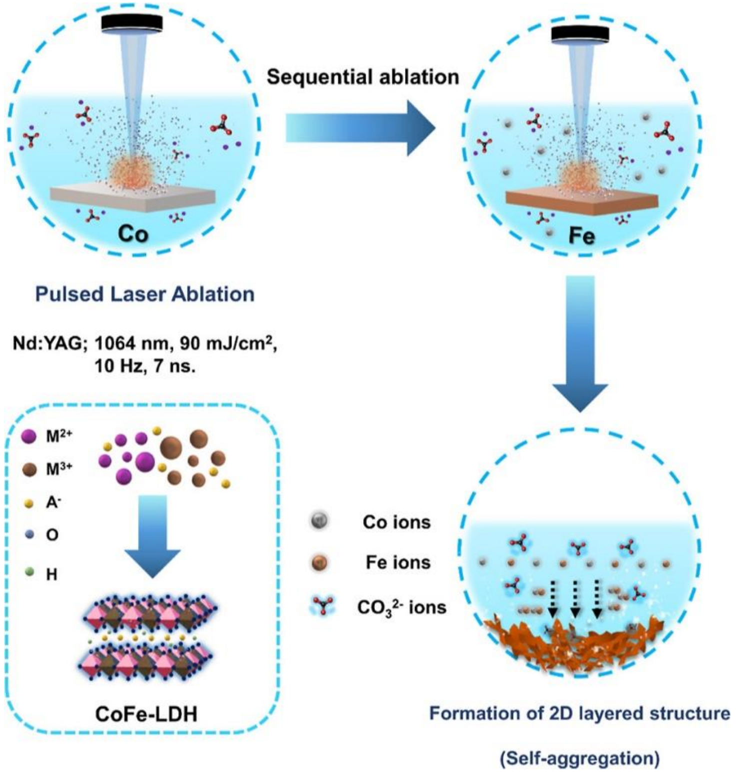
- **Surfactant-free mixed-metal hydroxide water oxidation nanocatalysts** synthesized by pulsed-laser ablation in liquids
- In a series of [Ni-Fe]-layered double hydroxides with intercalated nitrate and water, $[Ni_{1-x}Fe_x(OH)_2](NO_3)_y(OH)_{x-y}\cdot nH_2O$, higher activity was observed as the amount of Fe decreased to 22%
- Addition of Ti^{4+} and La^{3+} ions further enhanced electrocatalysis, with a lowest overpotential of 260 mV at 10 mA cm^{-2}
- Electrocatalytic water oxidation activity increased with the relative proportion of a 405.1 eV N 1s (XPS binding energy) species in the nanosheets

https://doi.org/10.1021/ja506087h
https://doi.org/10.1039/C6EE00377J
https://doi.org/10.1021/acs.chemrev.6b00398



- **Two-dimensional cobalt–iron-layered double-hydroxide (CoFe-LDH) ultrathin nanosheets** by pulsed laser ablation in an aqueous medium exhibiting abundant electrochemically active sites and a large surface area

https://doi.org/10.1021/acscatal.2c05017

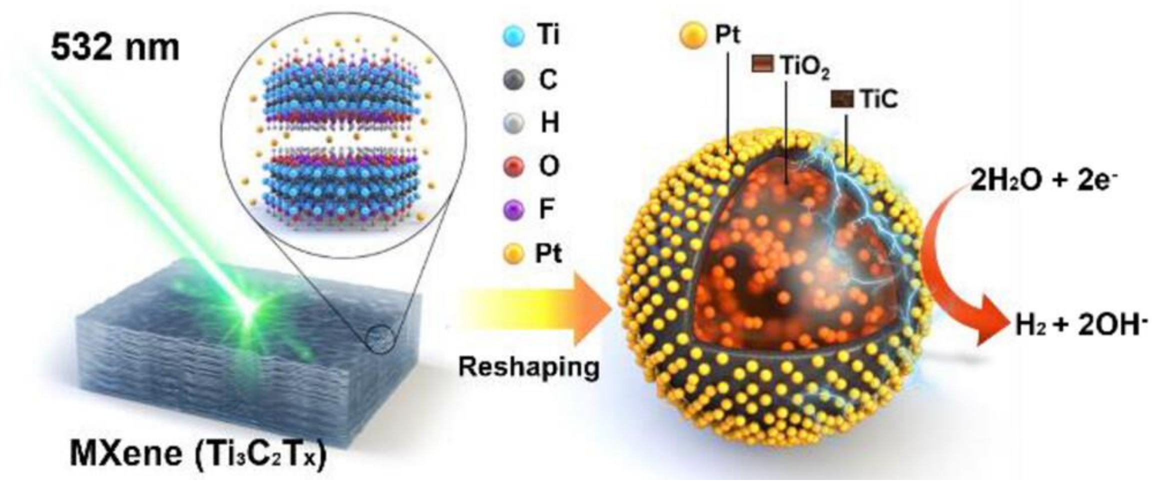


LSPC enables the easy access to a library of uncommon or metastable materials, sometimes otherwise inaccessible

Hybrid compounds

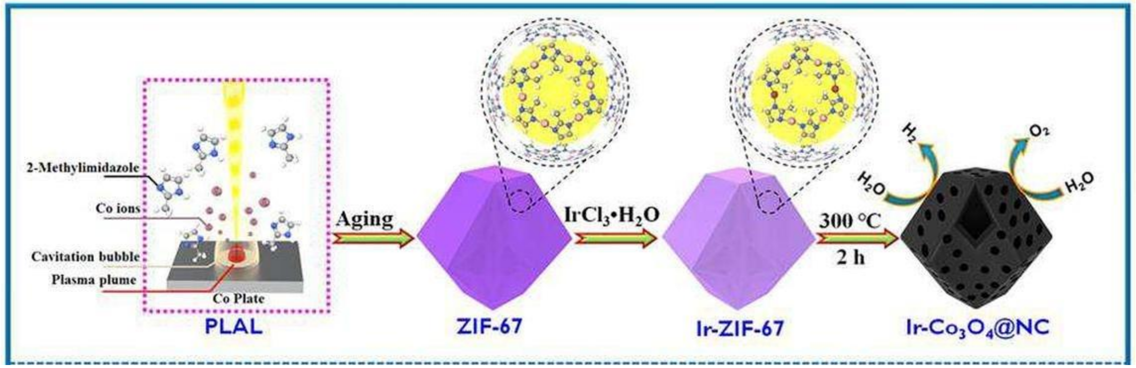
- A 2D MXene ($Ti_3C_2T_x$) was converted in **TiO_2@TiC core–shell spheres** with sizes of 200–350 nm **decorated with ~2 nm ultrasmall Pt NPs** on the surface using the single-step PLIL method
- These advances allow for a significant increase in electrocatalytic hydrogen evolution reaction (HER) activity under visible light illumination

https://doi.org/10.1021/acsnano.2c12638



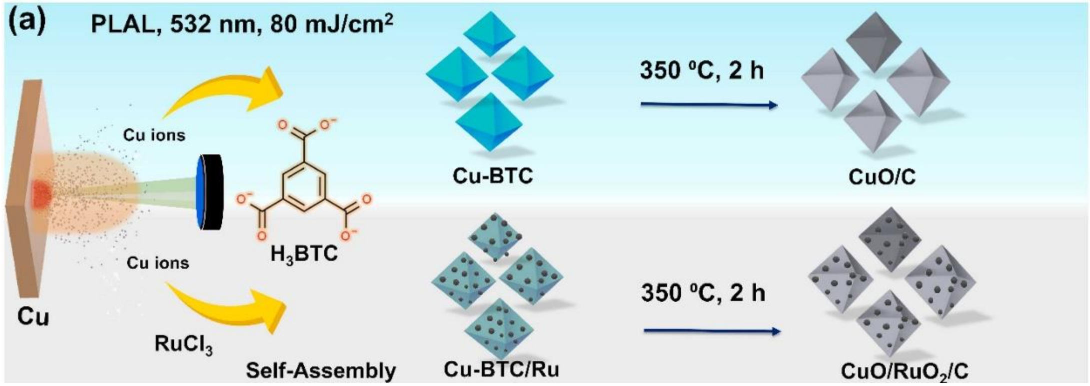
- **Ir-doped Co_3O_4@NC hybrid (MOF)** synthesized via advanced pulsed laser technique

https://doi.org/10.1016/j.cej.2023.143717



- **Cu-MOF-derived CuO/C and CuO/RuO_2/C** were fabricated via PLAL and calcination

https://doi.org/10.1016/j.apcatb.2023.123164



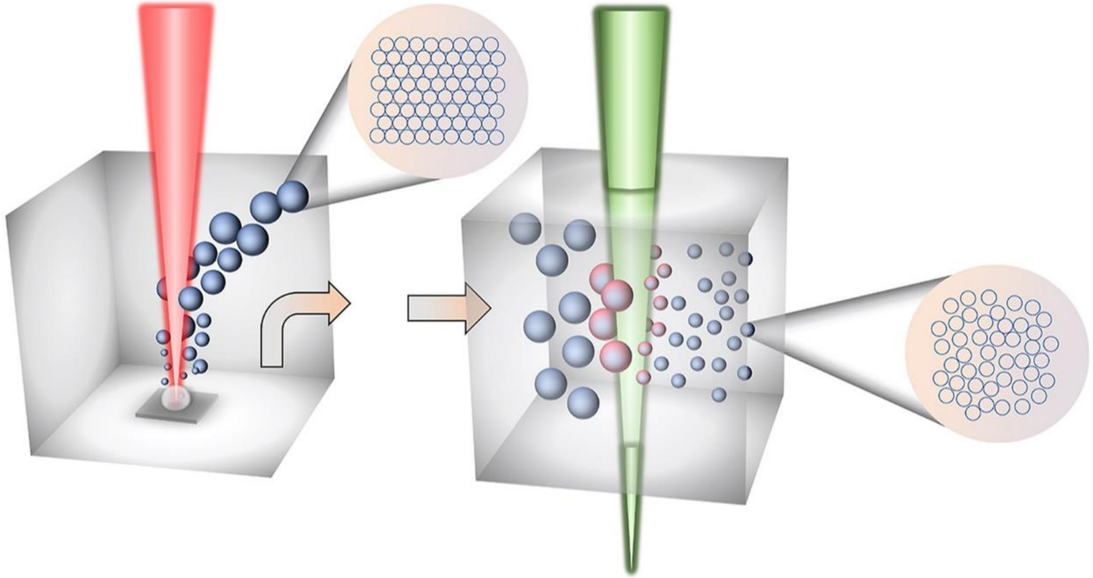
V. Amendola
University of Padova

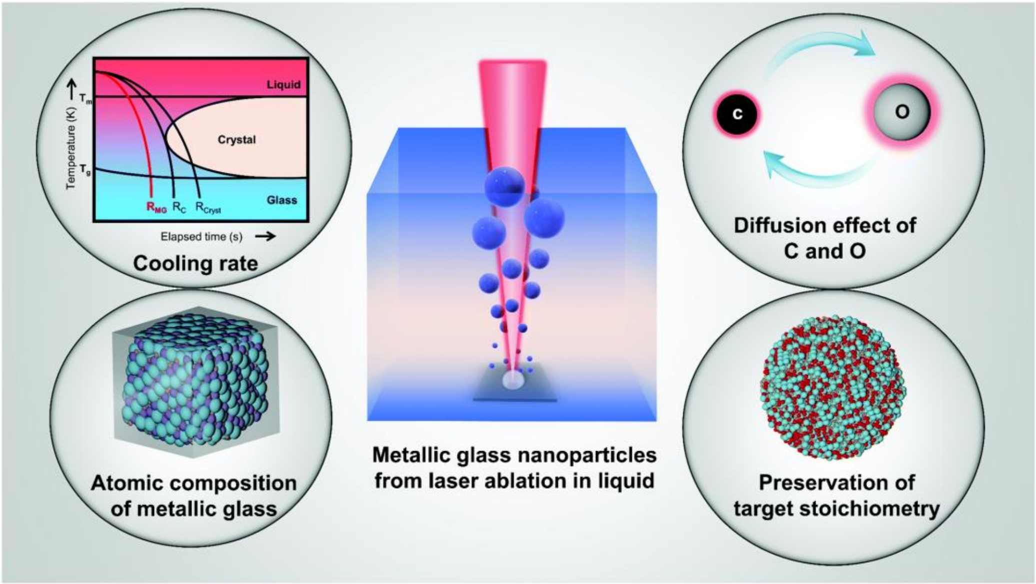
LSPC enables the easy access to a library of uncommon or metastable materials, sometimes otherwise inaccessible

Amorphous phases

- Laser ablation in liquid (LAL) and laser fragmentation in liquid (LFL) showed promising potential for the production of **amorphous metal oxide and carbide NPs**
- Yet, the amorphization in such methods still lacks sufficient rules to follow regarding the formation mechanism and criteria
- Liquid selection, target elements, laser parameters play a significant role in the competitive relationship between amorphization and crystallization
- There are also prospects of laser-generated metallic glass nanoparticles (MG-NPs) from MG targets

https://doi.org/10.1016/j.mtchem.2023.101544
https://doi.org/10.1039/D1CP00701G





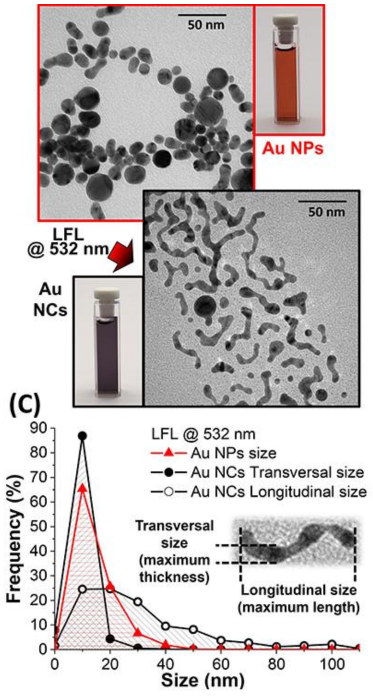
V. Amendola
University of Padova

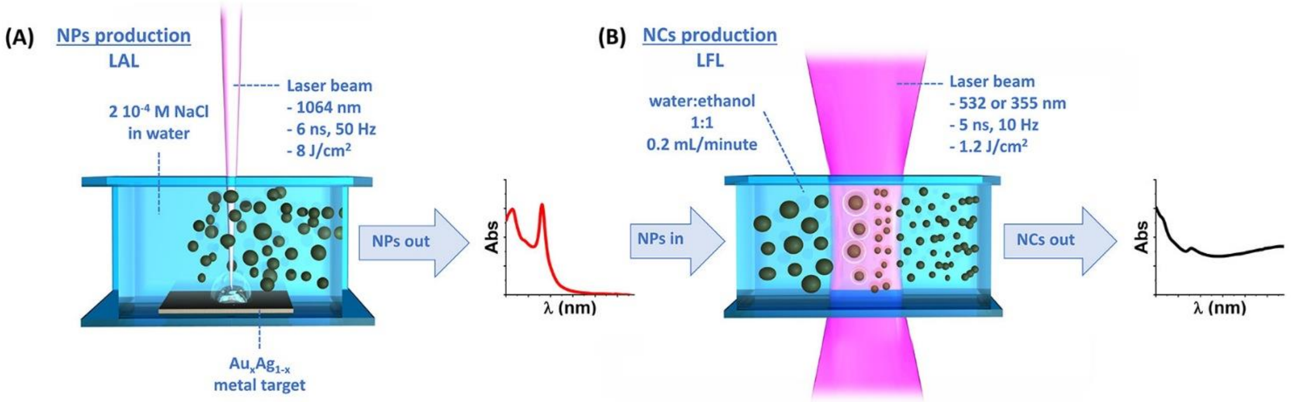
LSPC enables the easy access to a library of uncommon or metastable materials, sometimes otherwise inaccessible

Unconventional shapes

- **Au and Au-Ag nanocorals (NCs) are formed in two stages by photofragmentation of LAL-generated NPs**, followed by spontaneous unidirectional assembly of the nanocrystals
- The whole procedure is without chemicals or templating compounds, hence the NCs can be coated with thiolated molecules in one step or embedded in matrixes
- NC have broadband absorption from UV to NIR

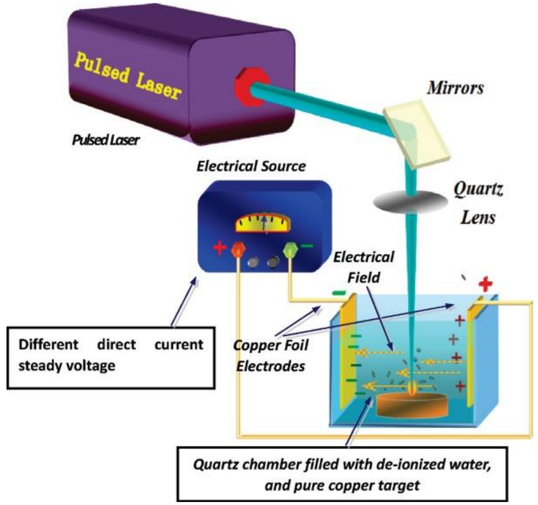
https://doi.org/10.1039/C5NR03442F
https://doi.org/10.1021/acsami.2c05983

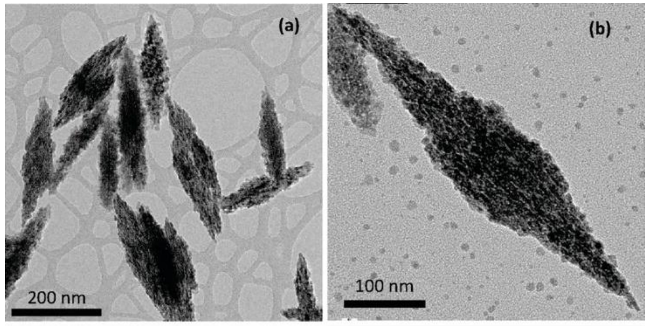


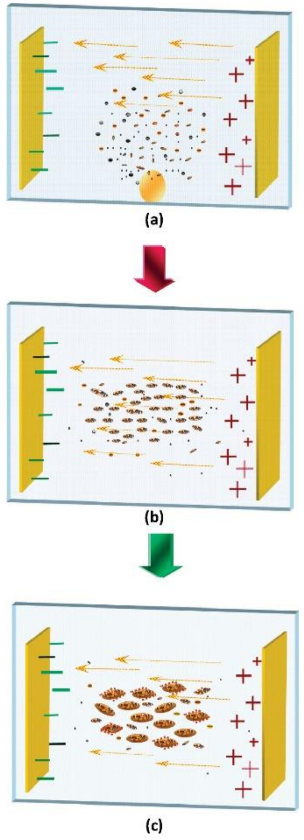


- Using **electrical field assisted laser ablation in liquid** (EFLAL), CuO nanocrystals are obtained in water and sequentially assembled into **CuO nanospindles**

https://doi.org/10.1021/jp907237q







UNCONVENTIONAL AND METASTABLE STRUCTURES

V. Amendola
University of Padova
DiSC

LSPC enables the easy access to a library of uncommon or metastable materials, sometimes otherwise inaccessible

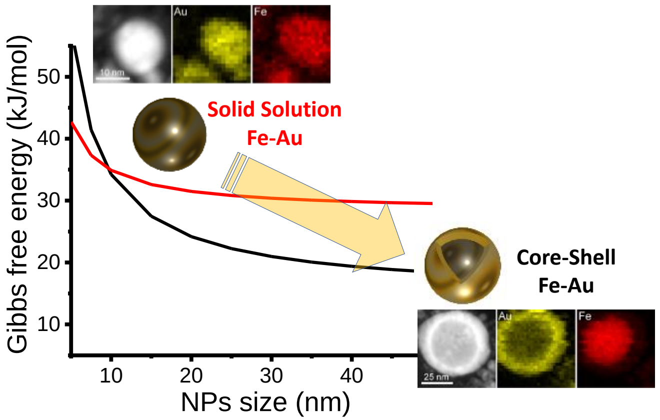
Unconventional shapes

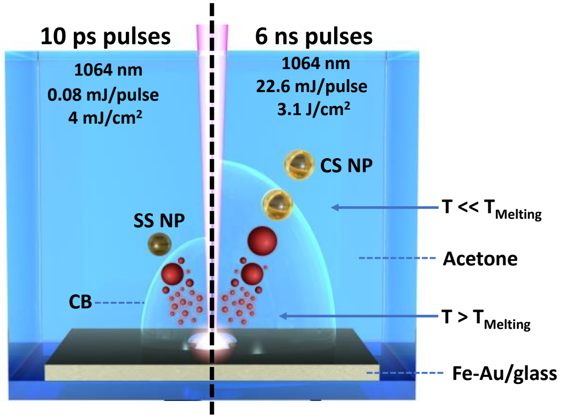
- The **thermodynamic driving force to minimization of surface and interface energy** can be exploited to produce colloidal **Fe–Au core–shell nanoparticles in one step** and with a yield approaching **99.7% in mass**
- This is obtained by laser ablation with nanosecond pulses of thin bimetallic films immersed in acetone
- The Fe–Au core–shell nanoparticles show magnetic and plasmonic properties, and a surface available to bioconjugation and analytical assays

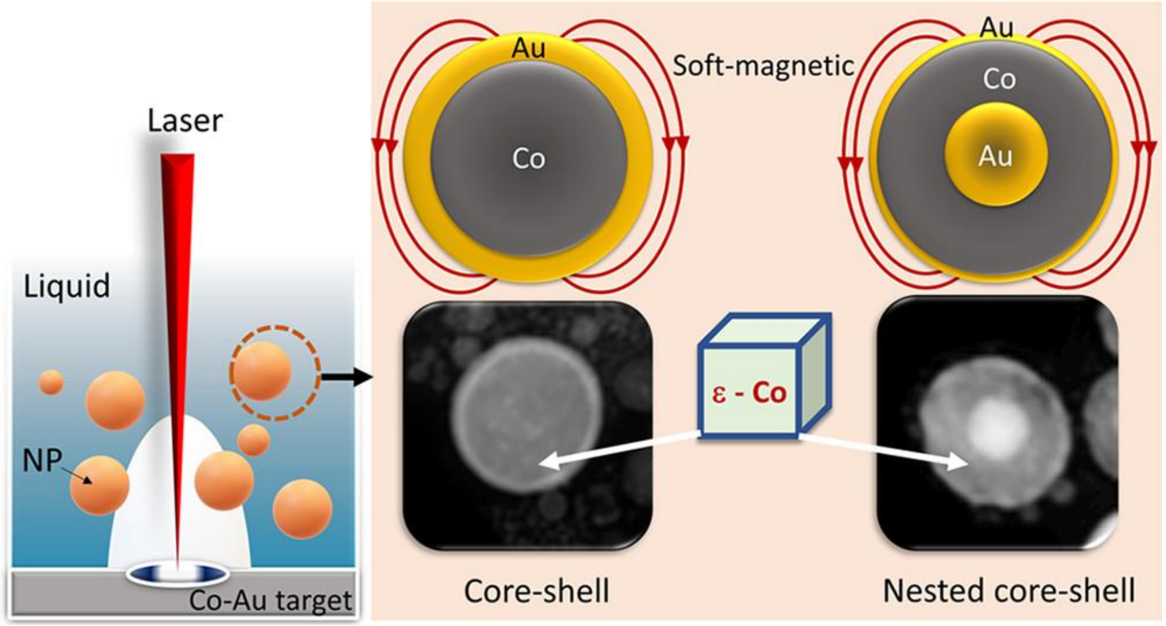
https://doi.org/10.1039/C9NH00332K

- laser ablation in liquid fabricateted colloidal **Co–Au core-shell NPs with core–shell yields up to 78% in mass**
- Presence of a unique nested core–shell structure with a very thin gold-rich shell, a nanocrystalline ε-cobalt sublayer, and a nested gold-rich core

https://doi.org/10.1021/acs.jpcc.1c02138





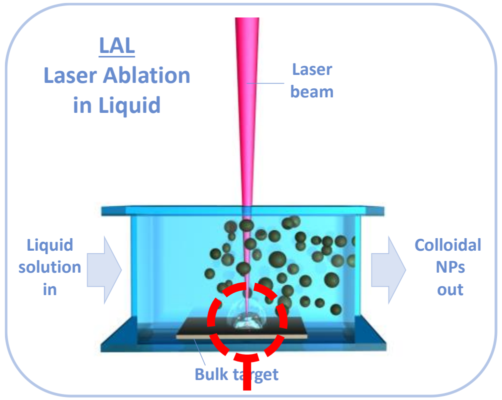


UNCONVENTIONAL AND METASTABLE STRUCTURES

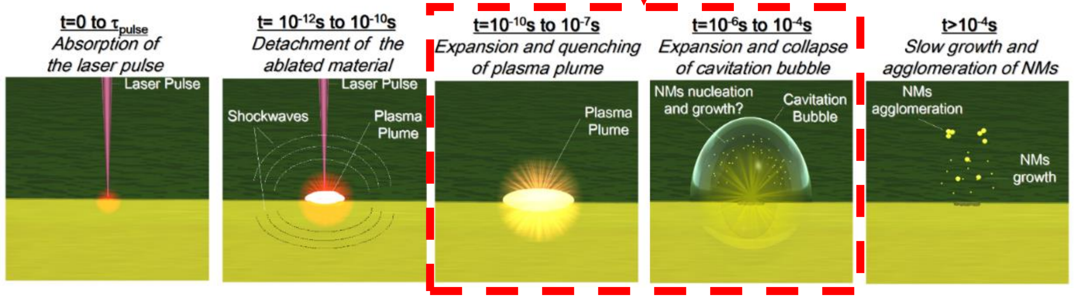
V. Amendola
University of Padova

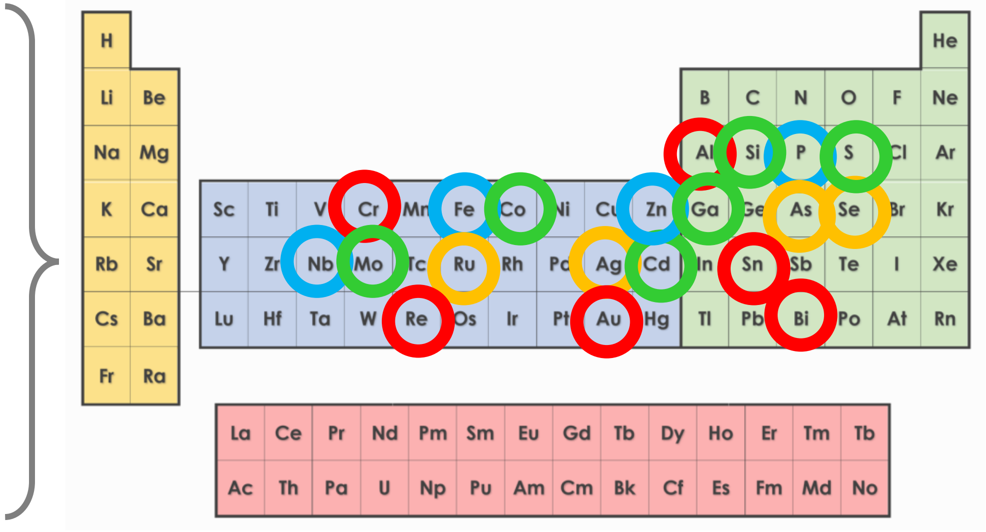
LSPC enables the easy access to a library of uncommon or metastable materials, sometimes otherwise inaccessible

Nanoalloys for plasmonics, catalysis, nanomedicine, etc.



Timeline of LAL





The **rapid dynamics of LAL and other LSPC methods** have proven compatible with the mixture of immiscible elements, opening up countless possibilities in the field of nanoalloys

https://doi.org/10.1117/12.3005137

https://doi.org/10.1002/cphc.202200136

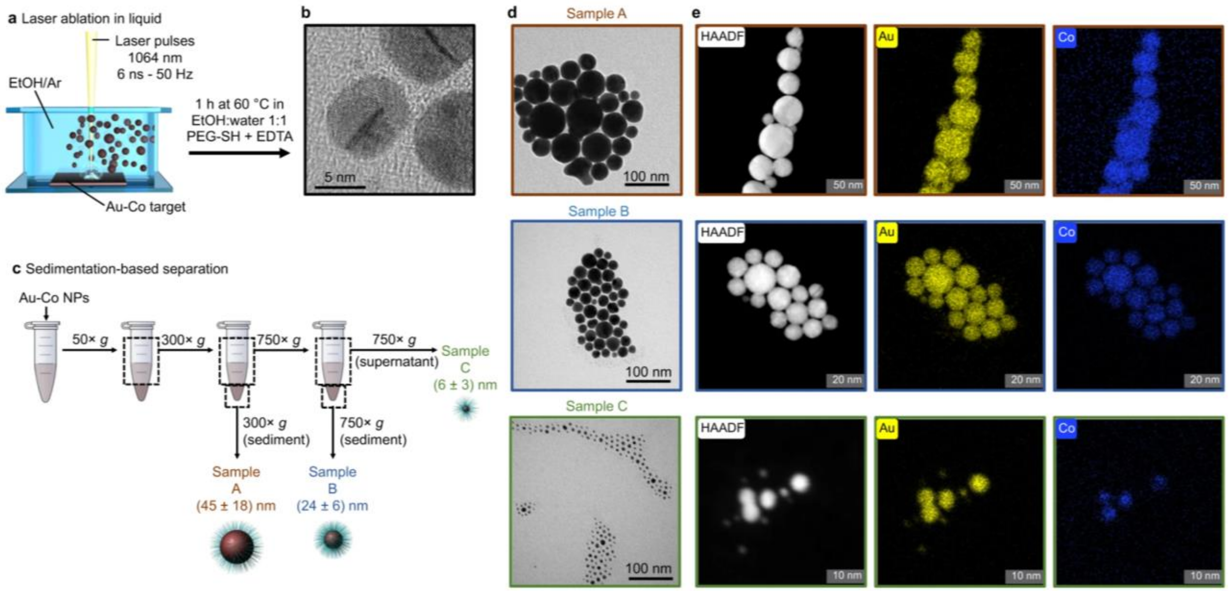
V. Amendola
University of Padova

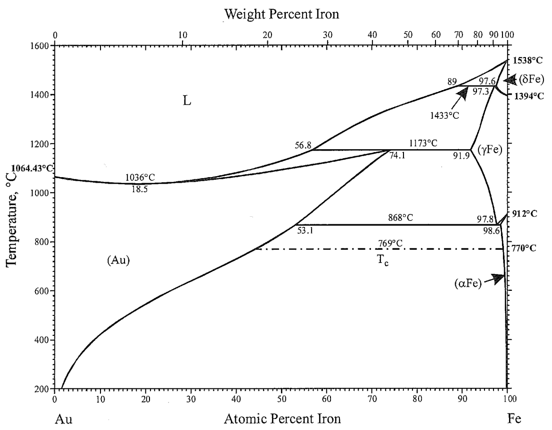
LSPC enables the easy access to a library of uncommon or metastable materials, sometimes otherwise inaccessible

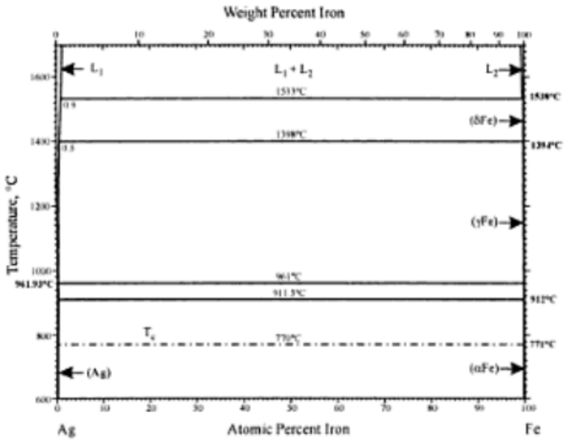
Nanoalloys for plasmonics, catalysis, nanomedicine, etc.

- Accurate calculation and conceptual understanding of the optical properties of metastable alloys of both **plasmonic (Au) and magnetic (Co, Fe)** elements obtained through a tailored laser synthesis procedure

https://doi.org/10.1038/s41467-024-45137-x
https://doi.org/10.1021/acs.nanolett.9b02396

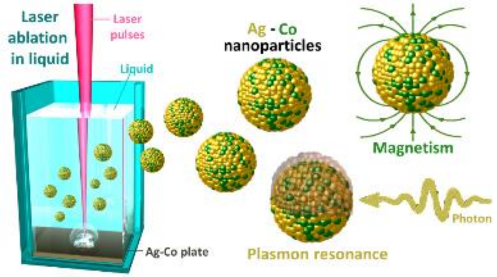


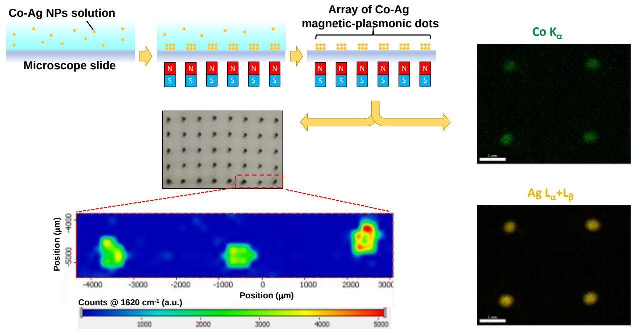




Au-Fe (Au-Co) Phase Diagram
SS Kinetically stable

Fe-Ag (Co-Ag) Phase Diagram
SS NOT even kinetically stable





- LAL of **magnetic-plasmonic Ag-Fe and Ag-Co NPs**

https://doi.org/10.1016/j.jcis.2020.11.089
https://doi.org/10.1039/c9na00143c

UNCONVENTIONAL AND METASTABLE STRUCTURES

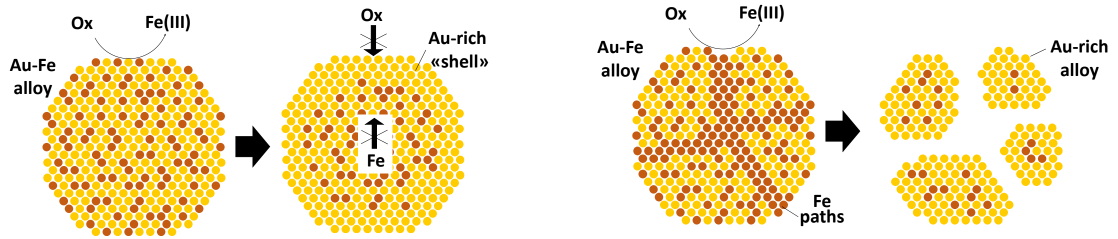
V. Amendola
University of Padova

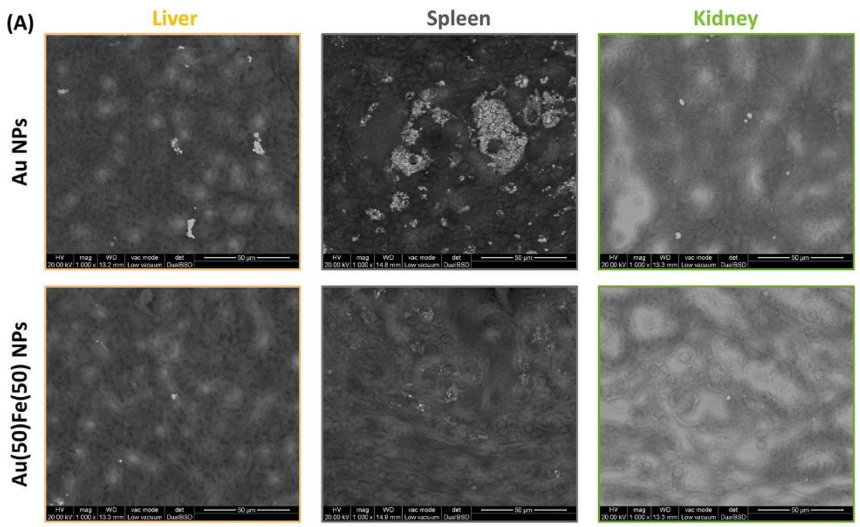
LSPC enables the easy access to a library of uncommon or metastable materials, sometimes otherwise inaccessible

Nanoalloys for plasmonics, catalysis, nanomedicine, etc.

- LAL generated **nonequilibrium gold–iron alloys behaving as shape-morphing "4-D" nanocrystals** with the properties of **self-degradable** multifunctional nanomedicines

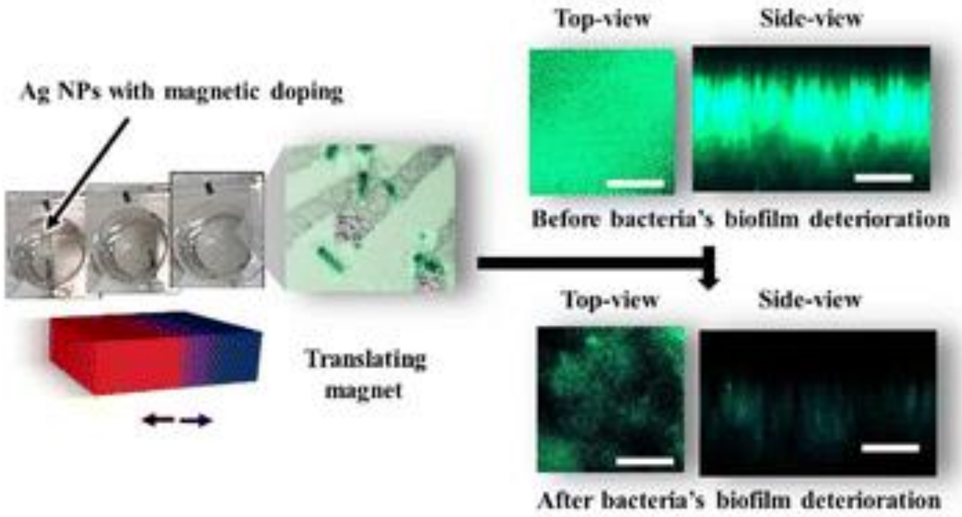
https://doi.org/10.1021/acsnano.0c03614





- Antimicrobial formulations should combine toxicity for bacteria, biofilm permeation ability, biofilm deterioration capability, and tolerability by the organism without renouncing compatibility with a sustainable, low-cost, and scalable production route as well as an acceptable ecological impact after the ineluctable release in the environment
- **Silver NPs doped with magnetic elements (Co and Fe)** allowed the standard silver antibacterial agents to **perforate bacterial biofilms through magnetophoretic migration** upon the application of an external magnetic field

https://doi.org/10.1039/D2NR03902H



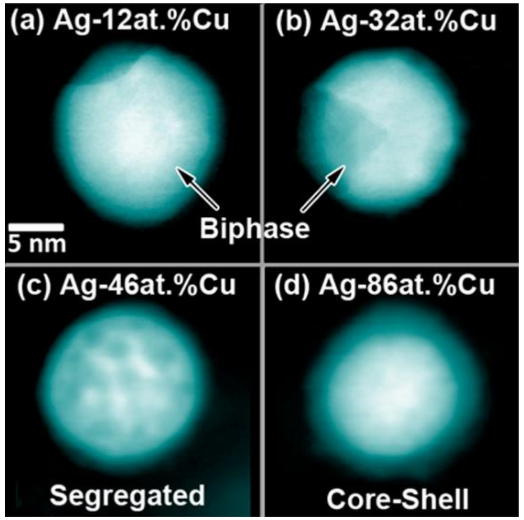
V. Amendola
University of Padova
DiSC

LSPC enables the easy access to a library of uncommon or metastable materials, sometimes otherwise inaccessible

Nanoalloys for plasmonics, catalysis, nanomedicine, etc.

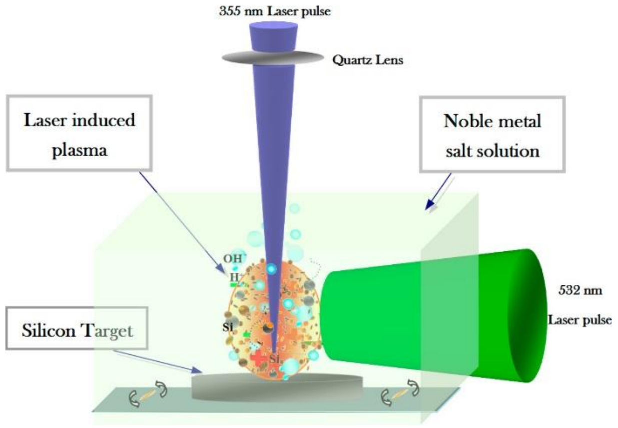
- **Ag–Cu alloy nanoparticles** of four different compositions obtained by the laser ablation technique with the target under aqueous medium
- A morphological transition in the **nanoparticles from a normal two-phase microstructure to a structure with random segregation and finally a core–shell structure** at small sizes as a function of Cu concentration
- The results could be rationalized through the thermodynamic modeling of free energy of phase mixing and wettability of the alloying phases.

https://doi.org/10.1021/jp502327c



- Fabrication of **Si/Au Core/Shell Nanoplasmonic Structures** with Ultrasensitive Surface-Enhanced Raman Scattering for Monolayer Molecule Detection by reactive LAL

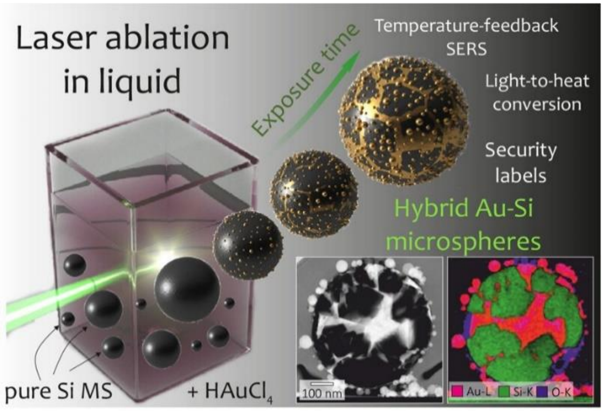
https://doi.org/10.1021/jp5111482



- Multigram-Scale Production of **Hybrid Au-Si Nanomaterial by Laser Ablation in Liquid** (LAL) for Temperature-Feedback Optical Nanosensing, Light-to-Heat Conversion, and Anticounterfeit Labeling

https://doi.org/10.1021/acsami.2c18999

https://doi.org/10.1021/acsanm.4c01289



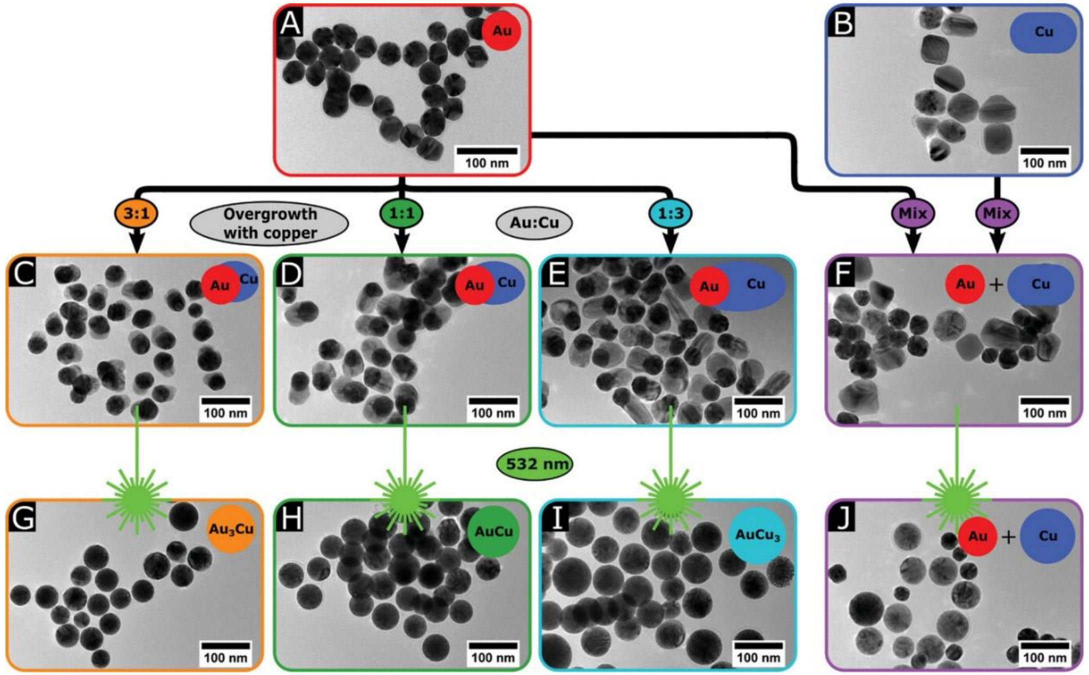
V. Amendola
University of Padova

LSPC enables the easy access to a library of uncommon or metastable materials, sometimes otherwise inaccessible

Nanoalloys for plasmonics, catalysis, nanomedicine, etc.

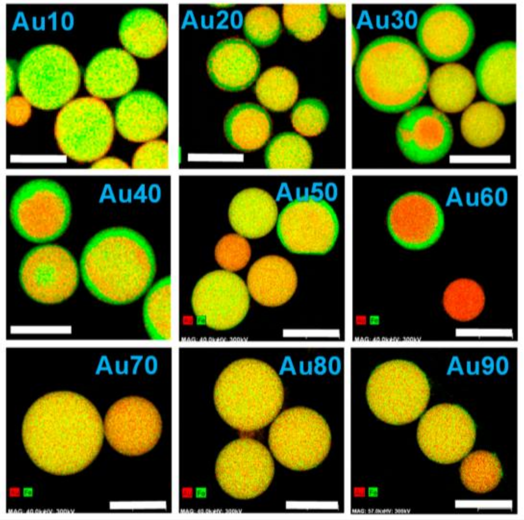
- After preparing **Au–Cu** hetero nanoparticles by wet-chemical synthesis, nanoalloys with previous adjusted composition can be formed by **postsynthesis laser treatment**

https://doi.org/10.1002/ppsc.202300021



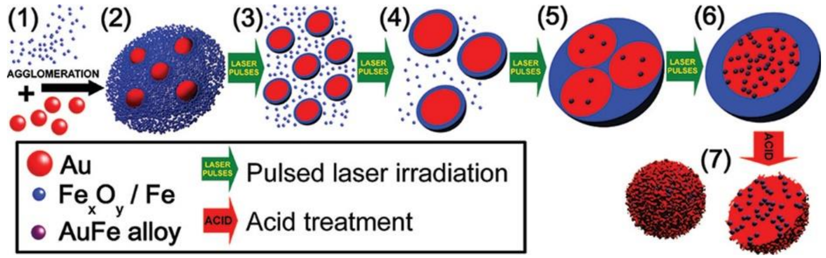
- **Submicrometre spherical particles made of Au and Fe can be fabricated by pulsed-laser melting in liquid** (PLML) using a mixture of Au and iron oxide nanoparticles as the raw particles dispersed in ethanol using a 355 nm pulsed laser

https://doi.org/10.3390/nano9020198



- **Au-based** submicrometer-sized spherical particles with uniform morphology/size and **integrated porosity-magnetic property** in a single particles are synthesized by a two-step LML and acid treatment

https://doi.org/10.1021/la2038334

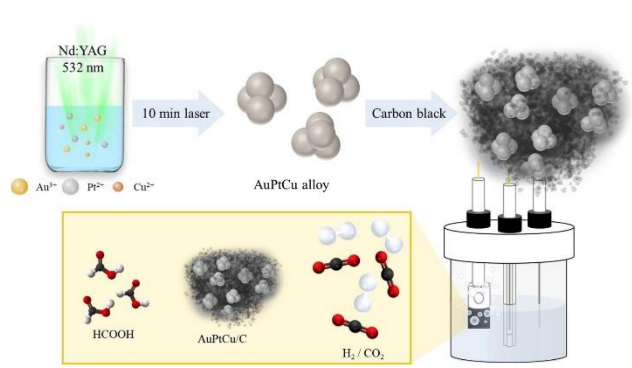


V. Amendola
University of Padova

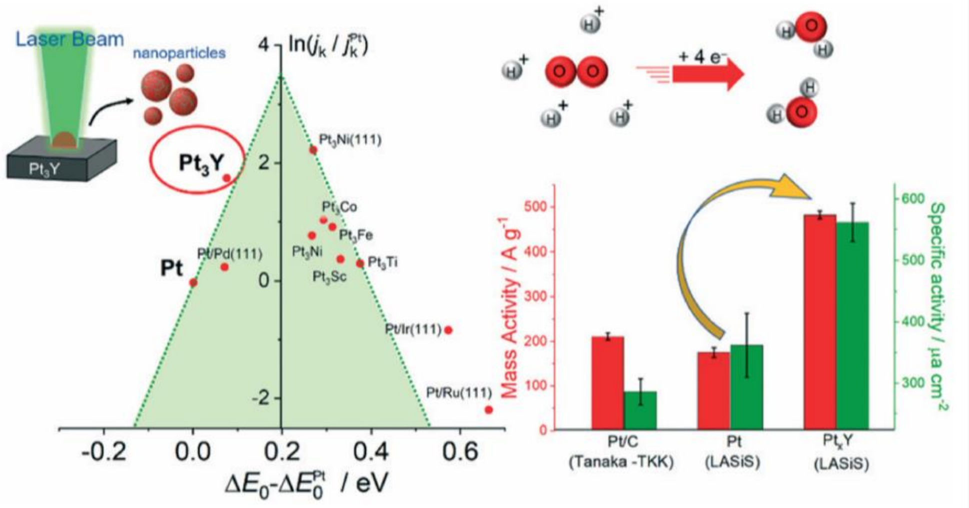
LSPC enables the easy access to a library of uncommon or metastable materials, sometimes otherwise inaccessible

Nanoalloys for plasmonics, catalysis, nanomedicine, etc.

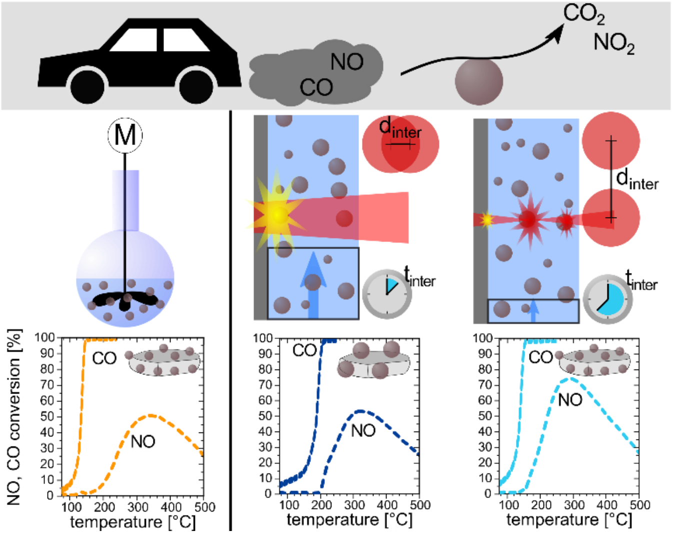
Pulsed laser-driven green synthesis of trimetallic **AuPtCu** nanoalloys for formic acid electro-oxidation in acidic environment
https://doi.org/10.1016/j.fuel.2022.126164



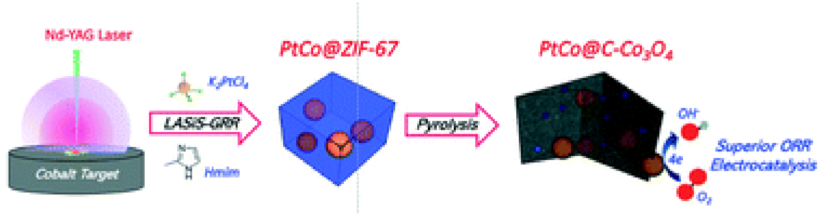
Climbing the oxygen reduction reaction volcano plot with laser ablation synthesis of Pt_xY nanoalloys
https://doi.org/10.1039/D0CY00983K

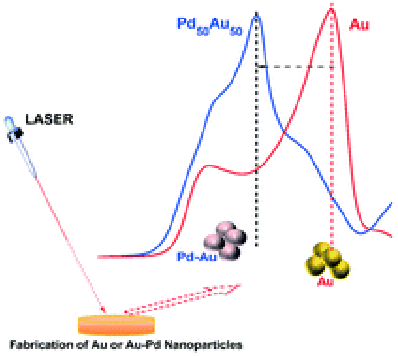


Pt-Pd NPs cope with the industrial gold standard catalyst
https://doi.org/10.3390/nano10081582



MOF-derived **PtCo/Co3O4** nanocomposites in carbonaceous matrices as high-performance ORR electrocatalysts synthesized via laser ablation techniques
https://doi.org/10.1039/D0CY02099K





Bare laser-synthesized **Pd-Au** alloy nanoparticles as efficient electrocatalysts for glucose oxidation for energy conversion applications
https://doi.org/10.1039/D0CY01323D

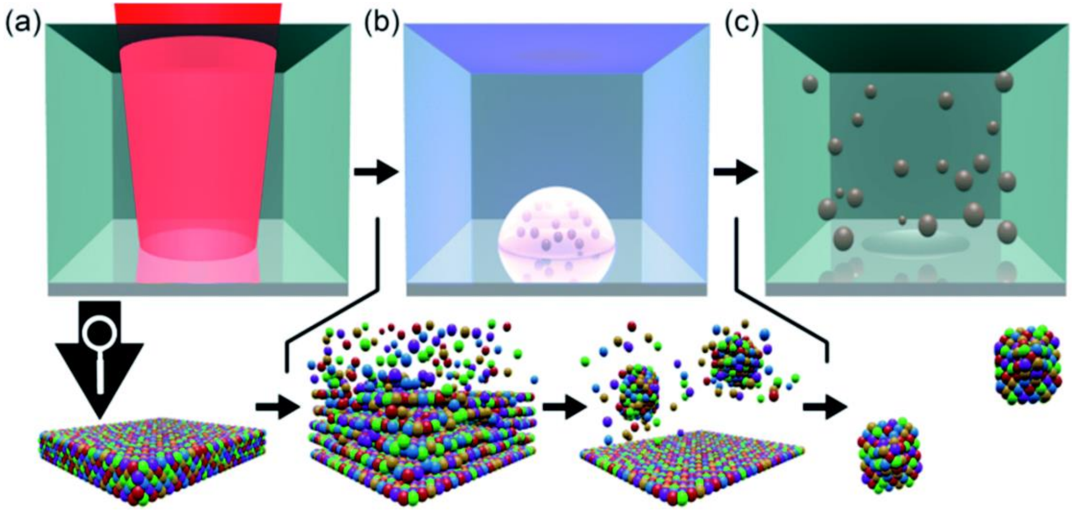
V. Amendola
University of Padova

LSPC enables the easy access to a library of uncommon or metastable materials, sometimes otherwise inaccessible

Nanoalloys for plasmonics, catalysis, nanomedicine, etc.

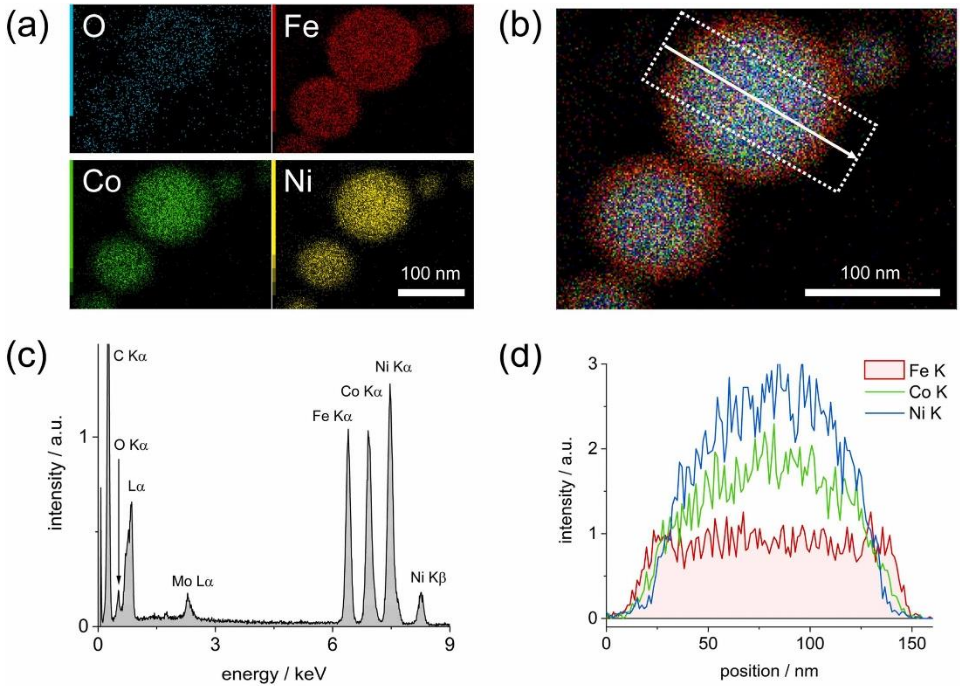
- Single-step synthesis of colloidal **CoCrFeMnNi HEA** nanoparticles with targeted equimolar stoichiometry and diameters less than 5 nm by liquid-phase, ultrashort-pulsed laser ablation of the consolidated and heat-treated micropowders of the five constituent metals
- Productivity of 3 grams of colloidal HEA nanoparticles per hour
- Laser synthesis is the only room temperature synthesis that gives access to HEA NPs with their composition freezed by kinetic control

https://doi.org/10.1039/C9RA03254A

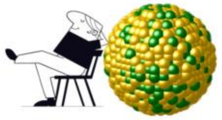


- **FeCoNi** medium-entropy alloy-core Fe-shell nanoparticles produced from equiatomic target by LAL
- Chain-like superstructures of spherical nanoparticles formed by overstriking ablation
- Ni-rich nanoparticles originating in UV ultrashort laser pulse ablation

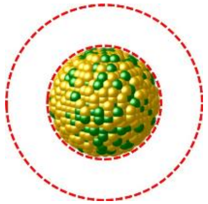
https://doi.org/10.1016/j.jallcom.2023.169896



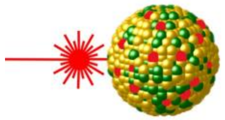
V. Amendola
University of Padova



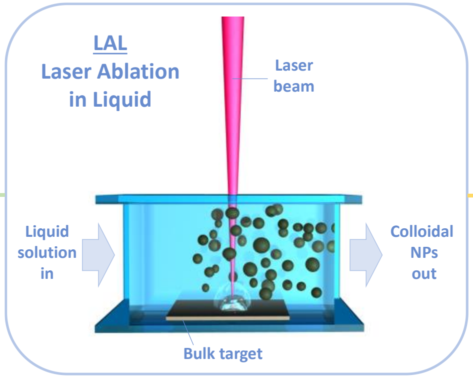
AUTOMATIC AND SCALABLE SYNTHESIS

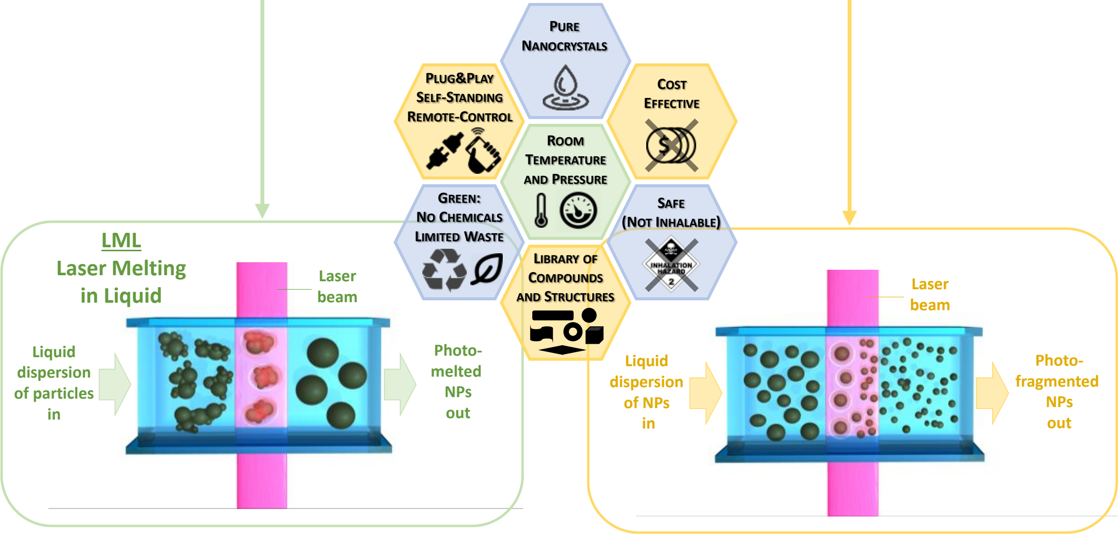


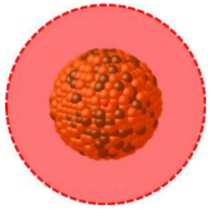
PURITY AND STERILITY



DEFECT ENGINEERING

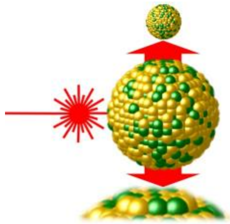




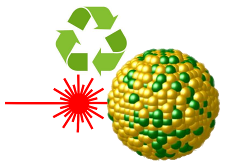


INCLUSION IN A MATRIX OR MIXTURE

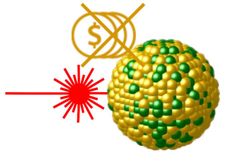
UNCONVENTIONAL STRUCTURES



SIZE TUNEABLE WITH LASER PULSES



GREEN SYNTHESIS AND GREEN PRODUCTS



COST AFFORDABLE

LASP
www.chimica.unipd.it/lasp

V. Amendola
University of Padova

DiSC

Università di Padova
Prof. Denis Badocco
Prof. Stefano Agnoli

CNR-ICMATE
Dr. Daniel Forrer
Dr. Luca Nodari

San Raffaele Hospital
Dr. Antonello Spinelli
Dr. Riccardo Vago

University of La Plata
Dr. David Muneton A.
Prof. Marcela F. Van Raap

Thomas Reffatto
Riccardo Biso
Clara Goncalves de Faria
Michael Bissoli
Jaurel Kagho
Maria Assunta Lacavalla
Runpeng Miao
Sara Cazzola
Lorenzo Demuru
Giulia Spataro
Julia Voss
Vito Coviello

Federico Pini
Giuliano Coletta
Andrea Guadagnini
Veronica Torresan
Arianna Fabris
Arianna Palumbo
Carlo Bravin
Matteo Moretto
Enrico Rossi
Michele Mariz
Stefano Scaramuzza
Annamaria Poletti

nanomaterials@mdpi.com
nanomaterials
an Open Access Journal by MDPI

MDPI OPEN ACCESS

IMPACT FACTOR 5.719
CITESCORE 6.6

Special Issue

"Innovative Biomedical Applications of Laser-Generated Colloids"

Guest Editor: Prof. Dr. Vincenzo Amendola
Website: https://www.mdpi.com/journal/nanomaterials/special_issues/VU7JS241N3
Deadline for manuscript submissions: **END OF 2023 TO 2024**

DISCOUNTS AVAILABLE
ON ARTICLES PROCESSING FEE FOR THIS SPECIAL ISSUE

University of Verona
Prof. Pasquina Marzola
Dr. Alice Busato
Dr. Giulio Fracasso

University of Pavia
Prof. Silva Bortolussi
Dr. Ian Postuma
Prof. A. Lascialfari
Prof. Paolo Ghigna

University of Belgrade
Dr. Marina Bekic
Prof. M. Colic

Funding:

MUR PRIN 2022 PNRR
PRIN-PNRR

AIRC
AIRC – MFAG 2021-ID. 25681

Università degli Studi di Padova
Internationalization Funds PRAT – P-DiSC

STARS UNIPD
STARS

Ministero dell'Istruzione Università e Ricerca
FFABR PRIN-PNRR

Farnesina
Ministero degli Affari Esteri e della Cooperazione Internazionale
Great Relevance Projects