

Vincenzo Amendola  
Dipartimento di Scienze Chimiche  
Università di Padova  
vincenzo.amendola@unipd.it

## LASER ABLATION SYNTHESIS IN SOLUTION (LASIS) OF FUNCTIONAL NANOPARTICLES

*LASIS showed a great potential as a cost-competitive and green technique for obtaining easily functionalizable nanoparticles and complex nanostructures in solution, hence it is an interesting alternative to wet chemistry methods for the synthesis of functional nanoparticles.*

**T**he role of nanoparticles (NPs) in nanoscience and nanotechnology is well known and ranges from catalysis to photonics, from photovoltaics to electronics, from bioanalytics to nanomedicine. In the last decades, considerable research efforts have been directed towards the study of NPs properties, their structure-properties relationship and the development of efficient synthetic procedures. These efforts produced striking results and the bottom up approach of wet chemistry emerged as one of the most power-

ful methods for the synthesis of NPs [1]. However, some issues about the synthesis of NPs are still waiting for a fulfilment. These issues principally deals with the reproducibility of the synthetic methods, the functionalization of nanoparticles and the problems related to byproducts of the synthesis [1].

The problem of reproducibility is intrinsic in the bottom-up wet chemistry methods, because they are a wide ensemble of different procedures for the synthesis of NPs. Consequently, even a slight difference in the struc-

ture of NPs may require a drastic variation of the synthetic procedure, as it happens in the synthesis of gold nanoparticles coated with different types of surface ligands [1].

A general feature of these methods is that crystal growth stops when the mechanism of growth limitation prevails. In wet chemistry methods, crystal growth is in competition with surface conjugation by ligands. Therefore, the surface of NPs is coated with a dense layer of ligands, that also play an important role for the stability in solution of particles. The type of surface ligands has a great importance for the final product of the synthesis, since ligands influence particles size, size dispersion, shape, and, sometimes, the phase and the quality of crystal order. Most surface stabilizers are strongly bound to nanoparticles and further functionalization of NPs can be really difficult. Surface functionalization of NPs is the most important step for many applications, because it can add new properties like solubility, selective targeting or labelling abilities. Usually, functionalization is carried out in two ways: *i)* by using stabilizers with chemical groups that allow the conjugation of the desired molecules by chemical reactions after particles synthesis; *ii)* by place exchange reactions between the stabilizers and the functional molecules. Both are complex because they require the accurate refinement of the experimental conditions and, most important, they do not favour the multifunctionalization of the same particle with different functionalities. In other cases, the stability of NPs in solution can be the main difficulty to overcome for obtaining surface functionalization. Furthermore, ligands and synthesis byproducts can have undesired effects for the real application of NPs, like toxicity, poisoning of catalytic activity or degradation of optical and electronic properties. On the one hand, synthesis byproducts can be removed by purification procedures, that is like to say that their undesired effects cause larger costs and environmental concerns. On the other hand, ligands are indispensable for the stability of NPs and sometimes they are chemically bound to NPs surface, therefore they cannot be removed from particles in many cases.

It is worth to point out also that, in last years, the research about the synthesis of NPs faced a new ambitious targets, namely the development of a "sustainable nanotechnology", that is considered necessary for NPs to cross from science to applied technology [2]. The use of environmental harmful chemicals and the production of pollutant byproducts are common drawbacks in wet chemistry approaches for the synthesis of NPs. Consequently, large scale applications of nanoparticles can be hampered by high costs for waste disposal according to environmental regulations, in addition to the costs for chemicals supplies and chemical lab equipments.

The laser ablation synthesis in solution (LASiS) is an alternative to wet chemistry method for the synthesis of NPs [3]. LASiS is a top-down physical method consisting in the laser ablation of a solid target dipped in a solution for obtaining nanostructured materials as a colloidal suspension. The main formation mechanism of NPs consists in condensation of the plasma plume generated by laser irradiation of the solid target. The so obtained NPs are highly available for further functionalization or can be used wherever unprotected nanoparticles are desired. NPs with com-

plex nanostructures can be obtained by chemical reactions between the ablated material and the solvent or the solutes.

By using a physical technique for the synthesis of NPs, some of the above recalled disadvantages of wet chemistry methods are avoided. The main point is that LASiS can be a unique approach for the synthesis of a variety of nanomaterials in a variety of solvents in the presence of a variety of solutes [3, 4]. Moreover, LASiS does not necessarily require any chemicals and does not necessarily produce waste, that is LASiS is usually compatible with the 12 principles of green chemistry [2, 3]. Manual operation and the experimental set up of LASiS are minimal [3, 4]. When LASiS is used for the synthesis of noble metal nanoparticles, one step functionalization as well as multifunctionalization are straightforward, since the functional molecules can be simply added to the colloidal solution. Furthermore, laser irradiation after LASiS has been demonstrated as an effective technique for the chemical-free size control of noble metal nanoparticles [3]. On the other hand, not all the advantages of the synthesis by wet chemistry are retained by LASiS. In particular, the control on particles size and size distribution is lower and the control of particles shape at nanoscale was not obtained by LASiS until now. Most important, LASiS is a smart technique for the production of NPs on the gram scale, but the scalability to mass production of NPs is not straightforward and requires a careful evaluation of costs in comparison to wet chemistry methods, due to the need for laser sources.

These aspects are discussed with more details in the following sections.

## Technical outline of LASiS

Laser ablation is a well known technique in various technological areas like mass spectrometry by matrix assisted laser desorption ionization (MALDI-MS), thin film fabrication by pulsed laser deposition (PLD) in ultra-high vacuum chambers, material processing and patterning for microelectronics or tissues removal in surgery. The application of laser ablation to the synthesis of nanostructures in liquids is dated to the early Nineties, thanks to the pioneering work of A. Henlgein [5].

The experimental set up for LASiS is simple, which is a strength point of

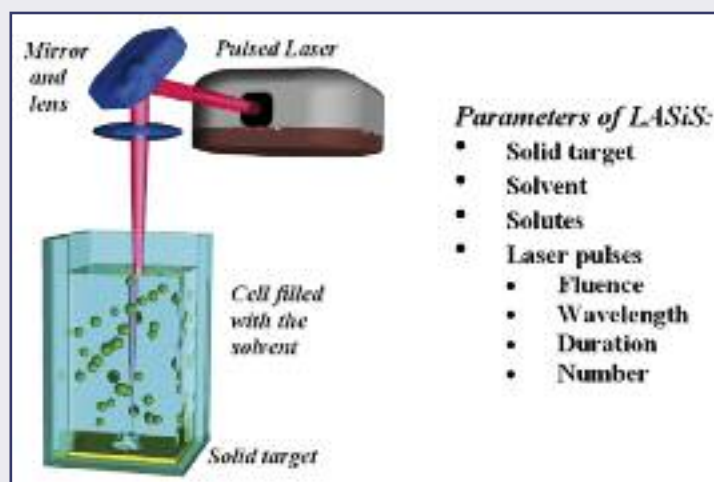


Fig. 1 - The principal components of the experimental set up for LASiS with a list of its main parameters

# CRITICAL REVIEWS

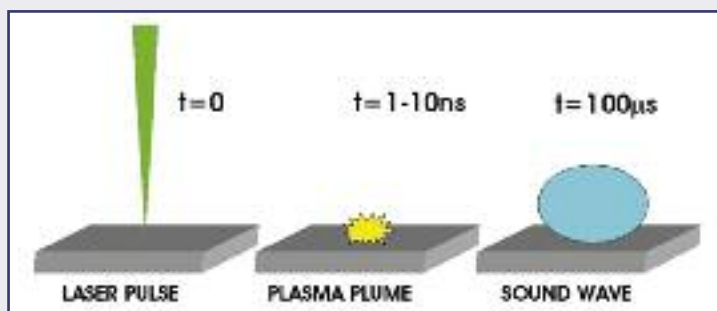


Fig. 2 - Cartoons sketching the main stages of the ablation process after laser pulse arrival (time  $t=0$ ), that are the formation of a plasma plume (from few ps to tens of ns) and a sound wave expansion (time scale of hundreds of  $\mu$ s)

this technique. It consists in a pulsed laser, a set of focusing optics and a cell containing the solid target and the liquid solution (Fig. 1). The main parameters of LASiS, that will be discussed in the following, are the target material, the solvent type, the solutes type and the ablation parameters (duration, wavelength, fluence and frequency of laser pulses) [3].

The only relevant cost is the laser source, that requires some thousands euros for a compact instrument with output energy appropriate for obtaining LASiS. However, such lasers are present in many research laboratories for other applications. Some authors reported the use of target scanning systems and fluxed cells for intensive NPs production. In other cases, sealed cells have been used for LASiS in controlled atmosphere and in volatile or in toxic solvents. LASiS has been obtained with fs, ps, ns and even ms pulses at wavelengths from the near infrared to the near ultraviolet and in a wide range of fluence between hundreds of  $\text{mJ}/\text{cm}^2$  to thousands of  $\text{J}/\text{cm}^2$ , though the results about NPs synthesis are strongly affected by pulse parameters.

Laser ablation at solid/gas and solid/vacuum interfaces has been investigated much deeper than at solid/liquid interfaces. Consequently, the mechanism of NPs formation by LASiS is not completely clear. Further understanding of these processes is necessary to get the best performances by LASiS and to overcome present limitations of this technique. Until now, the molecular dynamics simulations and experimental studies about laser ablation at solid liquid interfaces provided a qualitative or a semi quantitative description of the ablation process but did not provide the indications necessary to a refined control over NPs synthesis [4, 6, 7]. This is also a consequence of the strong variability of LASiS results when changing the ablation parameters. Indeed, the Italian scientific background in theoretical and experimental aspects about PLD and MALDI-MS is excellent, as well as about the physics and chemistry of plasmas, hence we believe that useful indications can come out in the future by collaborations with groups working in these and other related areas.

Some general characteristics about LASiS emerged in these years. First of all, laser fluence must be high enough to produce a plasma plume on the target in order to obtain NPs by LASiS [3, 4]. The formation of a plasma plume expanding in the liquid is accompanied by the formation of a sound wave propagating in the liquid, also called cavitation bubble (Fig. 2). The formation of the cavitation bubble due to solvent vaporization during the ablation process attracted the attention of many scientists

active in this field, because it strongly interferes with the ablation rate and with the homogeneity of the products [4]. Spectroscopic investigations by streak cameras and shadowgraphic investigations, together with molecular dynamics simulations, provided useful informations about the basic dynamics of these processes in liquids [4, 8]. The plasma plume duration is in the range of few nanoseconds to tens of nanoseconds, depending on laser fluence and pulse duration, while the expanding sound wave duration is in the range of hundreds of microsecond. One must point out that the presence of the liquid induce a quenching of the plasma plume one order of magnitude faster than for laser ablation in vacuum or in low pressure gases, as well as the sound wave expanding in the liquid induces a relevant density modification around the target. Moreover, the liquid produces a strong confinement at the plasma plume, that is compressed on the target, with the consequence that the interaction of the plasma with the target is stronger than for laser ablation in gases or vacuum [9-11].

Additional ablation mechanisms other than plasma plume formation can be the ejection of melted drops or solid fragments due to boiling and/or photoionization and consequent Coulomb explosion of the target [3, 9-11], that are relevant at high fluence or with ultrashort laser pulses. The morphology of the ablation craters is indicative of what is the prevailing mechanism, because explosive processes originates rugged craters [9-11]. Since high ablation rates are obtained by high fluences, explosive mechanisms are frequent in LASiS of NPs.

The use of laser pulses with duration in the nanosecond regime or longer can be useful for improving the phase homogeneity of the ablated material. Energy conversion from incident laser radiation to the heat in the target happens on the time scale of thermal relaxation in solid state, that is few picoseconds [3]. Experimental and theoretical studies confirmed that plasma plume begins few ps after that laser irradiation starts. Therefore, ns or longer pulses overlap effectively with the ablation process, whereas overlap is absent for ps or shorter pulses. Some authors suggested

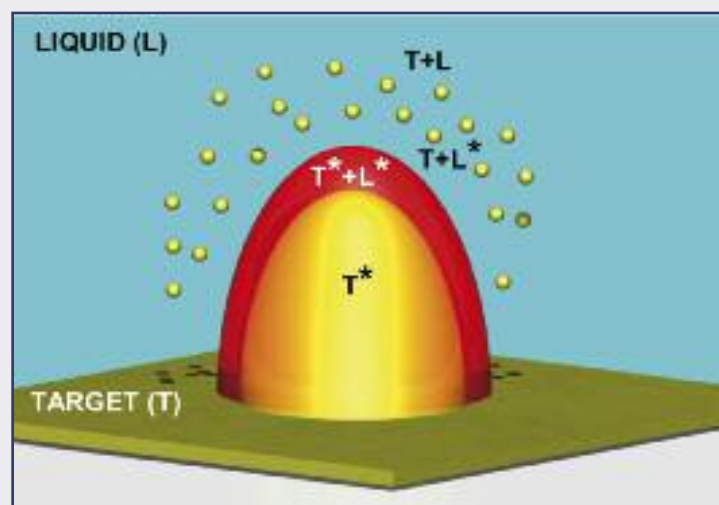


Fig. 3 - Sketch of the plasma plume formed by laser ablation of a solid target. Four principal combination of solution and target species can be identified due to different distribution of temperature, pressure and composition in space and time. The \* denotes excited and/or ionized states

that laser irradiation of the ablated material, occurring with ns pulses, improves the vaporization of the ejected material, explaining why NPs obtained by ns pulses often show sharper size distributions than particles obtained with shorter pulses [3, 9-11].

Laser wavelengths in the near infrared are sometimes preferred for avoiding the reabsorption of laser pulses by NPs, that is especially probable with pulses in the near ultraviolet or when NPs have strong absorption bands like Ag and Au NPs. This process can produce a broadening of the size distribution of NPs.

When LASiS is carried out with ordinary energies, NPs are obtained by a nucleation and growth mechanism during plasma cooling [3, 4]. The growth mechanism is fed by the diffusion of vaporized target atoms and by the coalescence of particles embryos in solution, that last hundreds of nanoseconds after the laser pulse. The coalescence mechanism is a relevant process, because NPs obtained by LASiS are prominently polycrystalline. LASiS proved to be useful also for obtaining NPs with metastable phases because nucleation and growth of NPs are fast processes that occur out of equilibrium, when temperature and pressure are much higher than in ambient conditions [4].

The atomic density and composition, the pressure and temperature in the plume determine the structure and the size of NPs obtained by LASiS. Unfortunately, all these parameters are not constant in time neither uniform in space in the LASiS process, because two boundary regions exist between the plasma plume and the surrounding liquid or the metal target. Moreover, the expansion of the plume in the liquid buffer produces a concentration gradient of atomic and molecular species from the solution, that is complementary to the concentration gradient of target atoms. One can identify four class of species involved in particles formation (Fig. 3) [3, 4]: species coming from the target or from the solution at high temperature and pressure or at ordinary temperature and pressure. Where the concentration of target species is dominating during particles formation, as it happens in the inner part of the plasma plume, the formation of NPs with same composition of the target is favoured. If both target and solution species are present at high temperature and pressure, as it happens at the boundary between the expanding plume and the liquid, new chemical reactions may happen, producing NPs with a different composition from the target. When NPs have already formed in solution, only particles surface can be affected by chemical reactions with solution species.

When LASiS is carried out with high energy laser pulses, explosive mechanisms are present and particles formation by ejection of melted drops or hot solid fragments should be also considered.

The highly ionized conditions experimented in the plasma and the likelihood of chemical reactions with ionized solution species favour the surface charging of NPs obtained by LASiS [3, 4, 12, 13]. Consequently, LASiS basically produces colloidal suspension of charged nanoparticles. It is an important advantage of LASiS, because it allows the synthesis of nanometric particles in the complete absence of surface ligands or stabilizers. Recently, Yang's group experimentally showed that the presence of intense pulsed electric fields during the ablation process can interfere

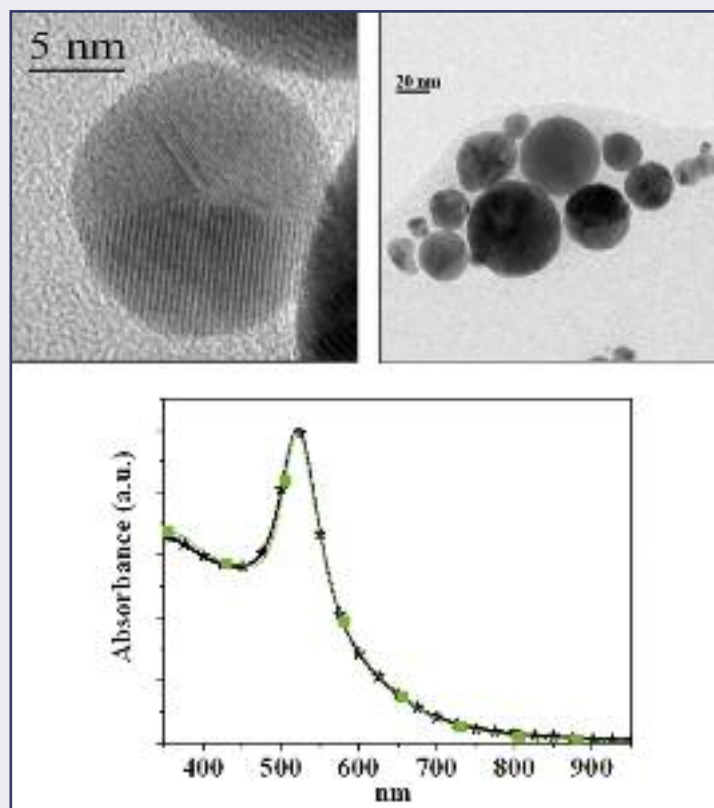


Fig. 4 - Top: Transmission electron microscope images of Au NPs obtained by LASiS in water. Both shows a polycrystalline structure typical of metal nanoparticles obtained by LASiS. Bottom: Typical UV-visible spectra of Au nanoparticles in water. The prevalently spherical shape and the size on the order of tens of nm originates a single sharp plasmon absorption at about 530 nm. The experimental UV-visible spectrum (black stars) is well fitted by the Mie-Gans model (green squares), as described in [15]

with the embryos coalescence process inducing a templating effect that originated acicular instead of spherical particles [14].

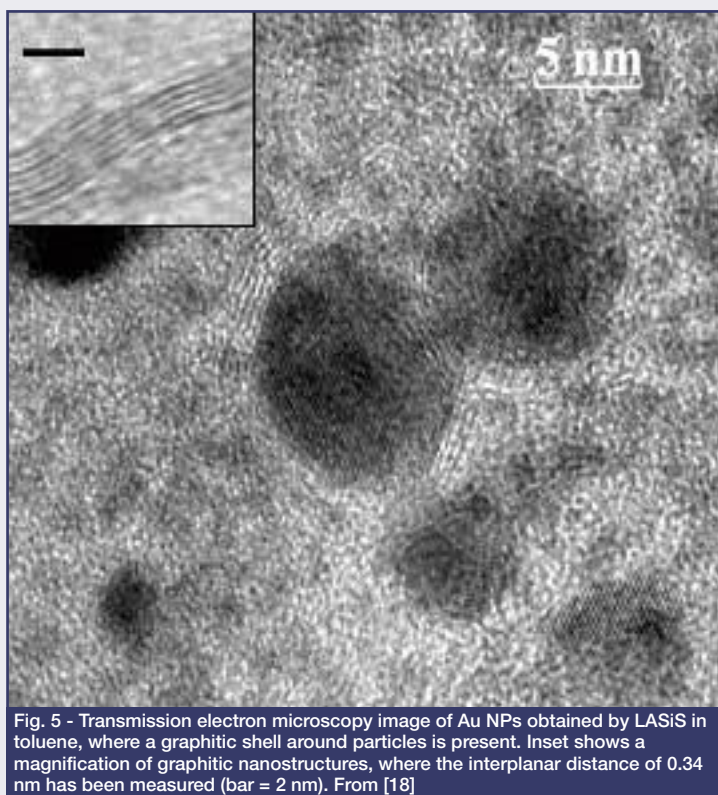
The above considerations suggest that, on the one hand, the formation mechanism of NPs is rather complex and, on the other hand, that LASiS has the potential for the synthesis of a wide variety of nanomaterials with simple or complex structures, that still wait to be fully explored. Some examples of this potential are provided in the next sections.

## LASiS of noble metal nanoparticles

The synthesis of noble metal nanoparticles (NMNPs) like Au, Ag, Pt, Cu and their alloys by LASiS was studied more frequently than for other types of NPs [3]. This may be due to various reasons. The first one consists in the chemical inertness of noble metals in water and other common solvents, which allows the laser ablation synthesis of stable colloidal solutions of NPs. Other reasons are the interesting properties of NMNPs like the presence of an intense absorption band due to the resonance of plasmonic modes, the easy surface chemistry based on surface conjugation by metal-sulfur bonds and the physical and chemical stability (originating the biocompatibility of Au NPs and some catalytic properties of NMNPs) [3].

The size of NMNPs obtained by LASiS is usually between few nm and tens of nm [3]. The shape of NPs is prevalently spherical or slightly spheroidal, although particles aggregation can occur during or after the syn-





thesis when the colloidal system is not sufficiently stable [3]. When a sharp plasmon band is present, like in gold, silver and copper NPs, their characterization can be easily carried out by UV-visible spectroscopy [15]. The plasmon band is sensitive to particles size, shape and composition. For instance, our group developed a simple model for the evaluation of the average size and for a semi-quantitative estimation of the aggregation level by fitting the UV-visible spectrum of Au NPs solution (Fig. 4). The fitting program can be downloaded freely at [www.chimica.unipd.it/vincenzo.amendola](http://www.chimica.unipd.it/vincenzo.amendola).

NMNPs have been synthesized in pure water and in various pure organic solvents [3]. Higher stability has been observed in water, while a significant aggregation takes place in polar organic solvents like alcohols, acetonitrile, tetrahydrofuran, dimethylsulphoxide and dimethylformamide [16, 17]. In general, no stable NMNP solutions have been obtained in pure nonpolar solvents, because the colloidal system is poorly stabilized. In general, one can observe that NPs stability in pure solvents is affected by the metal type, the solvent type and particles concentration. For instance, Au NPs obtained by LASiS in pure water can be indefinitely stable, while they can undergo a rapid precipitation in some organic solvents [3]. For instance, Au NPs obtained in alcohols showed increasing aggregation for increasing length of the solvent aliphatic molecular chain [16]. LASiS in alcohol or other organic solvents is especially useful when direct encapsulation of NPs in a polymeric matrix is desired.

The impurities eventually contained in the solvents can have a strong influence on the stability of nanoparticles. Recently, Compagnini et al. showed that linear carbon chains obtained as byproducts during LASiS can have a important role in affecting the stability of colloidal NMNPs [18].

On the other hand, salts with micromolar concentration or higher can improve NMNPs stability in water by enhancing their net surface charge, as reported in various experimental studies [3, 13]. Some authors also observed that the presence of additives in organic solvents like antiperoxide stabilizers in tetrahydrofuran can enhance particles stability [3]. When LASiS is carried out in liquids that have a poor thermal stability, pyrolysis can take place during the ablation process. This is the case of LASiS of Au and Ag NPs in aromatic solvents like toluene, where metal nanoparticles are obtained embedded in a graphitic shell due to solvent pyrolysis (Fig. 5) [19].

A large number of experimental investigations are devoted to LASiS of NMNPs in the presence of solutes like surfactants or thiolated molecules [3]. Anionic surfactants like sodium dodecyl sulfate (SDS) are effective stabilizers for NMNPs in water and reduce the average particles size because the mechanism of surface coating with SDS competes with the mechanism of particles growth [20-22]. The same behaviour is observed in case of thiolated molecules, with the difference that thiols strongly bind to metal surfaces by chemical bonds. Consequently, thiolated molecules allow a strong reduction of the average size and an effective sharpening of the size distribution of NMNPs obtained by LASiS [23]. In best cases, the standard deviation on the average particles size is of the order of 50% for LASiS in pure solvents and can reach values of the order of 30% or less if coupled with size selection procedures like centrifugation or size exclusion chromatography. However, it can be as low as 10% if strong stabilizing agents are present in solution during LASiS, in a way similar to what happens with the wet chemistry methods [3].

The size and the shape of Au NPs can be controlled also by ligands free techniques based on laser irradiation procedures following the synthesis [3]. In particular, laser irradiation methods that make possible the reduction or the increase of nanoparticles size, even in absence of stabilizing agents or other chemicals, have been developed. These methods exploit the high selectivity of nanosecond laser pulses, due to the fact that photoinduced heating of NPs and thermal relaxation from the particles to the surrounding liquid occur on the same time scale of few nanoseconds [3]. The size reduction method is based on fragmentation by photothermal heating of nanoparticles (Fig. 6a) [24]. We were able to predetermine Au NPs size in a range between 25 and 4 nm by setting the appropriate fluence of the irradiation treatment. The standard deviation was progressively reduced from an initial value of about 60%, (that of AuNP obtained by LASiS) to 20% for 4 nm particles, without the addition of any stabilizer, hence preserving the surface availability for further functionalization. The size reduction was successfully applied also to Au NPs obtained by LASiS in organic solvents. Size reduction of NMNPs has been reported also in the presence of SDS, thiolated ligands and other stabilizers like dendrimers with ns, ps or fs pulses [3, 25, 26]. In these cases, the size of nanoparticles is predetermined by the ligands type and concentration rather than by the irradiation fluence.

The size increase method is based on a two steps process, consisting of a controlled aggregation of nanoparticles and of the following laser irradiation of the solution to obtain photomelting of aggregates into larg-

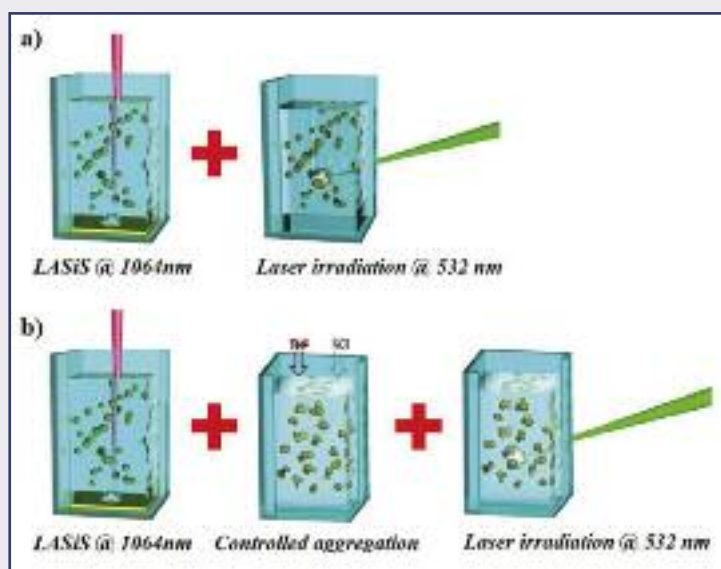


Fig. 6 - Cartoons sketching: a) the size reduction of Au NPs, consisting in the LASiS at 1064 nm and in the following laser irradiation at 532 nm; b) the size increase of AuNP, consisting in the LASiS at 1064 nm, the controlled aggregation of nanoparticles by addition of THF and KCl and the photomelting of aggregates by low fluence laser irradiation at 532 nm

er nanoparticles (Fig. 6b) [24]. We applied this method also to Au NPs obtained by LASiS in organic solvents. Moreover, photoinduced melting of NPs by laser irradiation at low fluence can be a general approach for removing particles aggregation, as demonstrated in water and organic solvents [3].

Photomelting or photofragmentation by laser irradiation has been used also for the synthesis of alloy nanoparticles like Au-Ag, Au-Pd, Ag-Pd and Au-Pt. The complete alloying can be achieved in most cases, while the formation of inhomogeneous or core@shell structures is sometimes observed [27].

## Functionalization of NMNPs

By monitoring protein or DNA integrity during LASiS of Au NPs in water, Pedersen et al. reported that no appreciable degradation of the solutes was observed during the synthesis [28]. Therefore, the insertion of one or more thiolated molecules in the solution can be a straightforward technique for obtaining functionalized NMNPs by LASiS. The functionalization of Au NPs with a fullerene derivative in dimethylsulfoxide, with  $\alpha$ -lipoic acid in acetonitrile and with thiolated oligonucleotides or bovine serum albumin in water have been obtained in this way, as well as conjugation with cyclodextrins in water by electrostatic interactions [17, 28-30].

Moreover, one of the main advantages of LASiS is the ability of obtaining ligands free NMNP in a variety of solvents (Fig. 7) [3]. Therefore, functionalization with desired molecules can be obtained after LASiS, by choosing the solvent suitable for both particles synthesis and molecules solubilization. We previously reported the one step functionalization of gold and silver nanoparticles obtained by LASiS in organic solvents with a variety of functional molecules like thermoresponsive polymers or standard stabilizers as mercaptoethanol, dodecanthiol or  $\alpha$ -lipoic acid

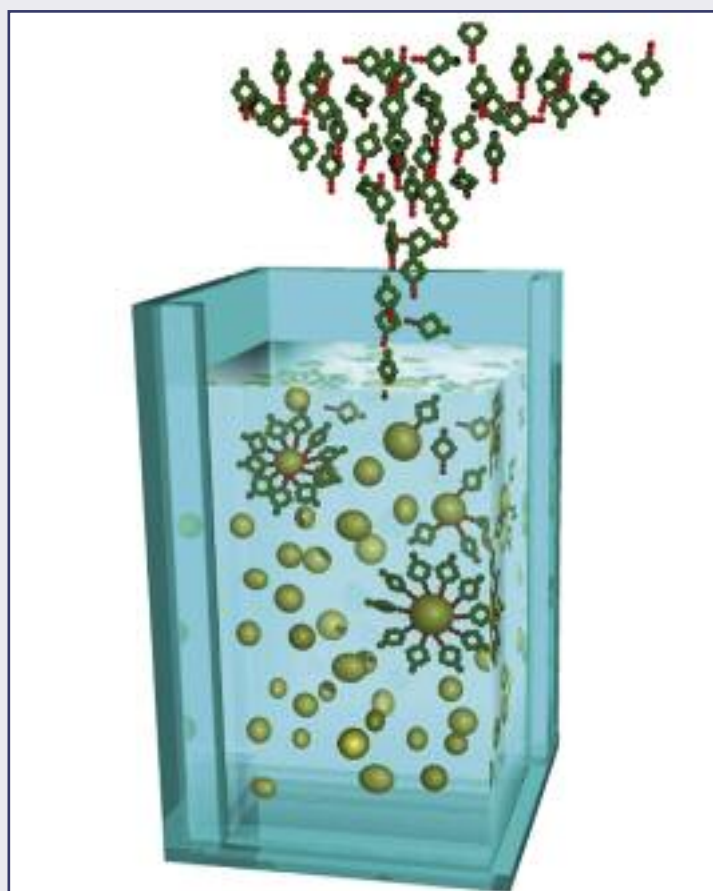


Fig. 7 - Cartoon reporting an important advantage of NMNPs obtained by LASiS: one step functionalization of ligands-free nanoparticles by addition of desired molecules in solution

[15, 31]. In case of thiolated molecules that are soluble in organic solvents only, the one-step functionalization procedure is much simplified with respect to the approach based on wet chemistry synthesis of NMNPs, for the following reasons: *i)* usually NMNPs synthesized in presence of thiols have sizes smaller than 5 nm, hence they show poor plasmonic responses; NMNPs with larger size can be obtained by LASiS in pure organic solvents and functionalized later, as done in our previous works; *ii)* more than a single type of thiols can be added to the same solution of NMNPs after LASiS, without affecting their size and plasmonic properties; *iii)* different types of thiols can be added to different solutions containing the same NMNPs, hence one can obtain the same NMNPs covered with different thiols, as done in our previous works about AgNP and AuNP.

We also demonstrated that the surface of Au NPs obtained by LASiS in water is highly accessible for bioconjugation and is suitable for UV-visible monitoring of surface coverage. It is well known that the plasmon absorption band of Au NPs is sensitive to the physical and chemical environment of particles surface. In our experiment, we added increasing amounts of bovine serum albumin or thiolated polymers like poly-ethylene-glycol to a solution of Au NPs obtained by LASiS in pure water [3, 24, 31]. By monitoring the red shift and the absorbance change of the surface plasmon resonance after the addition of ligands until saturation,

Fig. 8 - The yellow boxes in the periodic table correspond to the elements that are present as pure compounds, alloys, binary compounds, oxides, hydroxides, sulfides, nitrides or carbon particles in nanoparticles obtained by LASiS According to what reported in [3] and [4]

we obtained a quantitative estimation of the amount of molecules required for the complete coverage of particles surface. In our work about Au NPs surface coating with a thermoresponsive thiol terminated poly-N-isopropylacrylamide-co-acrylamide co-polymer, we used the red shift of surface plasmon absorption for estimating the polymer amount required for nanoparticles surface saturation [31]. The number of polymer chains for each AuNP was evaluated by the same measurements. In particular, we measured the red shift of the surface plasmon absorption for a ratio of thiolated polymer : AuNP varying from 310 : 1 to 61300 : 1 and we found surface saturation for a ratio of about 4000 : 1 (average AuNP size of 18 nm). These figures were in fair agreement with simultaneous iodine titration measurements on the unbound polymer obtained after centrifugation of the AuNP-polymer solution.

The use of this type of plots for the real time monitoring of nanoparticles multi-functionalization with high sensitivity is promising. Once the saturation concentration has been estimated by separate experiments for each ligand type, the sequential addition of ligands with the desired ratio is facilitated. Such a procedure is particularly important whenever ligands are scarce or precious, as often happen in case of NMNPs bioconjugation, because saturation concentration can be measured in a brief time and on volumes as small as those required for a UV-visible analysis. We also observed a very good stability for AuNP and AgNP solutions during the addition of ligands, i.e. negligible aggregation. This finding is compatible with the strong adhesion of stabilizing charges on the surface of NMNPs obtained by LASiS.

## LASiS of NPs with various composition

Many reports about LASiS of NPs with a variety of phases and compositions exist (Fig. 8), although only a part of them provided a deep characterization of the products and showed a good control over particles morphology. Some of these works have been reviewed in references 4. NPs of Pb, Ni, Co, Si, CdS, ZnSe, Zn, US, FeNi, Ag<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> have been obtained by laser ablation of targets with the same composition dipped in water or in organic solvents [3, 4]. Oxide nanoparticles like CuO, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, GeO<sub>2</sub>, FeO and ZnO or hydroxide nanoparticles like Mg(OH)<sub>2</sub> and Zn(OH)<sub>2</sub> have been obtained by laser ablation of pure

metals or pure semiconductors in water, by exploiting the oxidation of metal atoms that takes place in the plasma plume region [3, 4].

The stability of these NPs is usually poorer than NMNPs and extensive aggregation is observed, as in case of Zn(OH)<sub>2</sub> NPs [32]. Sometimes, the stability of NPs can be controlled by various parameters like the pH, the solvent and the presence of surfactants or other stabilizers [4].

The use of organic solvents reduces the oxidation of elements like Cu, since metal copper particles have been obtained in acetone while copper oxide nanoparticles have been obtained in water [3, 33]. The formation of

core@shell structures with a metal or semiconductor core and an oxide shell was reported in several cases like for Cu@CuO [3, 33], Si@SiO<sub>2</sub> [34], and Zn@ZnO [35]. These NPs can show high defectivity, that can be useful for obtaining new properties like photoluminescence in Zn@ZnO NPs [35]. The formation of linear carbon chains like polyynes or polycumulenes by LASiS of graphite targets in water and hexane was also reported [36].

LASiS of multi-elements compounds can generate NPs with a different stoichiometry also in absence of oxidation, as reported for the synthesis of HfS nanoparticles by ablating a HfS<sub>3</sub> target immersed in tert-butyl disulfide [37].

Alternatively, laser ablation in the presence of chemical reagents can originate compounds with new structures and shapes. In the case of laser ablation of Ni in aqueous solution of silver nitrate, Ag-Ni alloy nanoparticles with cigar-like shape were obtained [3, 38]. The silver-nickel alloy is not thermodynamically allowed in ordinary conditions, but it results from the fast kinetics formation of nanoparticles in the high temperature and pressure conditions produced by the laser ablation process. Other nanostructured materials like cubic and hexagonal phases of diamond, C<sub>60</sub> carbon and cubic BN NPs have been obtained by LASiS of graphite or hexagonal BN, as a further confirmation of the high pressure and temperature reached during the synthesis [4, 38].

The deviation from the ordinary spherical shape has been observed also for other materials obtained by LASiS in solution of electrolytes. In particular, the templating effects of electrolytes in solution allowed the synthesis of carbon and of GeO nanoparticles with cubic shape [39]. However, one must point out that, these samples containing metastable or nonspherical shapes are very heterogeneous and consist of a mixture of NPs with different shape, size and phase [4, 39, 40].

Good results have been obtained by LASiS in the synthesis of organic NPs made of dyes, fullerenes or organic anticancer drugs. In particular, Asahi's group showed that the phase and the size of organic nanocrystals can be controlled by varying the fluence, the duration and the wavelength of incident laser pulses [41]. LASiS of organic nanoparticles was obtained by laser ablation of sols composed of macroscopic powders suspended in the liquid instead of a solid target [41].



## Concluding remarks

LASiS is a top down physical approach for the synthesis of nanomaterials in liquids. Though the stability, the composition, the average size and the size distribution of the NPs can be very different from one case to the other, one should consider that a long list of different nanomaterials can be obtained by using the same simple experimental set up. LASiS allows minimum manual operation, requires raw materials for the synthesis (i.e. sensible money earning for the purchase of solid targets or powders instead of metal salts, organometallic precursors and other chemicals) and waste production is minimal or null. On the other hand, a careful evaluation of the costs with respect to other approaches like wet chemistry synthesis is necessary prior to the application of LASiS for mass production of nanoparticles. Recently, the production of NPs on the gram scale by LASiS has been reported for the first time [42].

The results obtained until now by LASiS of NMNPs show that a good control on the synthesis of nanoparticles can be obtained, with large opportunities for the fabrication of multifunctional nanostructures. Moreover, the interesting and heterogeneous results obtained in the synthesis of NPs with

various composition and shape suggests that this research field can be fertile for further investigations about the mechanisms of ablation and particles formation, aiming at higher degrees of control on particles morphology and at obtaining functional nanomaterials with complex structures.

**Acknowledgments:** The author is indebted with Prof. Moreno Meneghetti for the constant support and guide during his experimental work and during the writing of this manuscript.



Vincenzo Amendola (PhD in Material Science and Engineering) is Assistant Professor in Physical Chemistry (Dep. of Chemical Sciences, Padova University). Main research interests are LASiS of functional nanoparticles, plasmonics, nanomedicine, SERS and laser interactions with nanostructures. He is open to collaborations and scientific counseling. The complete cv can be found at [www.chimica.unipd.it/vincenzo.amendola](http://www.chimica.unipd.it/vincenzo.amendola)

## References

- [1] G.A. Ozin, A.C. Arsenault, *Nanochemistry: A Chemical Approach to Nanomaterials*, Royal Society of Chemistry, 2009, 820.
- [2] C.J. Murphy, *J. Mater. Chem.*, 2008, **18**, 2173.
- [3] V. Amendola, M. Meneghetti, *Phys. Chem. Chem. Phys.*, 2009, **11**, 3805.
- [4] G.W. Yang, *Prog. Mater. Sci.*, 2007, **52**, 648.
- [5] A. Fojtik, A. Henglein, *Ber. Bunsen-Ges. Phys. Chem.*, 1993, **97**, 252.
- [6] L.V. Zhigilei *et al.*, *J. Phys. Chem. C*, 2009, **113**, 11892.
- [7] L.V. Zhigilei *et al.*, *J. Phys. Chem. B*, 1998, **102**, 2845.
- [8] K. Saito *et al.*, *Appl. Surf. Sci.*, 2002, **197**, 56.
- [9] W.T. Nichols *et al.*, *J. Appl. Phys.*, 2006, **100**, 114911.
- [10] W.T. Nichols *et al.*, *J. Appl. Phys.*, 2006, **100**, 114912.
- [11] W.T. Nichols *et al.*, *J. Appl. Phys.*, 2006, **100**, 114913.
- [12] H. Muto *et al.*, *J. Phys. Chem. C*, 2007, **111**, 17221.
- [13] J.P. Sylvestre *et al.*, *J. Phys. Chem. B*, 2004, **108**, 16864.
- [14] X.Z. Lin *et al.*, *J. Phys. Chem. C*, 2009, **113**, 17543.
- [15] V. Amendola, M. Meneghetti, *J. Phys. Chem. C*, 2009, **113**, 4277.
- [16] G. Compagnini *et al.*, *J. Appl. Phys.*, 2003, **94**, 7874.
- [17] V. Amendola *et al.*, *J. Phys. Chem. B*, 2006, **110**, 7232.
- [18] L. D'Urso *et al.*, *J. Phys. Chem. C*, 2010, **114**, 907.
- [19] V. Amendola *et al.*, *J. Phys. Chem. B*, 2005, **109**, 23125.
- [20] F. Mafune' *et al.*, *J. Phys. Chem. B*, 2001, **105**, 5114.
- [21] F. Mafune' *et al.*, *J. Phys. Chem. B*, 2000, **104**, 9111.
- [22] F. Mafune' *et al.*, *J. Phys. Chem. B*, 2003, **107**, 4218.
- [23] G. Compagnini *et al.*, *J. Mater. Res.*, 2004, **19**, 2795.
- [24] V. Amendola, M. Meneghetti, *J. Mater. Chem.*, 2007, **17**, 4705.
- [25] F. Mafune' *et al.*, *J. Phys. Chem. B*, 2002, **106**, 7575.
- [26] A. Giusti *et al.*, *J. Phys. Chem. C*, 2007, **111**, 14984.
- [27] G. Compagnini *et al.*, *Chem. Phys. Lett.*, 2008, **457**, 386.
- [28] S. Pedersen, S. Barcikowski, *Adv. Funct. Mater.*, 2009, **19**, 1167.
- [29] V. Amendola *et al.*, *Synth. Met.*, 2005, **155**, 283.
- [30] J.P. Sylvestre *et al.*, *J. Am. Chem. Soc.*, 2004, **126**, 7176.
- [31] S. Salmaso *et al.*, *J. Mater. Chem.*, 2009, **19**, 1608.
- [32] C. Liang *et al.*, *Chem. Mater.*, 2004, **16**, 963.
- [33] R.M. Tilaki *et al.*, *Appl. Phys. A*, 2007, **88**, 415.
- [34] V. Svrcek *et al.*, *J. Appl. Phys.*, 2008, **103**, 023101.
- [35] H. Zeng *et al.*, *Appl. Phys. Lett.*, **88**, 171910.
- [36] G. Compagnini *et al.*, *J. Phys. Chem. C*, 2008, **112**, 20301.
- [37] M. Nath *et al.*, *Chem. Mater.*, 2004, **16**, 2238.
- [38] Q. X. Liu *et al.*, *Chem. Phys. Lett.*, 2003, **382**, 1.
- [39] J.B. Wang *et al.*, *Chem. Phys. Lett.*, 2002, **361**, 86.
- [40] P. Liu *et al.*, *J. Phys. Chem. C*, 2008, **112**, 13450.
- [41] T. Asahi *et al.*, *Acc. Chem. Res.*, 2008, **41**, 1790.
- [42] C. Sajti *et al.*, *J. Phys. Chem. C*, 2010, **114**, 2421.

## RIASSUNTO

### Sintesi mediante ablazione laser in soluzione (LASiS) di nanoparticelle funzionali

La LASiS ha dimostrato di avere un grande potenziale come tecnica a basso costo e "green" per la produzione di nanoparticelle facilmente funzionalizzabili e di nanostrutture complesse, dunque rappresenta una interessante alternativa ai metodi di "wet chemistry" per la sintesi di nanoparticelle funzionali.