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FUNDAMENTAL ASPECTS OF LASER ABLATION IN LIQUID: GREEN METHOD FOR NANOPARTICLE PRODUCTION

BY

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Abstract. Laser ablation of metallic targets in aqueous media is one of the most powerful tools that we have at this moment for the production of pure and sustainable nanoparticle with direct bio-medical applications. Understanding the fundamental aspects of this process can further pave the way for a better control of the nanoparticle properties and tailoring new pharmaceutical products with direct and localized effects.

Keywords: laser ablation; nanoparticles; liquid; cavitation.

1. General Aspects of Laser Ablation in Liquid

Laser ablation in liquid is coupled with the laser ablation of solids in gaseous media, from the late 80'. The pioneers of this technique are considered Patil *et al.* (Patil *et al.*, 1978) with the group of Needersen *et al.* (Mafune *et al.*, 2000) later reporting themselves the synthetic of colloidal solution through laser ablation of metallic targets in water and organic solvents. In the last two decades laser ablation in liquid has seen a resurgence, now being seen as a low-cost, green, versatile method which allows the synthesis of a wide range of nanoparticles. The versatility of the technique is reflected by the wide range of

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parameters (properties of the laser beam, properties of the target and those of the liquid solution) that can influence the mechanisms of particle removal, as is it the case for vacuum or gas (Compagnini *et al*., 2003). The particularities of laser ablation in liquid like extreme thermodynamic conditions (high values of the temperature, pressure and particle density), the confinement of the plasma plume by the liquid, the cavitation phenomena, are creating the perfect medium for the production of pure and sustainable chemical products. One main aspect of the whole process is the fact that during expansion the plasma plume resulted as from the interaction of the laser beam and the target contains now not only components from the target but also from the liquid, allowing the formation of nanoparticles with a both crystalline or amorphous structures, that can present themselves as full, hollow or core-shell nanoparticles (NP). The most investigated compounds, are bio compatible metallic NP of Au, Ag or iron oxides.

Their main applications are as passive agents in the administration of the bio-compatible compounds at cellular level and are often used as probes for electronic microscopy.

2. Fundamental Aspect of Laser Ablation in Liquid

For the laser – matter interaction in liquid can be distinguished 4 main parameters whose profile in time and space influences significantly the properties (phase, structure) of the final synthesized products: temperature (T), pressure (p), concentration of the ablated material (CM) and concentration of the solution species (CS). Laser – solid interaction is a complex phenomenon by itself and introducing a new phase (liquid). The main difficulty when investigating this process arises from the semi spherical symmetry of the phenomena, the 4 parameters previously mentioned are not uniformly distributed in space and time.

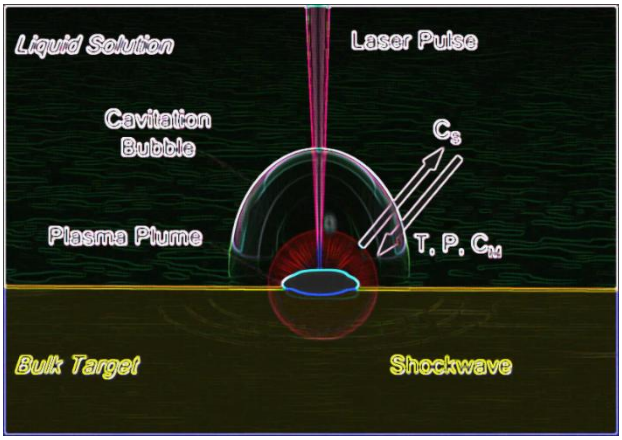

Fig. 1 – Schematic representation of the laser ablation in liquid process (Amendola *et al*., 2007).

In the process of laser ablation in liquid the primary interaction occurs between the laser pulse and the liquid environment. Therefore, the liquid properties (transparency of the liquid in respect to the laser wavelength, density, thermal conductivity, viscosity, etc.) can induce significant unwanted effects during the irradiation process. The main unwanted effect is the decrease in beam energy that reaches the target's surface.

Nanomaterials synthesis by ultrafast lasers has become a viable method and it constitutes the basis for a new independent science field. Many advantages emerge from using a liquid environment or a liquid film, such as lowering the heat on the target, confining the plasma, and increasing the shock pressure on the surface (Kang *et al*., 2008; Hwang *et al*., 2004; Zhang *et al*., 2017). There is a long range of lasers with different characteristic parameters that can be used in LAL. Regarding the wavelength, in literature we find utilized laser from ultraviolet (UV) (if the liquid allows UV transmission) and visible (VIS) to near – infrared (NIR). The pulse duration can be in the *fs* temporal regime to picosecond, nanosecond, microsecond and millisecond regimes, even extending to continuous – wave lasers (Zhang *et al*., 2017).

These losses are mainly caused by two phenomena: de-focalization and beam attenuation. The first phenomena, de-focalization, occurs in particular in the case of laser ablation in liquid medium. In contrast with laser ablation in gas, where the focalization conditions are determined just by the position of the target in respect to the focal lens, in LAL the focalization depends on the thickness of the layer of liquid. The de-focalization introduced by the liquid layer is in direct connection with the refractory properties of the solution. In the literature can be found other causes that can affect the focalization, such as vaporization of the liquid at the liquid – air interface and the self – focusing effect. The auto-focusing of the beam is a nonlinear optical phenomenon that occurs in the case of nanosecond and femtosecond laser regimes. The second phenomena (attenuation of the laser beam in the liquid) is due to the photon absorption and scattering on liquid molecules. Worth mentioning consequences of the absorption of the beam's energy are heating of the liquid and/or dissociation of the liquid molecules (in case of the UV lasers). The attenuation is also influenced by the presence of products produced by previous laser beams. The "shielding effect" appears as some collateral phenomena to the ones presented above, basically the already formed NP absorbed a significant part of the incoming beam which lead to the fragmentation and thus to the reduction of the NP dimensions.

The problem of particle removal during the laser matter interaction can be addressed in an analogous manner as in the case of laser ablation in vacuum. An accurate description of the exact ablation mechanisms becomes more difficult here as during the laser-matter interaction more than one mechanism can manifest themselves simultaneously. Thus, we can state here as a general fact that the main ablation mechanism that are responsible with particle removal and NP formation are evaporation explosive boiling and phase explosion.

3. Expansion and Quenching of the Plasma Plume

In the first picoseconds after the laser pulse interacted with the target the physics is similar to that involved in laser ablation in gas. But, after longer periods of about 10^{-10}-10^{-9} s an important difference is observed – the liquid strongly confines the plasma near the irradiation point (crater) area (Saka *et al*., 2000; Perez *et al*., 2008). The confinement slows down the cooling rate due to the fact that at the interface between the target and the ablated material there is a heat transfer. Maybe one of the most important consequences of the confinement of the plasma is that the ablation yield in liquid is higher compared to the ablation yield in gas. This happens because a larger target area reaches the energetic threshold for ablation (Tsuji *et al*., 2004; Saka *et al*., 2000, 2002). Moreover, an essential characteristic of the LAL process emerges from this observation - that the energy transfer is double sided, from the laser pulse to the solid target and from the plasma plume to the already heated target. The plasma– target energy transfer can take place for several nanoseconds after the end of the laser pulse (Mafune *et al.*, 2000; Amendola and Meneghetti, 2009). For moments of time that surpass 10^{-10} s the plasma plume expands in the liquid and cools down by heating the liquid as well as the target. The liquid can reach temperatures of about a few 10^3 K similar to the ones found for plasma generated in vacuum, these temperatures are appropriate for ionization processes and pyrolysis of the solution molecules. The gradients of the T, P, C_M and C_S are becoming more uniform and are defining fast transformation in both space and time for all the main parameters. Qualitative estimation of these gradients can be made using theoretical and experimental techniques while a quantitative evaluation is missing. In this stage the ejected species and liquid ones are mixing (Fig. 2). Now it will take place 4 types of chemical reactions both from a plasma plume perspective as well as the interface between the plasma and the liquid media.

The first type of reactions refers to the formation of metastable phases of the material induced by the extreme conditions within the plasma. The second type of reaction takes places in the plasma volume, here the involved reactants are the ionized species of the target and those of the solution. The species of the solution are particle resulted from the ionization and excitation generated at the interface liquid- plasma (Fig. 2). Thus, on the expansion direction of the plume it appears an area named “plasma-induced plasma” where we initially find the ionized species of the liquid media. This area will evolve while it’s unified with the primary plasma, once it is completely generated. Therefore, the first ablation mechanism like Coulomb explosion will lead to the formation of a plasma region which contains only liquid particle while with the manifestation of thermal mechanisms and the full generation of the primary plasma plume the two-plasma region and blending leading to a confined plasma plume containing both ionized species of the target and those of the solutions.

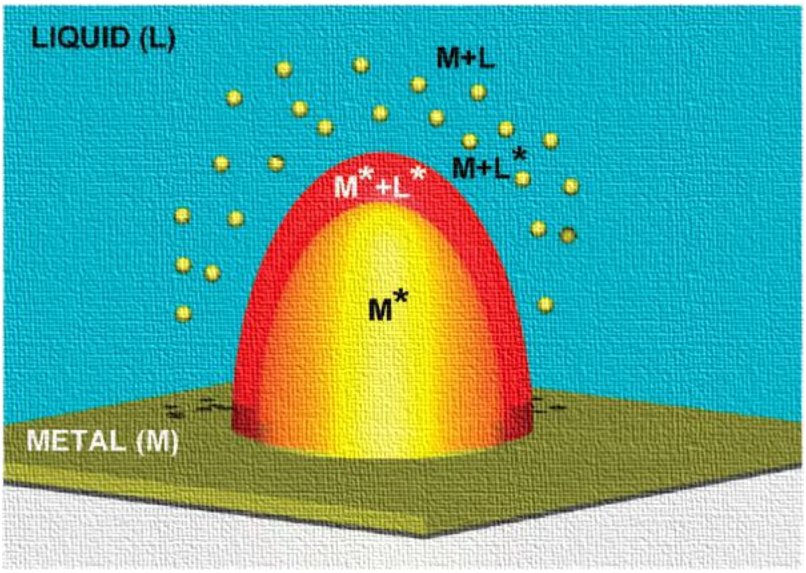

Fig. 2 – Schematic representation of particle distribution during the laser ablation process in liquid (Amendola and Meneghetti, 2013).

The third set of chemical reactions are conducted in the liquid – plasma interface. This is due to the fact that the thermodynamic state characterized by extreme values of the temperature, pressure and particle density, which create the perfect conditions for the chemical interactions between the ejected metallic particles and those of the liquid. The last type of interactions are happening in the liquid media. Due to the elevated values of the pressure at the plasma plume expansion front, the metallic particles will be ejected in the volume of the liquid media where it will interact with the solutions molecules (Yang, 2007). It is worth noting that 3 out of the 4 types of reactions presented here are involving both particles of the target and of the liquid. As such these chemical reactions coupled with the thermodynamic conditions can offer infinite possibilities for the tailoring of new sustainable materials by combining elements from both media (Sakka *et al*., 2000; Patil *et al*., 1978; Yang and Wang, 2000).

The main mechanism of nanoparticle formation generated by laser ablation in liquid is represented by nuclei growth. This process is assumed to the manifesting itself during the cooling of the plasma plume, followed by the growth of the supposed nuclei and their fusion (Fig.3).

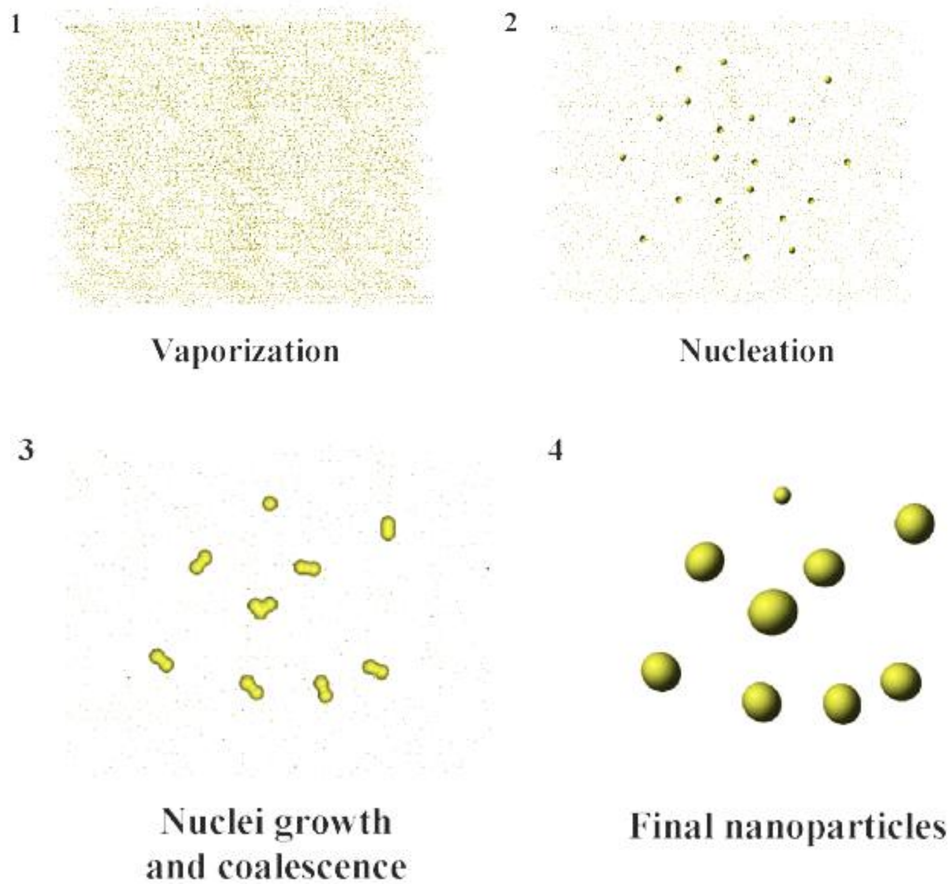

Fig. 3 – Representation of the nanoparticle formation process using the laser ablation in liquid (Amendola and Meneghetti, 2009).

In literature there are three experimental confirmation of this hypothesis. First it is represented by the experimental observation of crystalline structure in nanoparticles generate by laser ablation in liquid (Amendola *et al*., 2007; Amendola and Meneghetti, 2007). The second one is given by the fact that nanoparticles generated in the presence of ligands or polymeric solutions have a narrower dimensional distribution in comparison with the nanoparticles generated pure solvents (Mafune *et al.*, 2001, 2000). The thirs and last main confirmation from literature comes from the results that laser ablation in reactive solvents does not lead to the formation of pure metallic nanoparticles (Sakka *et al*., 2002).

The nucleation force present inside the plasma volume is given by the supersaturation. This is given by the ratio between the real vaporization pressure p and the equilibrium vaporization pressure $p_0(T)$. The free energy barrier ΔG_N

and the minimum radius R_N are thus depending on the supersaturation as follows:

$$\Delta G_N \propto \left[k_B T \left(\frac{p}{p_0(T)}\right)\right]^{-2}, \tag{1}$$

$$R_N \propto \left[k_B T \left(\frac{p}{p_0(T)}\right)\right]^{-1}, \tag{2}$$

where k_B is the Boltzmann constant, and T is the temperature describing the equilibrium state, while the well-known Gibbs free energy is a measure of the energy of a transformation state in in between competing states. For a better understanding of this concept we consider two phase that coexist in the same thermodynamic conditions. Between the two states the one with the lower free energy is steady while the other becomes metastable with the possibility of become a steady state as well. From a thermodynamic perspective the phase transformations are given by the differences in between the values of the free energy.

A major drawback of laser ablation in liquid as a technique for NP generation is the temporal imprecisions in pointing down the starting point of nucleation processes and those of NP formation. The exact moment at which the nucleation process is starting is strongly dependent on the concentration, temperature and pressure. For this reason, why, it cannot be related to the results obtained from laser ablation in gas. Some authors suggest that the nucleation jumpstarts after 10^{-9} s (Wang *et al*., 2005) while other propose an approximate time of 10^{-5} s (Tsuji *et al*., 2008; Itina, 2011). However, there is a lack of experimental proofs regarding the NP formation mechanism. It is still not clear if the nucleation and NP growth take place before or after the intensive mixing of the ejected species with those of the liquid. Moreover, due to the limitations of the experimental investigations techniques the correct ionization degree for some species it is difficult to find out. Optical emission spectroscopy confirms the fact that the there is a chemical interaction between the species of the target and those of the liquid even in the plasma. On the other hand, this information is not quantitative and thus not truly relevant to the NP formation phenomena.

Laser produced plasmas are complex media which contains besides electrons atoms, multiply ionized ions, atom, clusters also molten material fragments (Amendola and Meneghetti, 2013). Their presence is not negligible as in the past few years the group of Zighilei (Zighilei *et al*., 2009) has proposed a NP formation mechanism based of the phase explosion and the braking of the material in various structures. That being said there is not a consensus in the literature which could tell us if from these fragments it can result some precursors of NP. Therefore, a hypothesis can be made about these types of structures. The molten material, solid fragments and molecular clusters are directly ejected from the target and they could constitute preferential sites for the generation and characterization of nuclei. The direct conclusion of this would be in direct connection with the results reported by Zighilei *et al*., that the nucleation phase is not that relevant for the laser ablation in liquid as a whole, because the nuclei could be directly extracted from the target during the ablation process. In order to clarify this aspect further studies are needed for the understanding of the fundamental mechanism of ablation and material removal in the laser ablation in aqueous media. However, some nanoparticles obtained though this method are mainly polycrystalline thus at some point during the formation and expansion of the plume, the fusion of the nuclei still occurs.

In the framework of laser ablation in liquid, it is also possible the generation in specific conditions of liquid supersaturation of a mixture of clusters and atomic precursors. More precise, the vaporization pressure of the ejected species is higher than the equilibrium one thus the nucleation and growth process are accelerated. The dimensional distribution of the NP generated by laser ablation follows a lognormal function. On exception to this rule is the irradiation of already produced NP. Granqvist *et al*. showed that the NP are described by a log normal dimensional distribution when their growth is given by the diffusion processes of the atoms and nanoparticles which occurs produced simultaneously. The following agglomeration of NP do not affect the distribution as log as the drift moment of the NP is not affected.

The dimension of the produced NP can be controlled with the use of the external experimental parameters like wavelength, pulse duration, repetition frequency irradiated surface and the energy per pulse. As an example here in conditions of identical fluence the NP generated with UV laser beam would favor the formation of reactive species, the use of an IR beam would lead to an uneven energy distribution at the surface as the impurities have an preferential absorption. Finally, the use of a bigger surface would aid the formation of Np with a wider dimensional distribution.

4. Conclusions

Recent developments in laser ablation in liquid have led to the creation of a new exciting research area related to the formation of NP and generation of complex pharmaceutical compounds using one-step technologies. There is however a great need of fundamental research that would eventually allow researcher a better control on the NP distribution and properties. The use of complimentary investigation techniques and the ability to perform in situ investigations of the dynamics of atoms and ions leading into the nuclei formation could be of great help when attempting to clarify this problem.

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ASPECTE FUNDAMENTALE ALE ABLAȚIEI LASER ÎN LICHID: METODA ECOLOGICĂ DE PRODUCERE A NANOPARTICULELOR

(Rezumat)

În prezent ablația laser în mediul lichid este o tehnică ieftină, versatilă și ecologică ce oferă acces la sintetizarea unei plaje extinse de nanomateriale. Versatilitatea metodei se reflectă profund în plaja largă de parametri (parametri ai laserului, ai lichidului, ai țintei) ce influențează întregul proces de preparare a materialelor. Particularitățile procesului precum: condiții termodinamice “extreme” (valori mari ale temperaturii, presiunii, densității de particule), efectul lichidului de confinare a plasmei, fenomenul de cavitație, furnizează mediul perfect de sintetizare a unor produși puri, sustenabili și ușor funcționalizabili. Mai mult decât atât, în timpul expansiunii în lichid, plasma de ablație înglobează atât particule îndepărtate din material, cât și particule ale soluției. Astfel, pot rezulta nanoparticule atât cu structură cristalină cât și amorfă sub formă de sfere pline, sfere goale sau structuri de tip miez – capsulă ce reprezintă de fapt “semnături” ale ambelor faze (lichid, solid). Această caracteristică a procesului conferă posibilitatea generării in-situ de compuși stabili de tip nanoparticulă – polimer, care nu numai că împiedică agregarea nanoparticulelor pe termen lung, dar mai important astfel se pot produce compuși farmaceutici ce pot fi utilizați în diverse forme.