Applied Surface Science 348 (2015) 4–9

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Mechanisms and processes of pulsed laser ablation in liquids during nanoparticle production

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ARTICLE INFO

Article history:
Received 10 November 2014
Received in revised form
17 December 2014
Accepted 12 January 2015
Available online 20 January 2015

Keywords:
NPs
Laser ablation in liquids
Laser induced plasma
Laser induced bubble

ABSTRACT

In the last decade Pulsed Laser Ablation in Liquids (PLAL) has been widely investigated from the fundamental point of view, and various theories have been proposed. Although many important achievements have been obtained by the scientific community, many aspects still need to be clarified and many contradictions arise when comparing the interpretation of similar experiments carried out by different authors. In this paper we have reconsidered previous works focused on specific processes and stages of the PLAL, in order to outline a modern and comprehensive point of view of the overall physical aspects of PLAL. With this aim, several simultaneous diagnostic methods have been applied during the production of metallic nanoparticles (NPs), i.e. optical emission spectroscopy and fast imaging for the investigation of the laser-induced plasma, shadowgraph for the study of the cavitation bubble, and Double Pulse Laser Ablation in Liquid (DP-LAL) and laser scattering for the investigation of NPs location and mechanisms of release in solution. The connection between the various stages of the DP-LAL allows understanding the main characteristics of the produced NPs and the typical timescales of the basic mechanisms involved in PLAL.

1. Introduction

The great effort that the scientific community has put in the last decade in the study of nanoscience and nanotechnology has been leading the research toward the development of new methodologies of nanostructures synthesis. Among them, Pulsed Laser Ablation in Liquid, PLAL, is gaining an increasing interest thanks to several promising advantages, which include: environmental sustainability, easy experimental set-up (which does not require extreme conditions of the ambient of synthesis), long-lasting stability of the nanoparticles, which are produced completely free of undesired contaminants or dangerous synthesis reactants. The increase of the research products in this field in the period 1998–2011 has been already analyzed in [1,2], and until now their number has continued to grow. The nanomaterials and nanostructures that can be produced are extremely varied, as well as their applications. Refs. [3–5] present the most significant papers relative to the different typologies of nanostructures produced by PLAL with some of their applications, and focus on physical and chemical fundamentals of PLAL.

Precisely because of this great interest for PLAL nanostructures fabrication, studying the mechanisms of formation is extremely interesting in order to improve the fundamental understanding in this field. Until now, important goals have been reached, especially in the last decade, but much still needs to be clarified. In particular, the laser induced plasma and cavitation bubble dynamics during the laser ablation in liquids play crucial roles. In previous studies [6,7] we combined complementary optical techniques with high temporal resolution and investigated in details the roles of the laser-induced shockwave and plasma in the early time of these processes, as well as the connections between the cavitation bubble formation and dynamics and the formation of NPs [8–10]. On the other hand, theoretical studies were also carried out on the mechanisms of NPs formation [11,12]. This paper is based on some fundamental experiments, and its aim is to give and discuss a modern and comprehensive point of view on the mechanisms and the processes involved in the PLAL technique.

2. Experimental investigation of the processes involved in the production of NPs by PLAL

Laser induced breakdown of submerged targets is characterized by visible plasma emission and the production of shock waves and of cavitation bubbles. The duration of each of these processes is sketched in Fig. 1: after laser-matter interaction, laser-induced

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http://dx.doi.org/10.1016/j.apsusc.2015.01.082
0169-4332/

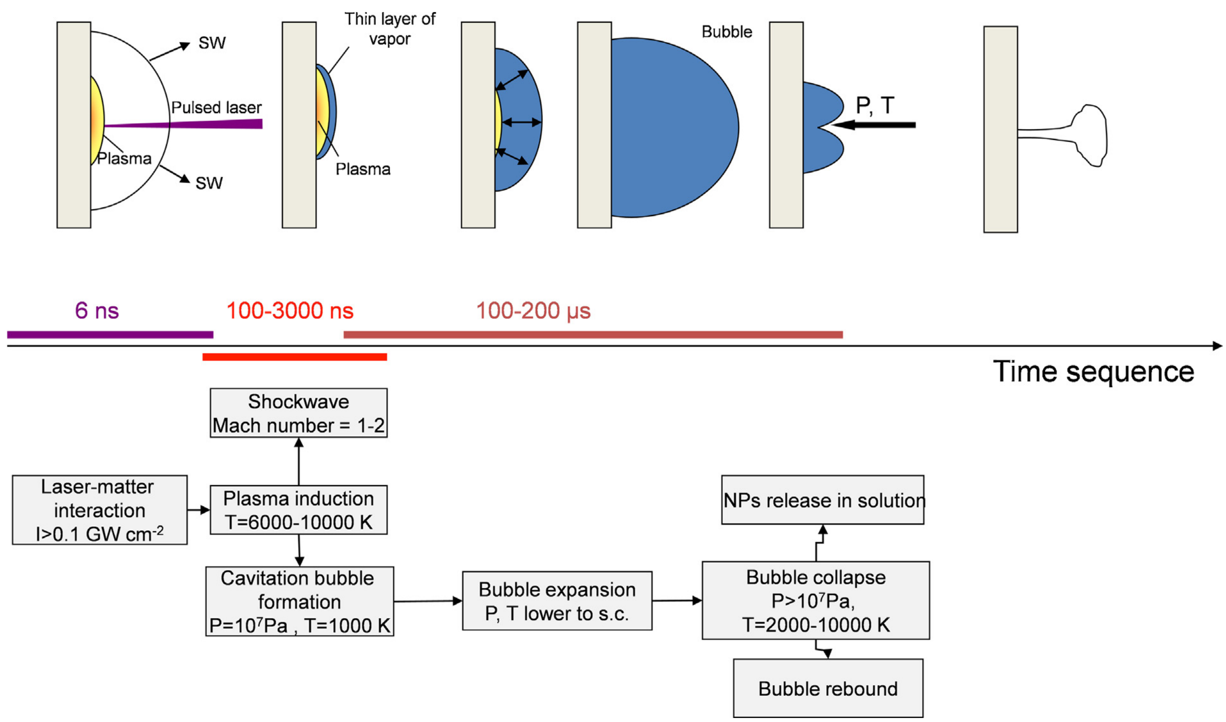

Fig. 1. Time sequence of the processes involved during the pulsed laser ablation in liquid.

breakdown occurs, followed by the shock wave formation, plasma expansion and cooling, and by cavitation bubble formation, expansion and collapse. Upon the bubble collapse, the nanoparticles, which are produced during the plasma cooling phase, can diffuse in the surrounding liquid and form a colloidal solution. Investigation of this series of processes is challenging because it requires different diagnostic techniques operating simultaneously. Moreover the dimension of the systems to investigate, i.e. the laser-induced plasma and the produced nanomaterial, requires detection methods with high sensitivity and high temporal resolution. In the frame of these considerations, we employed four different techniques for the experiments presented in this review: optical emission spectroscopy for the investigation of the laser-induced plasma [13], fast shadowgraph [6,14] for the measurement of the cavitation bubble dynamics, laser scattering [6,15,16] and Double Pulse-LAL (DP-LAL) [7] to monitor the laser-induced breakdown and the produced nanoparticles. Other techniques that can be used for this aim include, for example, laser induced fluorescence and X-ray scattering [8,9]. In order to better display some characteristics of the processes, targets with different geometry were employed to describe the phenomena involved in PLAL. In particular, in addition to the typical bulk targets (most usually disks or parallelepipeds of some mm of thickness), wire-shaped targets of hundreds of microns of diameter were used too. The main advantage of the latter target geometry, as already discussed in details in [6,17], is that it allows a larger field of view for the detection. Finally in this paper we analyze the mechanisms and the processes occurring during PLAL with a laser pulse with duration of few nanoseconds (6 ns) and irradiance >1 GW cm^{-2}.

2.1. Plasma production and cooling

When laser pulses with irradiance between 0.1 and 1 GW cm^{-2} interact with a solid target, seed electrons are ejected from the target by multiphoton ionization and then, as a consequence of the photon absorption by inverse Bremsstrahlung, the ablated particles form a hot atomic plasma [18]. When ablation occurs, the number density of the irradiated material can be expected to change with a continuous trend during the solid-to-gas phase transition. This means that initially a very dense and hot plasma is formed, so that instantaneous expansion occurs. The plasma expands supersonically driving a shock wave in the surrounding environment, and then it slows down compressing the surrounding liquid until the plasma itself extinguishes. The main elementary processes that sustain the plasma induced in a liquid environment are essentially the same that occur during ablation in air [19,20], the main differences being due to the different competition between the elementary processes and the different degree of energy exchange with the surrounding environment. Because of the low compressibility of the liquid, the plasma is suddenly confined so that it holds a density in the order of 10^{20} cm^{-3} and an ionization degree close to unity. At these conditions atoms and ions in the plasma phase are affected by the Debye–Hückel effect so that most excited levels are not allowed and radiative recombination is the predominant process [19,21].

Indeed upon 0.1–1 GW cm^{-2} laser ablation, the plasma is characterized by high-density effects [22] and, as a consequence of the limitation in the number of allowed excited levels, excitation and de-excitation by electron impact are replaced by ionization and recombination. In this scenario, the typical discrete spectrum, that reflects the Boltzmann distribution of atoms and ions, cannot be for the most of plasma evolution. Moreover, as a consequence of the recombining character of the laser induced plasma, radiative recombination becomes extremely efficient and is the main cause of deviation from the Local Thermal Equilibrium (LTE) condition, as discussed in details in [23].

The main effect of the predominance of radiative recombination on the other mechanisms is that the plasma emission spectrum is characterized by a continuum radiation. Since in the experimental conditions discussed in this work the plasma spectrum in liquid is a broad continuum that resembles a Planck-like distribution (though conceptually it is not a black body radiation), it can be used to determine the temperature of the plasma by applying the "Planck plot" method described in [24]. In previous studies [6,16], the temperature of a laser-induced plasma in water was found to be