

## Recent advances in nanoparticle generation in liquids by lasers: Revealing formation mechanisms and tailoring properties

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When Fojtik and Henglein [1] submitted in 1992 the first scientific paper on generation of nanoparticles (NPs) by laser ablation in liquids, the authors probably could not realize how it will revolutionize the nanoparticle science and technology. In 2017, marking a quarter century of this pioneering study, Amendola and Barcikowski [2] pointed out that the simple and bright idea of Henglein and Fojtik was an inspiration to hundreds of scientists worldwide over 25 years and opened a way to use lasers in synthesis of colloids. Since then, the method has significantly been evolved but the basic principle remains the same: a material immersed in a liquid is heated by the action of a focused laser beam and the subsequent matter expansion within liquid confinement results in formation of NPs. Comprehensive overviews of the progress achieved by 2017 in laser synthesis of nanomaterials and their applications are given in ref. [3]. A milestone was underlined regarding synthesis in liquid flow in combination with fast laser scanning over the target surface that allowed increasing the NP productivity to the industrial-scale level [3]. Of prime importance is that the laser-produced colloidal NPs often possess superior properties as compared to NPs obtained by other synthetic approaches that makes them attractive for a broad variety of applications [2,3]. In particular, a great advantage of these NPs is their ligand-free nature which allows to avoid side effects, such as blocking catalytically active sites, peculiar to chemically synthesized ligand-

coated NPs. Also, lasers allow to fabricate alloy NPs with controlled composition and homogenous elemental distributions and thus to tune their functional properties [3], a feature which is difficult to achieve by conventional chemical methods. Nowadays, several branches of the laser-based technique are developed with their established acronyms [2-4] such as (P)LAL for (pulsed) laser ablation in liquids, LFL for laser fragmentation in liquid, LDL or PUDDEL for (pulsed) laser defect engineering in liquid, LML for laser melting in liquid, and, in general, LSPC for laser synthesis and processing of colloids.

However, despite successful synthesis of an enormous number of functional nanomaterials by the LSPC method, many challenges remain to be solved [3]. In particular, this is related to the mechanisms of NP formation. Although the PLAL method is conceptually simple, the underlying mechanisms and highly nonequilibrium processes triggered by laser excitation of materials immersed in a liquid are at the edge of current experimental and theoretical capabilities. Therefore, despite of at least six proposed growth mechanisms [3], the exact picture on how the nanomaterials form during PLAL is still not completely clear and optimal LSPC regimes are found mainly by the trial-and-error method. Another challenge is associated with the surface chemistry of laser produced NPs. Although LSPC-produced NPs are often referred as ligand/surfactant-free, they are not naked and, due to reactions with liquid environments, surface atoms are

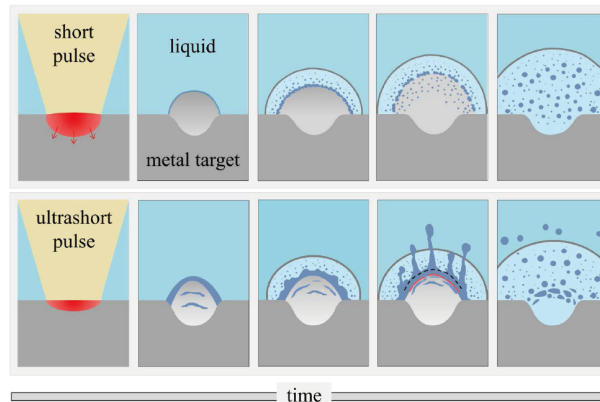
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often oxidized or complexed [3]. This subject is still poorly investigated whereas controlling the rich chemistry is crucial for obtaining NPs with desired phase and composition [2,3] and with good stability [4,5]. Finally, accurate manipulation of the size and shape of LSPC-produced nanostructures is still a challenge. Lasers usually generate NPs with broad size distributions, often involving populations of different sizes, while many applications require monodisperse NPs. Although considerable advances in size control have recently been achieved for metal NPs, especially using the LFL technique, colloids with a narrow size distribution are obtained at a sacrifice of the NP purity and throughput, and medium-sized monodisperse NPs of about 50 nm are still difficult to produce [3].

Excellent progress has recently been achieved in addressing the aforementioned challenges that was amply demonstrated in the 6th International Conference on Advanced Nanoparticle Generation and Excitation by Lasers in Liquids, ANGEL, which was held on June 16-18, 2021 in Hefei, China. In this forum, which provides essential space to discuss and enhance understanding of laser-matter interaction in liquids, a number of substantive breakthroughs in both the nanoscience fundamentals and applications of LSPC-produced NPs made in the last few years have been presented.

A great insight into the formation mechanisms of NPs under laser ablation of metals in liquid has been obtained by large-scale atomistic simulations in a wide range of laser pulse duration, from femtoseconds to nanoseconds [6]. The simulations have enabled to identify three different NP generation mechanisms working at different PLAL stages inside the emerging cavitation bubble and resulting in three groups of NPs with different sizes. The mechanisms are schematically illustrated in Figure 1 and include (1) formation of a thin transient metal layer at the ablation plume-liquid interface with subsequent decomposition of the layer into molten NPs, (2) formation of small NPs at the front of the bubble due to the nucleation, growth, and rapid cooling processes, and (3) the spinodal decomposition of the ablation products located below the transient layer, leading to generation of a population of large NPs. Overall, the initial dynamic stage of the PLAL process with formation of the transient metal layer is shown to play a key role in the nanoparticle generation. The fundamental difference between short (hundreds of ps to ns) and ultrashort (fs to tens of ps) pulse laser ablation in liquids is mainly related to the differences in the characteristics of this interfacial layer. In the case of ultrashort laser pulses, it is considerably denser and undergoes hydrodynamic instabilities leading to its decomposition with injection of large nanoparticles beyond the boundary of the cavitation bubble [6]. The coexistence of the different formation mechanisms provides an explanation for broad (or bimodal) NP size distributions typically observed



**Figure 1** (Color online) Schematic illustration of the evolution of processes occurring under ablation of a metal target in liquid by short (hundreds of ps to ns, upper panels) and ultrashort (fs to tens of ps, lower panels) laser pulses. The liquid is colored blue, the target is grey, the ablation plume is light grey, the cavitation bubble is light blue, nanoparticles and the transient metal layer are dark blue. For ultrashort pulses, the backside impacts (shown by the red curve) from the spallated metal droplets generate pressure pulses (dashed curve) that induce jetting of the molten metal due to hydrodynamic instabilities. With short laser pulses, all NPs are generated inside the cavitation bubble while they can be ejected beyond the bubble under ultrashort PLAL. Reprinted with permission from Shih et al. [6].

in PLAL experiments. The revealing in the simulations of the dynamics of NP generation opens a way for accurate controlling the NP formation process by appropriate adjusting PLAL conditions, e.g., using double pulse irradiation with a proper time delay between the pulses.

Significant progress has been recently achieved in experimental diagnostics of NP formation mechanisms under PLAL. Ando and Nakajima [7] developed a novel approach for the light-scattering technique by creation of a laser-induced transparent window. This allowed to clearly detect PLAL-produced NPs inside the cavitation bubble and to localize their main formation regions, around the central area and bubble apex. Another approach was suggested by Reich et al. [8] who used a set of synchrotron-based methods to detect and identify PLAL-produced species at different stages of the bubble evolution. For the case of Zn ablation in water, it is confirmed that, along with directly emitted NPs, a large fraction of the ablated zinc is present as isolated reactive species (atoms and small clusters) while oxidation occurs as a later step to already formed NPs.

Further insight into the formation mechanisms of LSPC-generated nanomaterials can be gained when dealing with multielement compounds due to different reactivity of the elements towards oxygen and liquid molecules. In its turn, this allows controlling the NP properties. For instance, alloys with transition metals are formed only by PLAL in a low oxidizing environment and, inversely, changing the oxidation efficiency of the solution allows to control the final composition of alloy NPs [9]. In addition, the PLAL process can mix different elements in NPs even for immiscible

starting materials [9]. By adjusting the PLAL conditions (laser parameters, type of liquid), it is feasible to control the structure of alloy NPs from a homogeneous mixture to phase-segregated core-shell NPs. Even surfaces of bare gold NPs can be chemically modified in colloids, e.g., by absorbed halogen atoms when performing PLAL in a halide solution, that paves the way for synthesizing metal NPs with on-demand-tuned work function [5]. The LSPC techniques are shown to be very promising for generation and healing of defects in colloidal NPs that can enhance their photocatalytic activity and may be used in the design of optimized solar fuels materials [10]. The recent review [11] summarizes the diversity of targets and liquids used for LSPC to demonstrate the capacity of LSPC for synthesis of different kinds of nanomaterials suitable for different applications.

The advances in controlling properties and scaling up production of LSPC-produced NPs promote their use in real-world applications. Far from pretending to provide a complete list of such applications, we will just mention here a couple of bright examples presented at the 6th ANGEL conference. A series of hybrid core-shell colloidal NPs were designed and synthesized as efficient broadband photocatalysts with tunable emissions upconverted from near-infrared to ultraviolet [12]. An efficient noninvasive technology to visualize fundamental biological processes of cell therapies in complex *in vivo* environments in real time has been developed based on femtosecond-PLAL-produced gold NPs assembled into chainlike clusters [13].

Despite the impressive efforts that have been made towards understanding and improvement of the LSPC techniques and their applications in different fields ranging from photocatalysis to sensing and bio-medicine, there are still remaining challenges to be addressed in order to achieve full LSPC potential. These challenges are seen in at least four directions: (1) achieving the control over NPs distributions towards narrow, single-peak ones; (2) control of composition of multicomponent NPs; (3) insights into the nonequilibrium chemical routes of NP fabrication by PLAL; (4) understanding the role of the thermodynamic critical phenomena developing during PLAL. Under ultrafast heating, chemical reactions are developing under nonequilibrium conditions that can result in generation of new metastable phases of nanomaterials [9]. Liquid media such as water and organics used for LSPC gain extreme reactive properties when reaching their critical or supercritical thermodynamic states. The role of critical phenomena in NP production by PLAL is still poorly explored although liquids in near-/super-critical states can swiftly dissolve solids with subsequent reassembling in chemically modified forms [14]. This is especially important at early stages of laser-matter interaction in a liquid layer adjacent to the irradiation spot [6] where, for instance, the critical opalescence can play a role as demonstrated by optical pump-probe measurements [15].

The direction (1) is expected to promote a wider practical use of laser-produced NPs as their polydispersity is currently one of the main limiting factors, in particular for plasmonic-related applications [3], since the optical properties of NPs are strongly size-dependent. Another limiting factor now is the relatively high cost of the LSPC-fabricated NPs. The laser techniques become cost-efficient (as compared with chemical methods) at a sufficiently high mass production level and the relative price of investment decreases considerably with laser power [3]. So, with the current rapid advances in the high-power laser technologies, this limitation is expected to be overcome soon.

Summarizing, we underline that the directions (1)-(4) are interconnected as they all are related to laser-stimulated chemistry, which in the case of (1) can help to limit NPs growth via surface reactions, in (2) and (3) involves both surface and gas-phase chemical kinetics in modification of NPs properties, while in (4) it manifests itself in extreme thermodynamic conditions that are yet poorly explored. The horizon of unexplored chemical phenomena in PLAL is wide, and in the near future, we can expect new discoveries in this field that will secure newly developed technologies for the benefit of society.

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