

Special
Issue

Opportunities and Challenges for Laser Synthesis of Colloids

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Nowadays, nanoparticles are pervasive in science and technology, and the prospect of being able to create an almost unlimited variety of different nanoparticles within minutes by using the same equipment has sparked the interest of scientists worldwide. In this context, laser synthesis and processing of colloids (LSPC) demonstrated that it is possible to obtain nanoparticles of various types, such as metals, oxides, carbon allotropes, or alloys.^[1,2] In fact, the list of candidate materials for LSPC is almost limitless, and every time when the question is if it will be possible to synthesize nanoparticles from a given target material, the answer is almost invariably: yes.

LSPC includes three main approaches: laser ablation in liquid (LAL), where nanoparticles are obtained by laser ablation synthesis in solution (LASiS) of a bulk target;^[3] laser fragmentation in liquid (LFL), where smaller nanoparticles are obtained by the fragmentation of larger nano- or micropowders dispersed in the liquid; and laser melting in liquid (LML), where nanoparticles are obtained by a mixed process of melting and vaporization of pristine nano- and microparticles (Figure 1).^[1]

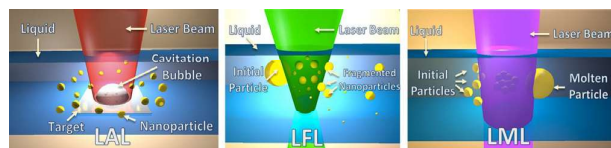


Figure 1. LSPC includes three main approaches: (left) LAL, (middle) LFL and (right) LML. Reprinted with permission from ref. 1. Copyright 2017, American Chemical Society.

Several limitations of LAL, LFL and LML have been solved in the past few years. LAL inherently leads to nanoparticles with wide size distributions, however, today we know that size quenching of metal nanoparticles, already within the laser-induced cavitation bubble,^[4] is possible by the addition of

minute amounts of ions.^[5] Additionally, LAL of a high-speed rotating target can also lead to very small nanoparticles.^[6] By using LFL^[7,8] and LML,^[9] metal nanoparticles can be further controlled in a wide size range while keeping the ligand-free character of the particle surface. The only existing gap in the addressable sizes is currently between 30 nm–100 nm.^[1] Compared to metal nanoparticles, oxide or non-oxide ceramic nanoparticles with a high proportion of covalent compounds still lack universal size-control and size-quenching methods, although precise size tuning has been demonstrated.^[10,11]

In the past, low productivity was a main disadvantage of the LSPC methods. With the recent demonstration of productivities $> 4 \text{ g h}^{-1}$,^[12] achieved by lasers with megahertz repetition rates,^[12] LSPC production of nanoparticles is able to compete with other colloidal synthesis methods and is—under certain circumstances—even more economical.^[13] A rich gamut of experimental techniques, including shadowgraphy,^[14,15] optical spectroscopy and small angle X-ray scattering,^[4,16] are used to study nanoparticle formation and cavitation bubbles induced by laser pulses. However, there still are several question marks over the formation mechanism of nanoparticles, and how the process changes going from low- to high-power LAL, that is, from low- to high-repetition rate lasers.

In organic solvents, LAL often leads to chemical byproducts due to the modification of solvent molecules in the proximity of the ablation site,^[17] and formation of gaseous compounds.^[18,19] This generates a rich chemistry between solution species and the ablated matter,^[20] which opens new avenues for the realization of complex nanostructures but also poses great challenges for the control of the composition and structure of products. Hence, beyond nanoparticle productivity, also selectivity towards one type of product is crucial. In some cases, such as laser generation of white carbon nanoparticles^[21] or nanodiamond,^[22] the output of these side-product materials remains limited.

Remarkable advances towards a better understanding of LAL mechanism have been made by numerical methods based on atomistic simulation^[23] or thermodynamic continuum approach,^[24] for instance by the theoretical reconstruction of the first 3 ns after laser matter interaction in liquids.^[23] These calculations supported the experimental evidence about the formation of oligoatomic clusters^[8,25] and also give possible explanations for wide size distributions observed for some LAL configurations. Also, finite element methods are being applied to study the cavitation bubble dynamics and, in particular, its collapse.^[26]

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An invited contribution to a Special Issue on Nanoparticles with Lasers

While LAL is an interplay between laser, liquid, and target, studies on the role of the target properties and the evolution of the target surface during laser ablation are just being recently conducted.^[27,28,29] In order to fully understand the mechanisms that lead to a specific nanoparticle composition or size distribution, such studies are highly required.

Bilal Gökce received his Diplom degree in solid-state physics from RWTH Aachen University in 2008 and his Ph.D. degree in physics at North Carolina State University in 2012. After working as a researcher on laser applications in the industry, in 2014, he joined the Faculty of Chemistry at University of Duisburg-Essen as a "Habilitation" to establish his own group, which focuses on functionalization of laser-generated nanoparticles and polymer-nanoparticle composites, strategies and applications for high-power ultrafast lasers, and laser materials processing. More about him can be found at <http://www.uni-due.de/goekce-group>.



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Stephan Barcikowski studied chemistry in Braunschweig and Hannover, and obtained his Ph.D. in Mechanical Engineering (Materials). At the Laser Zentrum Hannover e.V., Barcikowski built up the Nanomaterials group, and later led the institute's Materials Processing Department. In 2010, he cofounded the company Particular GmbH and the biannual international conference "ANGEL" on LSPC. Since 2011, he is Full Professor and chairs the Institute of Technical Chemistry I at the University of Duisburg-Essen. He has been scientific director of the Center for Nanointegration Duisburg-Essen (CENIDE) since 2015. More about him can be found at <http://www.uni-due.de/barcikowski>.



Also, acting on target geometrical structure is an alternative, yet scarcely explored, way to improve the control over nanoparticles size distribution^[27] or to access new interesting alloy nanomaterials.^[30] This approach can even be extended to LML, for the synthesis of bimetallic sub-micrometer-spheres by laser irradiation of reactive colloids in the presence of reducing agents.^[31] In general, LSPC proved to be a powerful method for the synthesis of nanoparticles with metastable of unconventional phases, and for mixing at the nanoscale of thermodynamically immiscible elements.^[32,33]

Today, thanks to the above-mentioned advances, LSPC came closer to real-world applications. Laser-generated nanoparticles are successfully used in catalysis,^[34,35] optics,^[36,37] spectroscopy,^[38,39] biology,^[40–42] or medicine,^[43] and many more fields of applications are within the range of LSPC.^[1] However, to reach the same maturity of older synthesis approaches such as the wet chemistry methods, and to enable industrial-grade applications, several issues are still waiting for the answers from the investigations yet to come.

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