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Editorial

Strategies to harvest the unique properties of laser-generated nanomaterials in biomedical and energy applications

Size matters. After decades of intensive nanoresearch, nanoparticles are widely implemented as functional elements on surfaces, into volumes and as nanohybrids, with application prospects as bioactive nanoparticle–polymer-composites and nanoparticle-bioconjugates. However, nowadays only a limited variety of materials that may be integrated into advanced functional products are available: Nanoparticles synthesized by conventional gas phase processes are often agglomerated to micropowders that are hardly re-dispersible into functional matrices, and chemical methods often lead to impurities of the nanoparticle colloids caused by additives and precursor reaction products. As alternative synthesis route, pulsed laser ablation in liquids (PLAL) has proven its capability to generate and conjugate elemental, nanoalloy, semiconductor or ceramic nanoparticles [1–4]. The working principle of the laser ablation process are depicted in Fig. 1.

Fabrication of nanoparticles using laser technology allows a rapid nanomaterial design with unique properties not accessible by any other synthesis route. Firstly, laser-generated nanomaterials in liquid are safe. In contrast to dry nanopowders, nanoparticle colloids cannot be inhaled during processing which leads to an improved occupational safety during product handling. Secondly nanomaterials from laser processes are known for their high purity as chemical precursors are not required by this physical synthesis route and thus the aqueous colloids are 100 percent pure and ligand free. In addition, laser-synthesised nanoparticles possess a unique surface chemistry attributed to partially oxidized surface atoms [8,9], which renders them stable in aqueous solutions by purely electrostatic forces. Finally, this method can be applied universally with almost unlimited variety of materials and solvents, giving access to metal, metal oxide, alloy, and semiconductor nanoparticles.

However, the field of laser ablation in liquids is still confronted with a number of challenges, which includes understanding the fundamentals of nanoparticle formation, the control of the particles' size and polydispersity and finally the productivity of the laser process. The mechanism of nanoparticle formation by laser ablation in liquid is still under vivid debate and entails plasma formation as well as cavitation processes [10]. Recent findings have revealed that crystaline nanoparticles of 2 different size regimes are already present within the cavitation bubble [11], though how they form during cavitation or in the plasma plume is not yet fully understood. As to size control many approaches have been developed including size quenching by organic ligands [9] and inorganic salts [12] as well as delayed conjugation in liquid flow [13]. Even though these techniques allow fabrication of monodisperse colloids at a size regime of 6–20 nm the size range is still limited compared to e.g. particles from chemical synthesis. To this end complementary laser post-irradiation processes namely pulsed laser fragmentation in liquids (PLFL) [14,15] and pulsed laser melting in liquids (PLML) [16,17] have been established to expand the particle size regime available by laser based methods to 4–400 nm (Fig. 2) [13]. Another recent approach entails the in situ grafting of small nanoparticles on catalyst supports [18]. However, synergetic effects between the different methods have not yet been fully explored and the presented size regime was predominantly examined for the model gold [13], while deviations may occur for other materials.

Finally cost-efficient upscaling of the productivity is a major issue as it would allow utilization of laser ablation in liquids in industrial processes. Here, application of flow through setups [19] as well as variations of laser parameters [20] and target geometry [5] were shown to significantly boost productivity and allow fabrication of these materials on a gram scale [21].

So PLAL and related laser-based techniques allow fabrication of multiple size-controlled materials with high purity and a unique surface chemistry. There is a broad variety of applications e.g. from the fields of biomedicine or energy technology which particularly profit from these unique properties. Firstly, high purity and ligand free surfaces are highly useful in bioconjugation experiments where laser generated gold nanoparticles were shown to possess a 5 times higher surface coverage compared to chemical counterparts [22], which could give these materials a significant edge in sensitivity during bioassays. Furthermore, ligand-free nanoparticles proved to be particularly suitable for deposition on support materials [23] for catalysis [30] as ligand shells which tend to hinder adsorption are completely absent. This allowed facile electrodeposition of laser-generated metal and alloy nanoparticles on the surface of electrodes [24] in order to alter their impedance and improve their biocompatibility in medical applications like deep brain stimulation for the treatment of neurological disorders. In addition, coupling of laser-synthesized ligand-free metal and alloy nanoparticles to oxide supports yields highly potent catalysts [25,26] profiting from the fact that calcination for ligand removal and hence heat-induced aggregation can be avoided. Another approach entails embedding laser-fabricated nanoparticles into polymer matrices. When this is done via an in situ process performing laser ablation in

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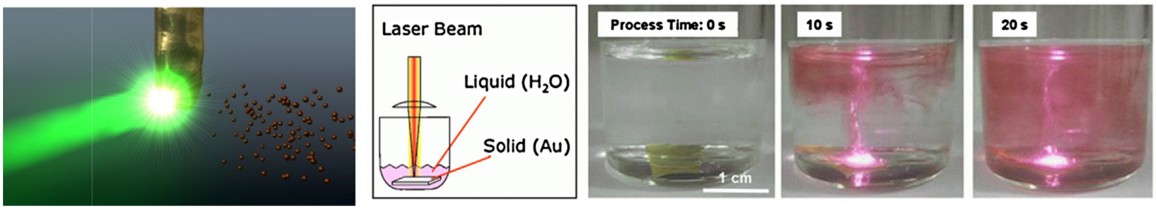

Fig. 1. Left: sketch of laser ablation in liquid using a wire-shaped target allowing both 100% material yield of increased ablation efficiency reproduced from [5] with permission from the PCCP Owner Societies. Right: widely applied, unoptimized setup for laser ablation in liquid batch using vertical beam focused on target below a high liquid level pictures were taken from one of the laser ablation in liquid videos [6], and the images were previously published in [7].

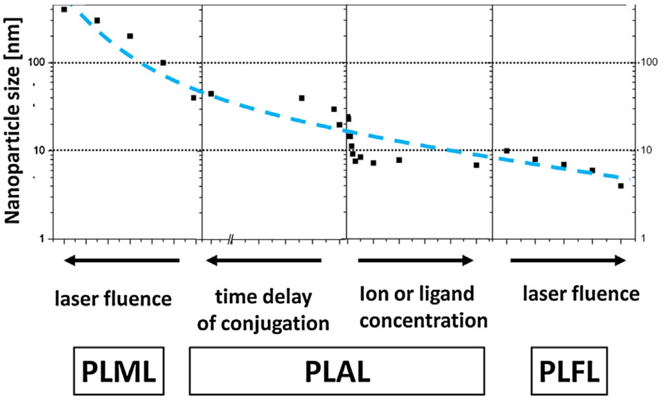

Fig. 2. Size control of gold nanoparticles by laser based methods pulsed laser melting in liquids (PLML), delayed conjugation, size quenching and pulsed laser fragmentation in liquids (PLFL) (adapted from [13]). The arrows indicate gradients of the respective variables.

the presence of monomer or polymer solutions a very uniform particle distribution in the composite as well as a very efficient matrix coupling may be achieved [27]. Nanocomposites based on laser-generated nanoparticles were successfully applied in antimicrobial medical instruments and wound dressings releasing metal ions [28], as well as in medical implants where embedded nanoparticles stimulated the growth of endothelial cells and hence enhanced biocompatibility [29].

Pulsed laser ablation in liquid (PLAL) has proven to be an emerging field and a vivid community has formed, whose progress is greatly stimulated during the biannual ANGEL conference.[1] PLAL particularly excels in fabricating a large variety of nanomaterials with unique properties. Research in this field has taken big leaps forward during the last decade as to the fundamental understanding of the laser ablation process as well as concerning the design of innovative materials. New research fields like pulsed laser melting or laser-induced chemical reduction methods have been successfully integrated which widened the scope of available materials and techniques. Furthermore, the number of contributions devoted to application e.g. in medicine, biology and chemistry has significantly increased. This development directed at real world applications shows that the unique properties of materials only matter when they can be harvested for a special purpose. Hence it is highly probable that successful nanointegration will be the key discipline meant to shape the future of this research field.

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