Circularly Polarised Laser Ablation in Liquids (CP-LAL)

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ABSTRACT

Chirality, a fundamental property of molecules, has garnered significant interest in recent years due to its implications in various technological and scientific advancements. Chiral nanoparticles (CNPs) provide an elegant route to combine the advantages of two worlds; the widespread applications of NPs and the specific benefits, gained due to their chirality generating a large body of opportunities, such as better performance of NPs in biological applications or circularly polarized light (CPL) emitters or high-surface features that are asymmetric catalysts to name a few. Accordingly, large-scale production of CNPs is an obvious demand, which is not easy to be realized with the methods that are commonly used, due to CNPs being either highly material specific or not easily scalable. We suggest the use of circularly polarized light for laser ablation in liquids (CP-LAL) as a chiral variant of LAL to fabricate CNPs, specifically benefiting from the advantageous properties of LAL such as scalability, universality, and green-synthesis principles conformity. The combination of circularly polarized light with laser ablation in liquid techniques (CP-LAL) presents a novel means of exploring the tangled relationships between circularly polarised light and chiral nanoparticle formation, paving the way for innovative applications and deeper insights into the fundamental light-matter interactions.

Keywords:
Chiral Nanoparticles, Pulsed Laser Ablation
in Liquid, Circularly Polarized Light, Light-
Matter Interaction, Chirality Transfer
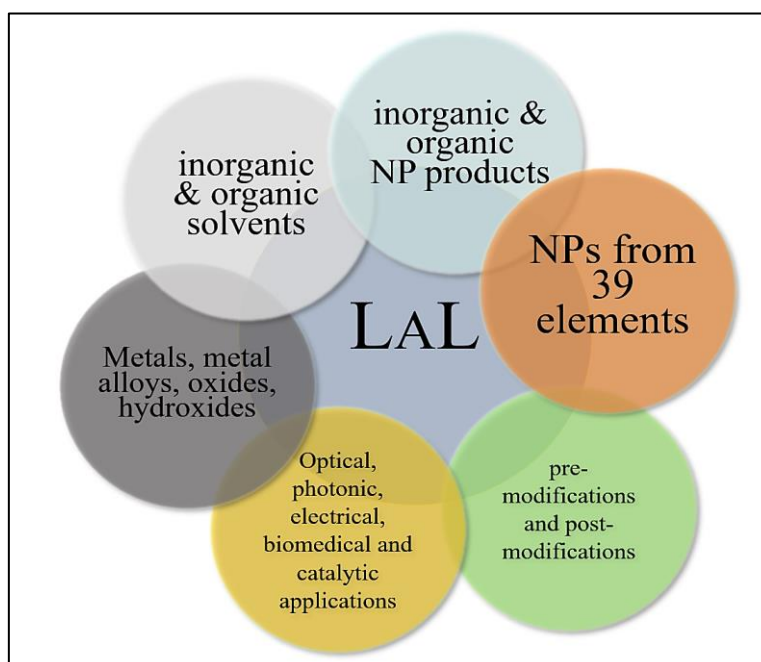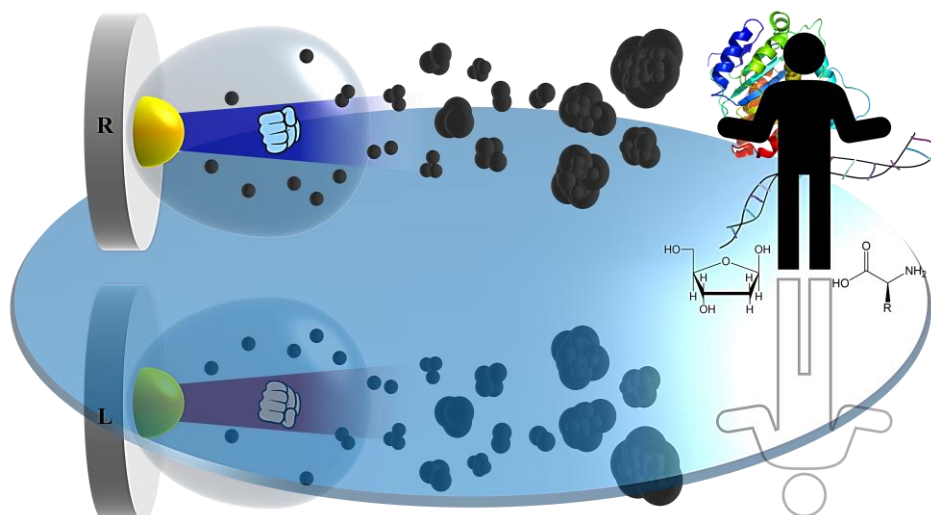
1. Introduction

Since their first mention in late 20th century [1], nanoparticles (NPs) have been attracting growing amount of attention and have greatly influenced modern day technologies. They can be found almost in every aspect of our daily life; from high-tech sunlight harvesting solar cells [2], to mitigation of heavy metal toxicity in green agriculture [3]. Adding an additional twist to NPs, thereby acquiring chiroptical activity, can enhance their applicability even more.

Interest in chiral NPs (CNPs) has been recently expanding, notably since their research boom in the late 2000s [4], not only thanks to the widespread chirality in living organisms, specifically human beings, but also due to chirality-related technological and scientific advances, such as the discovery of chirality-induced spin selectivity (CISS). In the following we will first highlight the role that CNPs can play, by showcasing some of their applications and then mention some of the methods by which they are fabricated. Fabrication of CNPs has been commonly based on an often-repeated pattern which has evolved from modifying existing methods; achiral NP-synthesis has been modified to include steps that introduce chirality, leading to the fabrication of CNPs either by asymmetrising the fabrication process itself [5, 6] or by applying post-fabrication modifications to the NPs [4, 7]. We will then be proposing to also apply the same recipe of modifying existing methods to a new one that, surprisingly, has not gone through this process yet.

In our opinion, laser ablation in liquids (LAL), a method whose interest has exponentially increased during the last decades [8], as a consequence of its beneficial features (Figure 1), can be easily adapted to include chirality and possesses great benefits as a method to fabricate CNPs (Figure 2).

Fig. 1. Summary of the LAL capabilities in terms of substance scope, imcorporability of LAL and its applications [50,66]

Fig. 2. Chirality and Chiral Nanoparticles (CNPs) in a nutshell: their production and examples of chirality in nature such as the left and right hand, biomolecules, etc. The blue pane acts as a mirror between the upper objects alongside their chiral counterparts below the mirror

2. CNPs as functional materials

Even in its long-standing existence, chirality remains a focal point of interest in modern scientific exploration [9]. Since chirality is an indispensable natural feature, modern science concludes towards imitating nature so as to accelerate the research landscape regarding both the chirality genesis inquiry and at the same time regarding the formation of unconventional and bespoke CNPs [10]. Approaching nature as it is, most high-tech applications exploit the benefits of chirality to address the needs of medicine and technology. CNPs have found their way into multiple application fields as summarized in multiple recent reviews [11-13], some of these examples are listed below.

2.1 CNPs as Asymmetric Catalysts

CNPs can be used to catalytically push a chemical reaction preferably towards the formation of one enantiomer over the other. Asymmetric catalysis is certainly one of the relevant technologies of our time, given the growing population of our planet and with it, the drastically increasing demand for pharmaceuticals, about half of which are chiral compounds [14]. A clear demonstration of the role of CNPs was presented by Kunz and coworkers [15], who used chiral ligands to functionalize supported Pt NPs and so fabricated CNPs with an appreciable catalytical stereoselectivity leading to an enantiomeric excess of 74% in hydrogenation of ethyl 3-oxo-3-phenylpropanoate. Chirality transfer from chiral ligands to metal atoms in catalytically active metal complexes have also been recently investigated in detail [16]. It was shown that the chiral ligands are more involved than only providing asymmetric steric hindrance. They directly affect the electronic structure of the catalytically active metal atom, and thus play a twofold role in the transfer of chirality from the catalyst to the product.

2.2 CNPs as Enantioselective Adsorbers

CNPs can also act at enantioselective adsorbers, which are of profound importance in enantio-resolution of chiral compounds. CNPs fabricated by asymmetrising gold NPs by cysteine coating,

was shown by Gellmann and et al. [17] to behave differently when exposed to enantiomers of propylene oxide from aqueous solution. This might appear trivial as it is no surprise that the diastereomers formed by propylene oxide and cysteine are expected to be different.

The role of the CNP here, however, is to enhance the detectability of the adsorption process. The authors could show that the size of the CNPs affects their optical measurements via three mechanisms; i) the smaller the particle, the lower the possible loading of the adsorbate; ii) the smaller the NPs, the higher the induced optical activity into them; and iii) the size-dependence of enantiospecific adsorption equilibrium constants.

2.3 CNPs as Highly Active Anode Material

Owing to the discovery of the CISS effect more than a decade ago [18], chirality has found its way also to energy-relevant processes such as photoelectrochemical water splitting, generating green hydrogen. Namman and coworkers showed that CNPs generated by chemisorbing chiral molecules to Fe_3O_4 NPs that were deposited onto an anode material leads to a spin-selective electron transfer from the solution to the anode [19]. Owing to this spin alignment, the formation of H_2O_2, which is the unwanted by-product, is suppressed and O_2 evolution in the triplet state is promoted. In this example the high surface area of CNPs combined with their chirality enabling the CISS effect, gives the anode a set of favourable properties; large currents of about 10 mA/cm^2, a lower overpotential and a dramatically lower peroxide yield, compared to an anode coated with achiral NPs.

2.4 CNPs as Phototheranostic Agents

CNPs have also found their way to tumour phototherapy. These materials show high efficiency of light conversion within the biological tissue's spectral window region and, owing to their handedness, exhibit selective absorption that can be utilized favourably. This provides a great advantage as it helps to minimize unintended damage to normal cells during the therapy. Xu and coworkers reported the efficient in vivo ablation of tumours by asymmetrised MoO_{3-x} CNPs in 2021 [20]. They could show that cysteine-capped molybdenum oxide CNPs possess chirality-dependent NIR absorption and high photothermal conversion efficiency. In addition, their rapid excretion in body administration removes any concerns regarding their toxicity, paving the way for a safe cancer therapy combining the advances of chiroptics and phototherapy.

3. Fabrication of CNPs

The applicability of CNPs relies heavily on the fabrication and manipulation approaches [4]. CNP fabrication is broadly categorized into bottom-up and top-down approaches based on the precursor materials [6, 21]. Bottom-up techniques involve atomic assembly, while top-down ones break down larger materials into nanostructures [6]. These methods focus on chiral nanoparticle synthesis for specific designs and properties. Synthetic methods can also be classified depending on when chirality is induced into the nanoparticle. The method of preparing non-chiral nanoparticles and then inducing chirality on them varies depending on the inducer and the interaction type. Chirality can arise without structural change via electrostatic interaction with a chiral organic inducer or by altering the atomic arrangement on the nanoparticle surface, creating a chiral footprint. Chirality is then transferred by binding chiral molecules to the nanoparticle surface through chemical reactions. After the nanoparticle synthesis, chirality can be induced through methods such as adsorbing chiral molecules onto the surface or chemical reactions or enhancing surface chirality. These steps are crucial

for adjusting nanoparticle structure and chirality to achieve desired properties. For the purpose of this perspective contribution, we classify chirality induction at the chemical/physical/optical level in a more general and comprehensive scope.

3.1. Chemical Asymmetrization

When synthesizing plasmonic chiral nanoparticles using a bottom-up approach, wet chemical synthesis accounts for an overwhelming proportion of the reports. Inducing chirality at the level of the nanoparticle itself provides versatility and high yields. Using a chiral ligand (or chiral capping agent) to induce chirality, together with an achiral reducing agent, it is possible to regulate the size, shape, and chiroptical activity of the nanoparticles by changing their composition as well as other physical and chemical reaction parameters [22]. In some cases the chiral molecule can act as a chiral inducer and a reducing agent at the same time, as for example cysteine, which has a thiol group interacting strongly with noble metals [23]. CNPs employing noble metals with optically active surface plasmon resonance (SPR) are highly demanded for their tunability and enantio-selectivity; their synthetic procedure requires external chiral inducing forces, electrostatic interactions, or the deformation of achiral structures through chiral ligands resulting in the formation of a chiral footprint [24]. However, it may require complex reaction conditions and purification steps especially for the applications of CNPs in the biomedical field.

Starting with achiral inorganic nanoparticles as a basis, chirality can also be induced during local growth, thereby imparting chirality to the entire structure. Transferring chirality via enantiospecific crystallization from initially achiral NPs, entails interaction with chiral organic molecules through electrostatic interactions or structural stress-induced deformation of metal nanoparticles. Another method of first synthesizing achiral nanoparticles and then creating a chiral NP assembly through asymmetrical bonding between each nanoparticle, is the self-assembly technique. In this case, chiral molecules are adsorbed on the surface of already-formed nanoparticles, and the chirality of the molecules is transferred to the surface of the nanoparticles, leading to asymmetric self-assembly, the so-called chiral assembly. Nanoparticles are spontaneously arranged in a specific direction due to the inherent chirality of the inducer species. For example, tetrahedral chiral carbon atomic species induce a pyramidal assembly, a chiral molecule with two non-parallel dipoles forms twisted dimer of nanorod, DNA double helix yields helical arrangement of nanorods and so on [25].

Template assisted synthesis of chiral nanoparticle is where the specific structure of the template guides the precursor species assembled in a chiral order [26]. Template-assisted synthesis employs chiral templates or scaffolds to guide the formation of chiral nanoparticles [27]. Techniques such as template-directed electrodeposition, templated self-assembly, and molecular imprinting facilitate the creation of chiral structures with precision. Advantages include precise control over chirality and scalability, although template removal can pose challenges [28].

3.2. Physical Asymmetrization

Directed self-assembly combines established self-assembly techniques with external forces to achieve tuneable nanostructures. For instance, Choi et al. demonstrated polarization-modulated terahertz radiation using herringbone-patterned plasmonic sheets [29]. Mechanical-instability-induced buckling is a method in which symmetry is broken in the starting material by applying asymmetric mechanical deformation such as stretching, twisting, compression, and expansion to generate nano- and micro-scale chiral forms. Kim et al. induced chirality in gold nanoparticle multilayers through mechanical torque during deposition [30]. Other methods include

thermomechanical strain for 3D chiral meta-atoms and helical magnetic fields for dynamic modulation of chiral superstructures [31].

Focused ion beam and electron beam induced deposition (FIBID/FEBID) are two classical examples of bottom-up methods used under vacuum conditions. Approaches such as chiral plasmonics, chiral field-assisted assembly, and chiral lithography offer unique pathways for fabricating chiral nanostructures. These techniques provide rapid and scalable fabrication options but may require specialized equipment and expertise. Generally-used approaches include removing local material from the bulk surface using technologies like direct laser writing (DLW), focused ion beam etching, and optical or electron-beam lithography to achieve the desired shape, layout, and properties. Although this method can be used to create a variety of nanostructures, preparing complex chiral assemblies has its own difficulties and limitations. Glancing- or inclined-angle deposition is a technology based on a bottom-up approach that creates chiral nanostructures by controlling the structure at the nanoscale through spatial control at the macroscale without a chiral inducer. Kotov and his colleagues achieved controlled symmetry breaking by obtaining both left- and right-rotation isomers of asymmetric gold nanoshells via vacuum evaporation at different tilt and rotation angles on pristine achiral nanopillars of ZnO [5]. Fischer and co-workers combined low-temperature shadow deposition and nanoscale patterning to achieve nanocolloids with anisotropic three-dimensional shapes, feature sizes down to 20 nm, and a variety of material choices [32]. Recently, a case was reported about creating a 3D folded nanorod in which the structures of different materials are connected at different angles by adjusting the tilt and rotation angles [33].

3.3. Optical Asymmetrization

Although a chiral organic inducer may be an external force, there are also cases where the chiral force transmitted by circularly polarized light provides asymmetry. With circular polarization of light, chiral NPs can be created without using a chiral-organic capping agent, reducing the cost of synthesis and removing the need for post-synthesis removal of the agents. Light induced crystallization can be alternative to a chiral-organic inducer, and amplification of enantiomeric excess can be achievable [34, 35].

AgNPs were shown to deform into a racemic prism-like shape under illumination using unpolarized light [36, 37]. Circularly polarized light induces enantio-specific crystallization through plasmon manipulation and achieves enantioselective polymorphic transitions via laser irradiation. The first example of using CPL-induced assembly of metal clusters in solution to synthesize chiral gold nanostructures were reported recently by Kim et al, who showed that illumination of gold salt solutions with CPL induces the formation of NPs. Subsequently, these NPs assemble into chiral nanostructures with 10-15 nm in diameter [38]. Using sodium chlorate chiral crystallization as a model system, Niinomi and colleagues demonstrated significant enhancement of chiral photosynthesis efficiency on a Mie-resonant silicon metasurface excited by CPL [39]. This resulted in a statistically significant large crystal enantiomeric excess of approximately 18%, surpassing the capabilities of CPL alone. Using CPL in the visible range, Qiao and co-workers initiated asymmetric photodeposition of PbO_2 on plasmonic gold bipyramids (AuBPs). They demonstrated for the first time the dependency of the asymmetric deposition on the wavelength of polarized light. The difference of deposition location was attributed to differences in electric field distribution resulting from varying excitation wavelengths and polarizations [40]. Tao Ding and his team demonstrate polarization-controlled growth of platinum oxide/sulfide nanoparticles via optical dipole interactions and near-field–enhanced photochemical deposition [41]. The complex manufacturing process and

poor scalability of 3D lithography can be overcome through a light-matter chirality transfer approach, so called 'CPL-print'.

Kim and co-workers reported single-step, mask-free direct-write printing, using silver salt aqueous solutions, which enables simple and versatile direct-write 3D printing of chiroplasmonic nanostructures on a variety of substrates [42]. Achieving three-dimensional and planar chiral nanostructures extendable to cadmium sulfide have been reported by adjusting polarization or using vector beams. This method offers a simple approach to create versatile chiral and complex platinum oxide configurations by modulating the laser beam polarization [41]. By using the ablation method with circularly polarized light in both spin- and orbital-angular momentum of photon, the fabrication of chiral nanostructures on a metal surface (not nanoparticles) was reported [43, 44].

4. Circularly Polarised LAL

4.1. LAL Technique

Fabrication and processing of innovative and unprecedented substances has become imperative for the needs of science. One of the assistants to that end are lasers which constitute a broad scientific branch, namely micro- and nano-engineering. There is a plethora of laser-assisted techniques that fall into that category for either the de novo synthesis of nanomaterials, as well as for the post-production processing and the size-growth control of NPs [45]. One of the most promising methods in this field are summarised under the umbrella term of PLA.

Since its advent in the early 1960s, pulsed laser ablation (PLA) has been employed for multiple uses in industry and research [46]. LAL (or otherwise specified as pulsed laser ablation (PLAL) [8], Pulsed laser ablation in liquid (PLAIL) [47] laser ablation synthesis in solution (LASiS) [48]) is a variant of PLA in which the absorbing target is fully immersed inside a liquid, whereby the confining environment is causing the violently ejected species by the high-power laser to form agglomerates by the rapid reactive cooling at the bubble-liquid interface transition [47, 49]. This rapid series of actions render LAL suitable for NP-generation [50] and by breaking down these sequential phenomena into timescales, one can acquire a picture of the LAL landscape.

Nevertheless, the precise sequence of the LAL-induced phenomena are target- (metal, semiconductors, dielectrics, alloys etc.) and time- dependent (between fs-ps, ps-100ps etc.) [49] and it is a subject still under debate, although the fundamental principles were settled around the 2000s, originally by Wang's et. al motivating assumptions [51, 52].

The generally accepted LAL mechanism, which is primarily described by physicochemical terms [53], and leads irrespective of the target to NP-generation, is illustrated in Figure 3. This simplified rendition of the LAL procedure is still amenable to a more exhaustive probing because there are some facets of LAL that are still obscure [54]. The main steps, however, broken down into time intervals, include: laser-matter interactions, plasma and bubble formation and shortly after the plasma formation and condensation (Figure 4), many different species are being released in the liquid phase: atoms, clusters, primary and secondary NPs [55-58, 53]. The ejected nanoparticles from the ablated area of the absorbing target linger in the liquid ambience, resulting in their coalescing into NPs [59, 60].
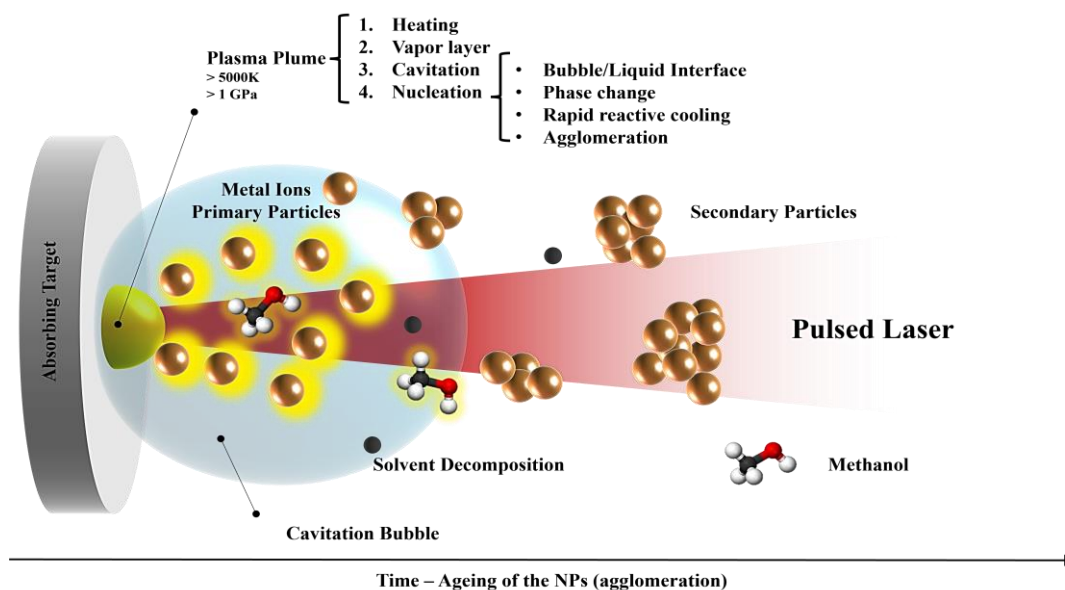
Fig. 3. Snapshot of an ablating surface. Three of the main steps of the LAL technique are captured: The plasma plume (yellow), the cavitation bubble (light blue) and the main laser beam irradiating the target. The ejected NPs (brown spheres) can be found as primary particles in the bubble or they become agglomerated (secondary particles) with the time [53]
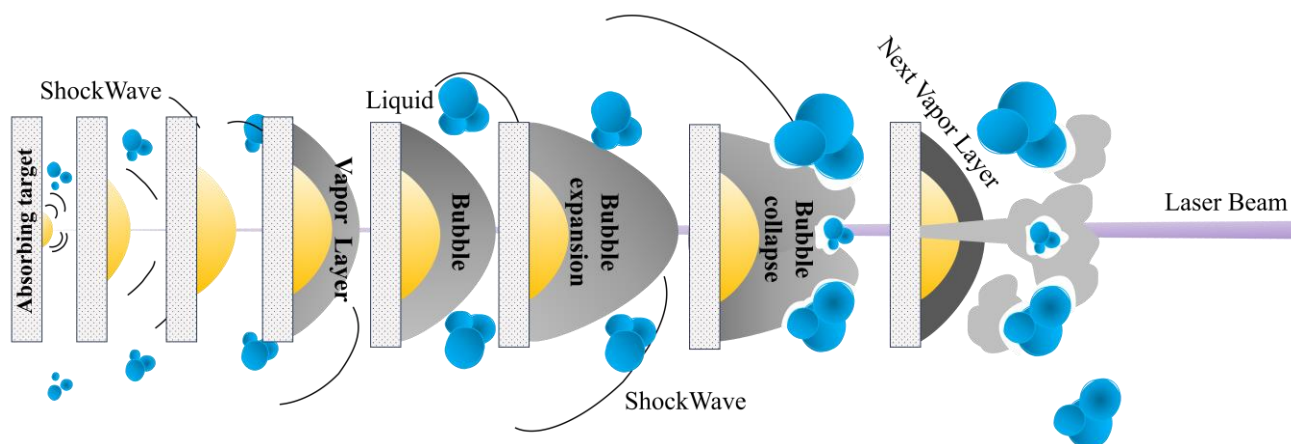
Fig. 4. The time evolution of physical phenomena taking place on the absorbing target (dotted light grey rectangular) in a liquid medium (blue bubbles); the plasma plume (yellow semi-ellipsoid on the target) generating shockwaves (black lines); the vapor layer expanding to a bubble and then collapsing (grey bubble). The next laser pulse approaching, generates a subsequent vapor layer (dark grey layer) after the collapse of the pre-existing bubble, and continues to expand as long as the plasma plume is present (i.e. the incident laser beam in on) [55-58]

4.2. Benefits from LAL Techniques

As a technique for NP-generation, LAL combines two highly desirable properties, stemming from the top-down regime that LAL predominantly belongs to [61], but are seldom found jointly in other methodologies, which are commonly employed for NP generation. One of these is the applicability of LAL in "huge scale manufacturing" [61] having recently in 2016 & 2017 reports of LAL production effectiveness of some grams per hour [49]. The other beneficial property is its universality, i.e. the

ease to apply LAL to various materials (e.g. polymers, metal surfaces, organic and inorganic substrates etc.). The required equipment for LAL includes: laser, optics, solution, target and their container. It is evident by this setup that LAL can be applicable to virtually any target by conveniently modifying the laser and liquid parameters; the initially costly expenditure of the laser device can be compensated by its universal applicability [62]. In the following passage more details will shed light on the benefits of LAL.

4.2.1. Upscalabilitly

The need for upscaling NPs production is evident as NPs are used in many mass-consumption products, in biomedical applications, and LAL products especially, may be used in catalysis [50]. Considering which factor plays the most significant role during the LAL process that could possibly increase the ablation rate (in other words $m_{(ejected \, NPs)}$/time), Zhang et. al collected evidence that laser fluence "might be the most important factor for high LAL throughput" and not the pulse duration, which might eventually start boiling the liquid in the continuous-wave laser irradiation [50]. Furthermore, most of the evidence in the literature was based only on the side of the laser parameters and the shape of the absorbing target with the bulk 3D materials and the quasi 1D being the most efficient in LAL techniques but not on the side of the liquid, which is why there is great need internationally for further expansion on this field [50].

For this reason, Gökce et. al [63], scrutinised this time the plasma-substrate interactions; by minimising in space or in time preferably the cavitation bubble, which is initially released during the ablation, they achieved higher production efficiency values, as each present bubble has a shielding effect (for the absorbing surface) against the following laser pulses. Likewise, the group around I. Bar [64] realised a LAL framework which increased the productivity scales of LAL and subsequently those of NPs, by irradiating an SHG-LAL on inclined metal targets at their menisci. Scalability is thus assumed not to be dependent on the nature of the absorbing target, but with the experimental configuration and the method. This independent feature is akin to the next beneficial property of LAL.

4.2.2 Universality

By looking at the review literature on LAL [50, 56, 65, 66], one can surmise that the feasible LAL products spans both the organic and inorganic nanospecies. Apart from single-species production, composites are also possible by replacing the absorbing target with a different one, while (at the same time, then) re-irradiating the previously fabricated NPs in the same solution (Succesive LAL, SLAL) [65]. LAL's universality strength can be highlighted by the great variety of reaction types that can assist (oxidation, hydroxylation, phosphorylation, hydrogenation, sulfidation, nitridation, carbonization, galvanic replacement and reductive alloying [65].

The great potential of LAL alone lies also in the fact that the consecutive series of phenomena taking place, are considered together as a whole in a so-called one-step process [47], analogous to the single-pot syntheses in wet-chemistry routes. Hence, LAL approaches for NP synthesis can be extended almost to any kind of absorbing target by obeying the needs for each target in terms of their physicochemical conditions and parameters. This modulation is mostly chemical-free and chiefly without side products or waste.

4.2.3 Green synthesis

It is widely accepted that LAL protocols observe the rules of green chemistry [66, 67]. More specifically, the initial selection of the absorbing target as well as the resulting NPs can originate from non-toxic chemical species [68], whereas in time-honoured wet-chemistry protocols, other components of the experiment may clash with the aforementioned green rules (i.e. solvents, auxiliary chemical agents, side products and gasses etc) [62].

The ecological aspects of LAL methodologies have no impact on the production efficiency or the size of the generated NPs [68]; on the contrary, with this method, innovative NPs are possible, in terms of size, surface properties, plasmonic and electronic structures, all of which are key factors in top-notch applications, such as MRI and CT imaging [69] or contrast agents [70]. What is more, the liquid confining environment of the LAL regimes compared to ablations in air for example, prevent the production of airborne NPs and other particles throughout the LAL mechanism (e.g. through collateral reactions, further decomposition of the products or the solvents etc.), that could pose a threat to the human health [66].

Nevertheless, without loss of generality, not all LAL components are fully green; one can claim, that the use of any sort of laser runs counter at least to the ultimate principle of green chemistry, i.e. that of the "inherently safer chemistry for accident prevention" [67] as the laser risks are very high [71] and "inherently" probable. Furthermore, it can be said that the energy-efficient design, namely the 6th green principle, is being questioned when lasers are operating upstream the optical setup [72].

5. Summary

The essence of this paper is about chirality and particularly about chiral nanoparticles (CNPs) and a novel conception about the incorporation of CPL in LAL techniques. LAL is a method that has been successful to produce NPs as shown by the numerous publications on this topic. The auspicious perspective that CPL is a chirality inducer, owing to the plasmonic coupling between CPL and substrates [7], and the exploitation of this finding in tandem with the LAL technique still conforms to the best of our knowledge, to a minimum with the green chemistry regulations. CP-LAL systems could introduce chirality and thus a deeper understanding of the mechanism could be achieved, without having to mimic the complexity of nature but rather trying to investigate the chirality question with the least sufficient factors, i.e. CPL and LAL. In this manner not only will the chirality question be clarified, but also at the bio-level, there will be more credible assumptions about the universally preferred homochirality of the biomolecules.

As mentioned before LAL, on its own, is mechanistically a combination of entangled temporal and spatial phenomena [54], whereby its research obstacles lie. Hence, the integration of CPL into LAL underpins the significance of the interdisciplinary joint efforts needed to clarify the LAL framework parameters on the one hand and the origin of the observed chirality on the other.

However, taking into consideration the above stated benefits of LAL and utilizing it in tandem with CPL could further contribute to both the elucidation of the chirality emergence in nanoparticles and the mechanism of LAL by acquiring more conclusions about the interplay of light with matter.

This paper advocates for the exploration of CP-LAL as a method to fabricate CNPs by leveraging the advantages contrary to the shortages of wet-chemical methods, since by adding chirality in the LAL framework could enhance our capability to disentangle the involved steps mentioned above and explain further the mechanism of CNPs nanofabrication via LAL.

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