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Rapid nanointegration with laser-generated nanoparticles

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Abstract

After several decades of intense research in the field of nanostructures, nanoparticles are widely implemented for functionalization on surfaces, into volumes and as nanohybrids, with application in active nanoparticle-polymer-composites and as nanoparticle-bioconjugates. But nowadays only a limited variety of materials can be integrated into advanced functional products due to limitations of gas phase and chemical synthesis methods such as particle sintering or impurity. As alternative synthesis route, laser ablation and nanoparticle generation in liquids has proven its scalability and capability to generate totally ligand-free colloidal nanoparticle building blocks.
This contribution highlights how the unique properties of laser-generated nanoparticles can be harvested in prospective real-world applications rapidly via "nanointegration" into the fields of biomedicine and catalysis. Furthermore, it addresses how laser parameters, chemical environment and reactor design may be tuned in order to obtain monodisperse nanoparticles and to enhance the productivity of the laser process.

Keywords: laser ablation; ligand-free nanoparticles; nano-integration

1. Introduction

The methods for fabrication of highly pure nanoparticles are very limited. While wet chemical bottom-up synthesis usually requires additives to stop the induced particle growth (size quenching) mechanical comminution processes cause contamination by abrasion. Gas phase synthesis is a method to obtain high purity but fabricated nanoparticles are highly aggregated or agglomerated due to strong particle-particle interaction during product capture. Moreover, this gas phase synthesis can be problematic as it bares the potential risk of airborne particles being inhaled or exposed to the environment. A method delivering pure and stable nanoparticles in liquids, in an occupationally safe way, is pulsed laser ablation in liquids (PLAL). PLAL enables scalable generation of totally ligand-free nanoparticles in different solvents in a continuous process. Another advantage of PLAL is the wide variety of materials, which may be generated.

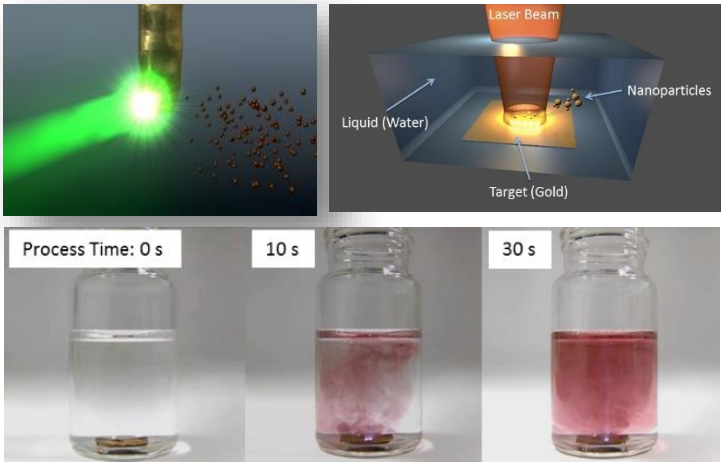

Fig. 1: Illustration of pulsed laser ablation in liquid of a thin wire (left image) and a planar surface of a gold target in water (right image and bottom) [1, 5]

During PLAL an intense pulsed laser beam is focused onto a bulk material surface. Nanoparticles are released from the initiated cavitation bubble that follows a laser-induced plasma plume [2, 3]. Figure 1 illustrates this process for gold in water. The left image illustrates a green laser beam interacting with the tip of a thin wire from which the nanoparticles are released. Thin wires are known to increase nanoparticle productivity compared to the conventional ablation of a planar surface (see Fig. 1 right) [4].

Being used for the generation of metal, alloy, metal oxide and semiconductor nanoparticles, ligand-free size control of noble metal particles may be achieved by addition of low salinity electrolytes or subsequent post-irradiation treatment. [5-7].

This technique has a nanoparticle yield of 100% (solid educt to nanoparticle) and gives access to a variety of nanoparticle materials in different solvents. Accordingly, for laser-generated nanoparticles many different potential applications have been explored.

2. Application of laser-generated nanoparticles

Purity Matters. The benefit of PLAL delivering ligand-free nanoparticles enables different applications where this purity is an advantage. Furthermore, laser-fabricated nanoparticles feature a unique surface chemistry and high surface charge due to partially oxidized surfaces [8, 9]. The following paragraphs highlight three key areas, namely polymer composites, heterogeneous catalysis and biomedicine, where laser-generated nanoparticles and their unique properties can be exploited in potential real-world applications.

2.1 Polymer doping with laser-generated nanoparticles

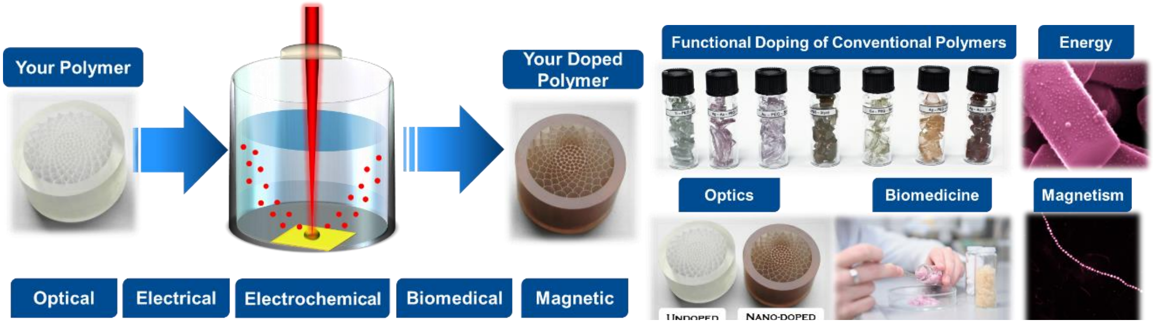

Fig. 2: Scheme of direct polymer doping by pulsed laser ablation in liquid monomer or polymer solution with ligand-free nanoparticles (left, structures manufactured by microTEC) and different application options (right)

Doping of polymers with laser-generated nanoparticles gives direct access to nanofunctionalization with an emerging variety of application, as recently reviewed in literature [10]. The nanoparticles can be generated either directly in the liquid monomer or in a solvent containing the monomer or polymer [10]. In a final step polymer-nanoparticle composites [11-14] which are optically [15] or biomedically [16-18] active are obtained. Laser synthesis is a powerful tool to synthesize nanoparticles that are directly incorporated into the polymer and hence feature strong interactions with polymer matrix. This can be achieved by the absence of surface covering ligands and therefore the resulting nanocomposites areless prone to phase separation due to tightimmobilization [10].

Fig. 2 illustrates the route to obtain nanoparticle-doped polymers and shows different products for various application. Basic idea is to simply use the monomer/polymer in liquid for nanoparticle dispersion which is identical to the solid polymer the prototype is made of, avoiding the use of any other additives.

2.2 Catalysis and surface structuring with ligand-free nanoparticles

Laser ablation synthesis in liquid releases highly charged particles. Hence, another benefit of the laser-generated nanoparticles is the possibility to structure surface directly forcing the charged nanoparticles to

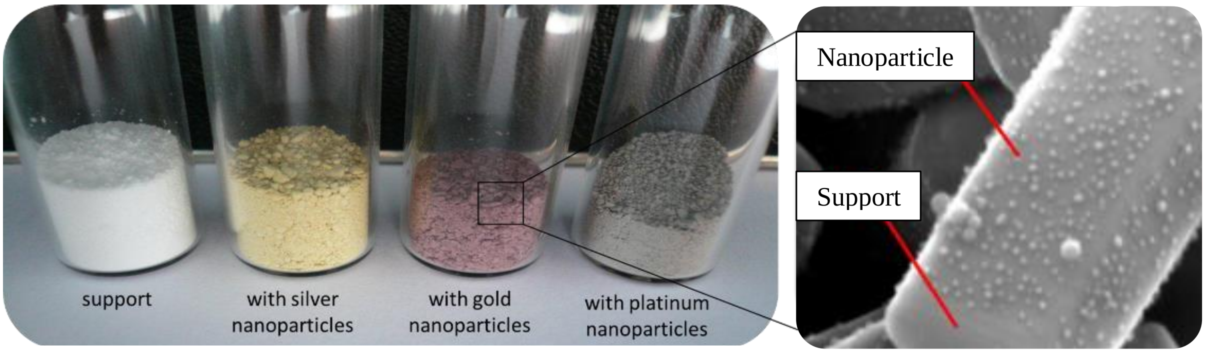

Fig. 3: Facile fabrication of heterogeneous catalysts by contacting laser-generated colloids with commercial powders. Photograph of a powder support without and with different laser-generated nanoparticles (left) and SEM image of gold nanoparticles attached to a zinc oxide mircoparticle [20]

attach irreversibly to oppositely charged particle supports added to the colloid [19, 20]. Thereby different nanoparticle/support ratios are achievable [21] as this adsorption yields 100% of nanoparticle onto the support up to several tens of weight% (depending on the surface provided by the support) [20]. In contrast to conventional chemical synthesis methods the nanoparticle size is constant for all particle loadings, which is relevant for model reaction-standards optimizing catalytic performances. Fig. 3 demonstrates different nanoparticles attached to a microparticle support. Before supporting of nanoparticles the support appears as white powder. Adsorption of, e.g. silver, gold or platinum nanoparticles results in coloring the support particles. The color accords with the colloidal appearance that indicates a prevention of particle aggregation. This can be confirmed by electron microscope images (right image in Fig. 3: gold nanoparticles on zinc oxide microparticles) giving insight to the surface structure on the nanoscale. Such metal/semiconductor nano/micro hybrid structures are relevant for several reactions in chemical industry such as alcohol oxidation [22], selective oxidation of propylene [23], low-temperature CO oxidation [24], direct synthesis of hydrogen peroxide [25], photocatalysis [26] or water splitting reactions [27].

Beside this, ligand-free gold nanoparticles are adequate candidates for catalytic model reactions as no ligands are present at particles surface that can potentially influence the reaction. A perfect match of kinetic model with the experiment was recently shown by Gu et al. using the laser-generated gold nanoparticles [28].

2.3 Laser-generated nanoparticles for biological and biomedical applications

The unique properties of laser-fabricated nanoparticles can also be utilized in biological and medical applications, where particularly the high purity of these particles is beneficial. Due to their "purity by design", toxic cross effects can be avoided and nanoparticle purification by labor intensive methods like filtration, dialysis and centrifugation is unnecessary. The field of biomedical applications comprises three key areas where laser-generated ligand-free nanoparticles have already been implemented. The first relevant area is surface structuring by electrophoretic deposition (EPD). In contrast to strategies described in 2.2. nanoparticle support interactions during EPD do not occur spontaneously but are initiated by an external electric field, while deposition is favored due to the absence of surface ligands [31]. This process was successfully applied to structure electrodes [32] or medical implants [33]. The key feature in this case is that surface roughness on the nanoscale tends to favor cellular growth and may hence increase biocompatibility. A second biomedically relevant application is the nanointegration of laser-generated metal nanoparticles into polymers by strategies specified in 2.1 and literature [10]. Main advantage of these nanocomposites in a biomedical context is

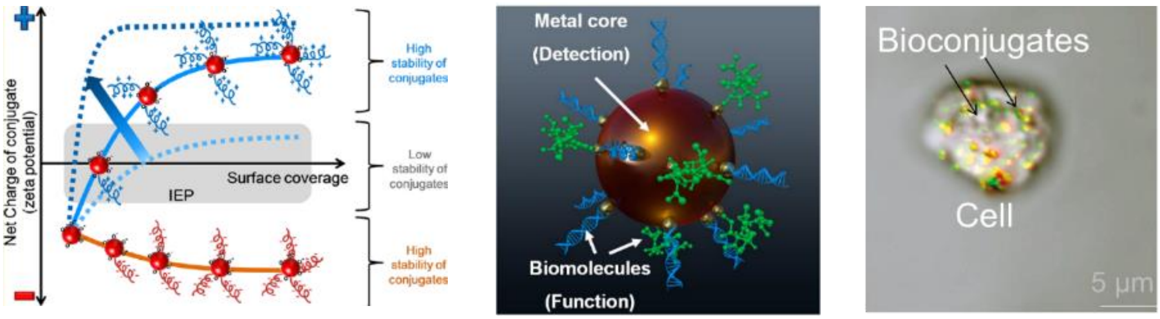

Fig. 4: Stability of nanogold-peptide conjugates dependent on the ligand´s net charge. In a range close to the isoelectric point (IEP), stability is lowest [29] (left). Illustration of a functionalized metallic nanoparticle conjugated with different biomolecules (middle). Representative confocal image of a somatic cell labelled with laser-generated nano-bio-conjugates [30] (right).

controlled ion release, which gives access to aseptic materials with high capacities and selective ion release systems e.g. applicable in wound healing processes [34-36]. The third relevant area comprises nano-bioconjugates composed of a metal core, predominantly gold, used for detection and a ligand shell of functional biomolecules. It was shown that laser-generated nanoparticles can be functionalized with higher surface coverage and conjugation efficiency than conjugates obtained by ligand exchange [37]. Furthermore, it was found that the colloidal stability of these conjugates is highly dependent on the charge of the applied ligand [29], a context illustrated in Figure 4. Bioconjugates, with functional units containing oligonucleotides [38], aptamers [39] and peptides [29] were successfully generated and could be used for cellular imaging in somatic cells [40] but also during sperm sexing [41].

3. Summary and conclusion

Nanoparticle generation by pulsed laser ablation in liquid is a constantly growing research field, where next to fundamental studies on the formation mechanism, nanointegration has become a key factor. Nanointegration entails that the properties of nanoparticles, namely their optical, biomedical or catalytic properties are integrated into half-finished materials or standard educts relevant for application. It could be shown that several research fields including catalysis, biomedicine and nanocomposites could greatly profit from laser-generated nanoparticles and several functional materials with improved properties are being implemented in the respective fields.

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