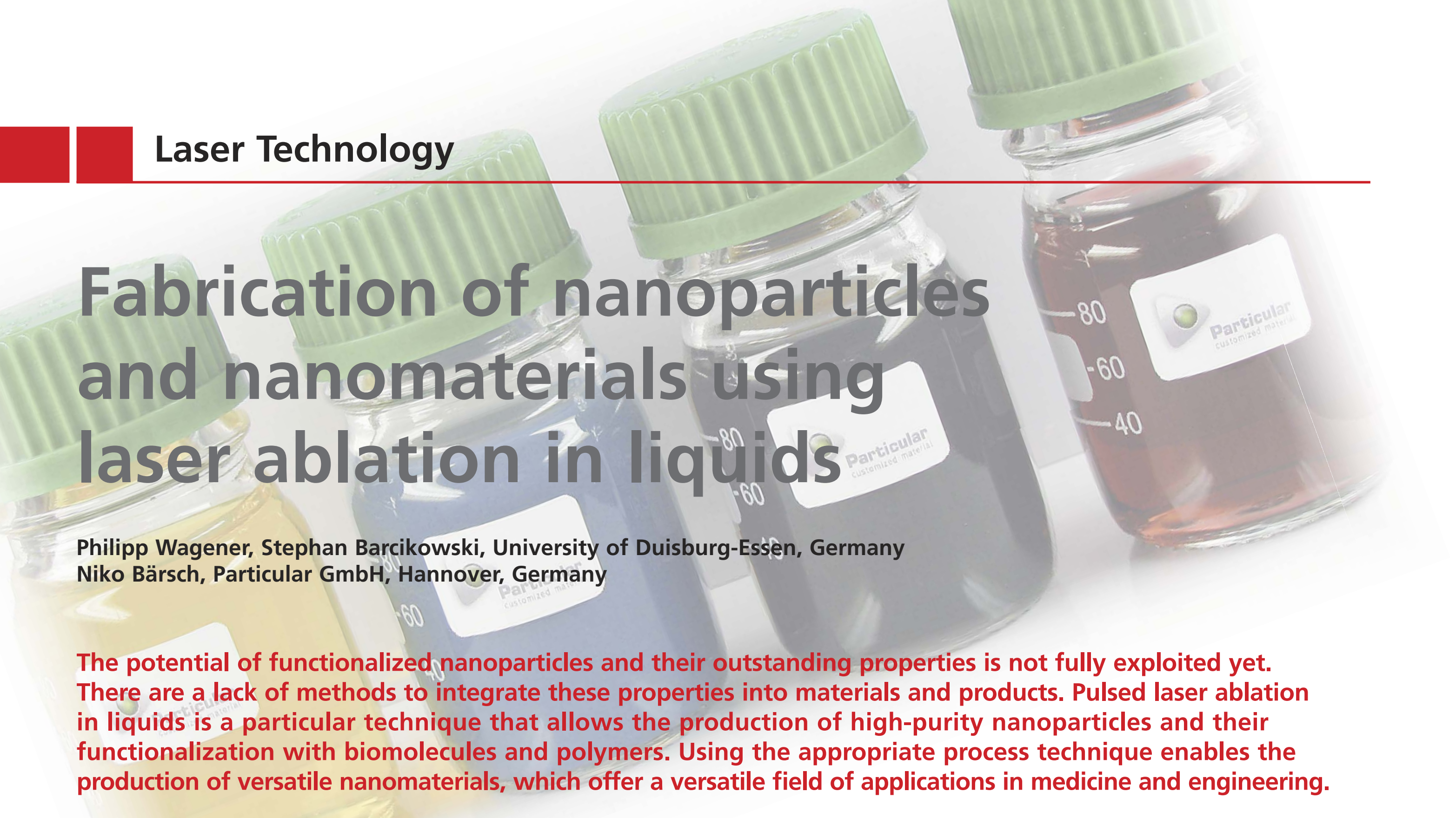

Fabrication of nanoparticles and nanomaterials using laser ablation in liquids

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The potential of functionalized nanoparticles and their outstanding properties is not fully exploited yet. There are a lack of methods to integrate these properties into materials and products. Pulsed laser ablation in liquids is a particular technique that allows the production of high-purity nanoparticles and their functionalization with biomolecules and polymers. Using the appropriate process technique enables the production of versatile nanomaterials, which offer a versatile field of applications in medicine and engineering.

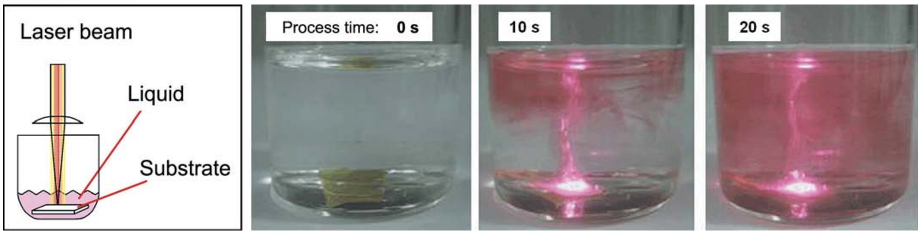

Figure 1: Laser-fabrication of gold nanoparticles in water

Nanostructures and nanoparticles differ in their chemical, optical, magnetic and electric properties from the bulk material of which they are made, and hence enable new application possibilities. For example, ceramic nanoparticles increase the scratch resistance of surfaces, silver nanoparticles give antibacterial properties to materials, and gold or iron nanoparticles open up new medical diagnoses and therapies. The challenge does not focus on the synthesis of nanoparticles, but rather on the integration of these nanoparticles into materials, on averting the deactivation of their unique properties due to agglomeration, and on methodically offering new compounds, alloys or material combinations in a nano-scale range.

Another important topic is the safety aspect, because in every production step the nanoparticles have to be contained in a formulation that prevents a possible health hazard and unwanted emission. There is always an inhalation risk when using the common nanopowders, because they can be transported into air easily. By contrast, nanoparticles in liquid (colloids) can be handled more safely.

In addition to the established chemical and physical processes for nanoparticle synthesis, the laser became more and better established as a varied instrument for generating high purity nanoparticles in liquid dispersions [1]. In such a procedure a substrate is ablated in a liquid medium using a pulsed laser beam. The released nanoparticles are stabilized by the surrounded medium against agglomeration and are readily suitable for further processing. These nanoparticles produced exclusively by physical means generated colloids are free from any contamination potentially originating from not reacted educts and typically there is no use of chemical toxic stabilization agents. Such high-purity nanoparticle colloids are especially interesting for challenging applications in medicine or as high-performance synthetics [2].

1 Generation of nanoparticles in liquids

The principle of the laser-based synthesis of nanoparticles in liquids is illustrated in **figure 1**. Here a pulsed laser beam is focused on a target in a solvent. After absorption of the laserpulse energy, the target material is vaporized and condenses in the solvent thus forming nanoparticles. The use of ultra-short pulses enables application of volatile organic solvents or monomers.

In general, every combination of target material and dispersion phase is possible. By varying the manufacturing process numerous material combinations can be tested in short time. The laser process can be called "rapid nanomaterial prototyping" or regarding the composite synthetics as "rapid nanocomposite manufacturing", both because of the nearly unlimited material variety and because it is easy to adapt the parameters [3]. Either metallic or ceramic nanoparticles can be generated in aqueous or organic solvents [4].

2 Conjugation

Laser-generated nanoparticles have, in comparison with chemically produced nanoparticles, certain particularities. Those generated by lasers have a positive surface charge [5], causing an electrostatic stabilization of the particles and making stabilization agents expendable. On the other hand, the charge enables an efficient interfacing to molecules

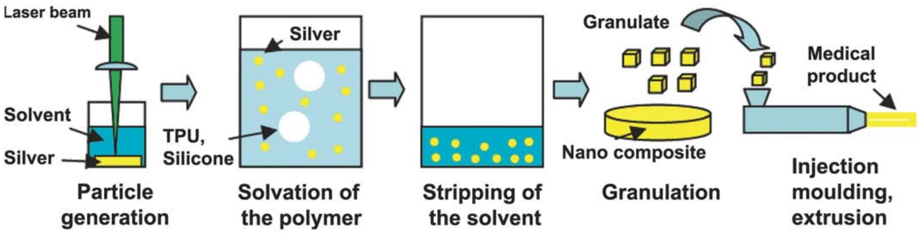

Figure 2: Scheme of laser-based synthesis of nanocomposites

with an electron donating function that are soluble in the surrounding liquid. This raises the possibility of generating conjugates from nanoparticles and biomolecules [6]. Such laser-generated nanoparticle-bioconjugates have a high potential for use in biomedical applications, such as contrast medium for microscopy (bio-imaging). It has been shown that the outstanding optical properties of the nanoparticles enable the quantitative intracellular detection even of single nanoparticles [7]. An additional application example is cell-specific active pharmaceutical ingredient routes (drug targeting), as has been shown with laser-generated nanoparticle-conjugates that were specific for prostate cancer cells recently [8].

Importantly, the biological functions must not be hindered due to the use of these nanoparticles. Because of their high purity the laser-generated nanoparticles assure bio-compatibility for different applications, such as nickel titan implants [9] and cell penetration in relevant nanoparticle concentrations

In addition to the bio-conjugation, the functionalization of a surface with polymer chains or monomers during the laser-ablation process (in-situ) enables the straightforward embedding into structures analogous polymers [11].

3 Integration of function

For gaining use of nanoparticles it is important that their function is preserved when they are embedded in a support material such as polymers. One example is the synthetic material for medical devices. After embedding of nanoparticles these materials have bio-active properties arising from the nanoparticles such as antibacterial or proliferation action.

Figure 2 illustrates the process route [11]. In the first step, nanoparticles are produced by laser ablation in a suitable solvent. Subsequently, the targeted polymer material (e.g. thermoplastic poly-urethane, TPU) is dissolved and the solvent is vaporized. This procedure results in the creation of a nanocomposite from the chosen synthetic material and the embedded nanoparticles. This nano-composite can be granulated and further conventional process steps can be carried out as commonly done in the synthetic materials industry.

The analysis by electron microscopy of the synthesized nanocomposites shows that the particles are distributed homogenously in the synthetic material matrix and do not lose their colloidal properties (shown in **figure 3**). This is extremely important with respect to the nano-functionalization of materials. For example, the antibacterial force of silver nanocomposites is caused by the release of metal ions by corrosion [2]. A continuous and adequate release is only possible if the particles are distributed homogenously within the synthetic material matrix. Also, other specific properties of nanoparticles, such as the optical adsorption caused by surface plasmon resonance without significant scattering losses, are only observed for colloidal and homogeneously dispersed particles.

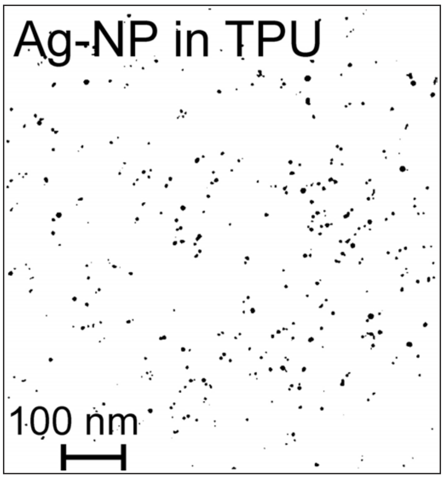

Figure 3: Electron micrograph of a nanocomposite made of silver nanoparticles embedded in polyurethane

Figure 4: Injection-molded prototypes made of laser-generated polyurethane nanocomposite with different nanoparticles (from left: gold, zinc oxide, silver, copper)

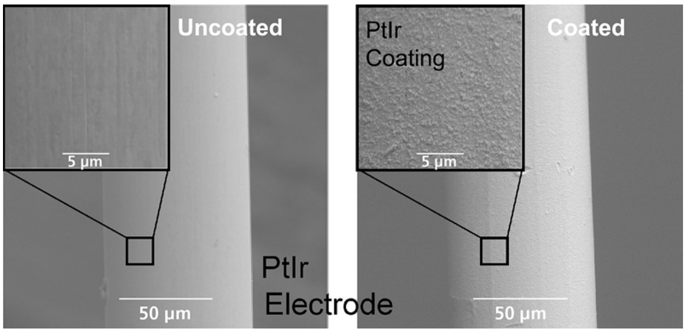

Figure 5: Surface of a PtIr electrode: uncoated (left) and after electrodeposition of PtIr nanoparticles (right)

4 Examples for application and profitability

Following a successful integration of function into a support material, laser-generated nanoparticles need to be processed to prototypes. Depending on the following industrial process, a minimum amount of laser-generated product will be needed. In scale up experiments it was possible to achieve, via using nanosecond lasers with high pulse energy, production rates such as gram per hour [4, 12]. This also depends on the laser parameters and boundary conditions such as solvent and required component concentrations.

In comparison with chemical mass products of filler material, the focus for laser-generated nanoparticles is on a high added value because of unique characteristics, such as purity, dispersability, and adjustable ion-release rates. The amount of pure nanoparticles in functionalized nano-composites lies at less than 1 wt%. This means that the productivity of the laser process is adequate for the production of sufficient amounts of e.g. biologically active nanocomposites. These can be compounded by conventional extrusion methods into prototypes and pilot batches. **Figure 4** shows a series of extruded parts (tension staff for stress tests) made from TPU and laser-generated metal nanoparticles (gold, silver, copper and zinc oxide) in different concentrations.

Besides the volume functionalization of synthetic materials with nanoparticles, metallic surfaces can be functionalized. Since laser-generated nanoparticles have a surface charge, they can be deposited using electrophoresis in this way giving an electric tension to the metal. One field of application is again the medical technology: via structuring of the surface the growth of cells can be specifically affected. In this manner the life-threatening narrowing of a stent (artificial tube) can be hindered. **Figure 5** illustrates the surface of a PtIr-electrode modified by deposition of laser-generated nanoparticles from the same material [13]. Hereby, the surface roughness can be tuned and varied on the nanoscale without changing the chemical composition.

5 Outlook

In spite of how well known laser-based nanoparticle generation and the demonstration of first applications have become, there are still: i) significant knowledge deficits in the basics of particle formation, ii) challenges in reproducibility, and iii) limitations in scalability.

i) It is known that cavitation bubble dynamics influence the subsequent particle nucleation in the liquid. However, the temporal sequence and kinetics of particle growth are subject to controversial international discussions until today. Thankfully, the scientific community is now operating from a platform (see *http://angel-conference.org*) that has established a regular knowledge exchange.

ii) Generation of colloids by means of pulsed laser ablation can be learned within minutes, but the fabrication of constant particle diameters is not trivial. Not mentioning the complex, parallel hydrodynamic processes in detail, one central aspect to be noticed is the competitive processes that particle generation by laser ablation and fragmentation of the generated particles in the fluid carrier undergo. Despite the simplicity of the method, every liquid/nanoparticle material combination for colloids with high quality requirements (e.g. for medical applications) has its own optimal process conditions. This does not only involve laser parameters, but especially the fluid chamber design.

Figure 6: Colloidal diversity of laser-fabricated nanoparticles (from left): nanoparticles made of silver, titanium, platinum and gold in acetone

iii) To maximize the nanoparticle generation productivity using modern ultrashort-pulsed and short-pulsed lasers with high output power, some effects need to be controlled that can constrict the efficiency. The shielding effect of the cavitation bubble in which the ablated material "precipitates" is one of the limiting factors for up-scaling. Compared to the pulse frequency, the bubble has a long lifetime, which makes beam sources at high repetition rates uneconomical. A pulse repetition rate of several kilohertz already correlates to a temporal pulse distance in the range of the bubble lifetime of typically .1 to .3 ms [14].

Although laser ablation in liquids has been described as a universal method for nanoparticle synthesis, there is still a requirement for coherent investigations of basic processes for scale-up and laser fragmentation. The majority of the presented research work was carried out at Laser Zentrum Hannover and recently at the University of Duisburg-Essen.

6 Conclusion

Laser generation of nanoparticles in liquids enables to synthesize a variety of highly pure nanoparticles that can be integrated into different materials as functional components. The laser method is especially suitable to generate new and unexplored nanoparticles, to prepare prototypes and pilot series, and to produce stable nanoparticle dispersions of high purity especially from metals and alloys (**figure 6**). The world's first industrial user of the technology for the commercial production of nanomaterial, Particular GmbH, is supported by the program "EXIST Transfer of Research" of the German Federal Ministry of Economics and Technology (BMWi).

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