Pulsed laser generation of clean colloidal metal nanoparticles

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ABSTRACT

In colloidal chemistry, diversity and purity of available nanoparticle dispersions are still limited. In contrast to salt-based precipitation or sol-gel processes, pulsed laser ablation in liquids is a physical process that generates nanoparticles e.g. from precious metals or alloys directly in water or organic solvents [1-8]. Zeta potential values up to -80 mV lead to high stabilities.

The innovation benefits from the increasing capabilities of modern pulsed laser systems. By optimization of production chambers and fluidics, nanomaterial ablation rates have reached the gram/hour scale [9]. Solid raw materials for laser-based colloid production are 5 to 10 times cheaper than commonly used chemical precursor compounds.

Laser-generated nanoparticles are highly pure and possess a large surface activity: the particle surface is not blocked by chemical ligands or rests of reducing agents. This leads to potential applications in biotechnology, medical technology, or catalysis.

Keywords: nanoparticles, colloids, metals, laser, synthesis

1 RELEVANCE OF CLEAN METAL NANOPARTICLES

The vast majority of commercially applied nanoparticles are produced by the chemical industry, using specific precursor substances. Oxidic nanoparticles, in particular, are often processed in mass products to adjust absorption properties or viscosities.

The main "new nanomaterials" with the largest growth rates are metal nanoparticles, carbon nanotubes, and polymer nanocomposites. Their synthesis traces back to a world-wide need for product innovations in different kinds of markets [10,11].

Most of these innovations make use of the fact that nanoparticles can interact intensively with their environment due to their **large specific surface.** The following three examples show applications of metallic nanoparticles that make use of their large surface ratio:

- In **biotechnology,** the biocompatibility and optical absorption characteristics of gold nanoparticles are used in combination with their affinity to thiol groups to mark or transport biological molecules, including in-vitro diagnosis in test kits ("point of care testing").
- In **medical technology,** the release of metal ions from nanoparticles (e.g. from silver, copper, or zinc) is used for antibacterial or wound-healing effects.
- In **catalysis,** the large specific surface and defect density of nanoparticles from platinum, ruthenium, and other catalysts is utilized to increase process efficiencies.

Almost all applications also have in common that the efficacy of the nanoparticles does not only depend on their specific surface (i.e. on the particle size), but at the same time on their **surface activity.**

The less a particle surface has been saturated with chemical bonds (ligands), the more reactive nanoparticles behave in their respective application. Highly pure nanoparticles without rests of chemical precursors and without any addition of stabilizing ligands increase the efficiency - which applies to nano-applications in medical technology, catalysis, biotechnology, and other nanotech fields. In addition, expensive follow-up treatments and cleaning steps (like the calcination of catalyst supports or the filtration of bio-conjugates) become unnecessary.

2 LASER ABLATION IN LIQUIDS

Pulsed laser ablation in liquids (see Figure 1) leads to the generation and homogeneous dispersion of highly pure nanoparticles with high surface activities from nearly any solid. As even the liquid medium can be selected, nano-particles can also be synthesized directly in solvents that are applied in a production chain, or can be conjugated with biological molecules during the generation process.

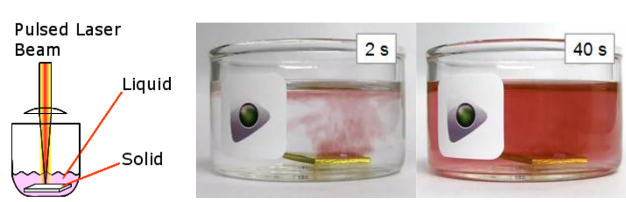


Figure 1: Basic principle of laser ablation in liquids, demonstrated at a gold foil in an open glass vessel: http://youtube.com/watch?v=pxaOChCL6kM

Using different process techniques and laser sources, the technology can generate stable nanoparticle dispersions of high quality from solids (e.g. precious metals or alloys) or from micro- and nano-powders (e.g. oxides) [1-7].

2.1 Productivity

For many application fields, productivity is one of the most important aspects of the innovation. To increase productivity, the fluid technology is crucial. Focusing laser light in liquids is one of the determining factors for chamber constructions, in which changes of the refractive index become decisive - often even non-linearly due to high laser intensities [7]. Another important factor is the influence of cavitation bubbles in the laser focus, the geometry and duration of which must be considered for the adjustment of temporal and spatial pulse-to-pulse distances. This allows significant productivity enhancements [9].

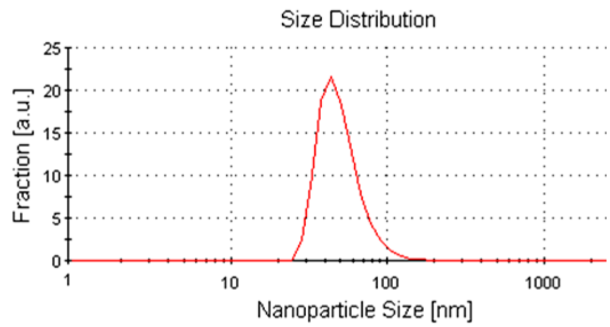
The definition of productivity aims is based on the respective applications that use active nanoparticles diluted in carrier media (e.g. 0.1 to 2 % in polymers or 0.001 to 0.01 % as gold conjugates). In a laser ablation process, the concentration can be set up during the synthesis. For these applications, lot sizes typically amount to nanoparticle masses on the milligram to gram scale. With a laser output power of 20 W, productivities can already reach several grams per hour [9], with modern high-power lasers and optimized fluid technology, this can increase respectively.

Examples: 5 tons of polymer per year (containing 0.5 % of nanoparticles) can be furnished with laser-generated nanoparticles economically with a productivity of 20 g/h that can already be reached in one-shift operation. For a typical lot size of gold conjugates, several minutes of laser processing time are usually sufficient.

2.2 Nanoparticle Size

Typical size distributions of aqueous laser-generated nanoparticle dispersions show a polydispersity index below 0.3, as demonstrated in Figure 2. For many applications, it is necessary that particle sizes are adjustable by laser and process parameters. This can be realized in three ways:

- **Quenching:**
  By adjusting the concentration of a biomolecule quencher (e.g. a peptide in a cell culture medium) dissolved in water, defined particle sizes esp. around 10 nm can be achieved, as has been investigated intensively e.g. for gold and zinc oxide [12,13].
- **Dwell time:**
  Process variations in a flow reactor allow the adjustment of nanoparticle sizes in a range of about 20 to 50 nm [12]. Further optimization of fluidics have the potential to extend this size range.
- **Fragmentation:**
  By means of laser fragmentation of suspensions, different particle sizes > 50 nm become available, depending on the processing time. Starting material (microparticles) and product (the colloid) can be separated using ultrasonics [13].



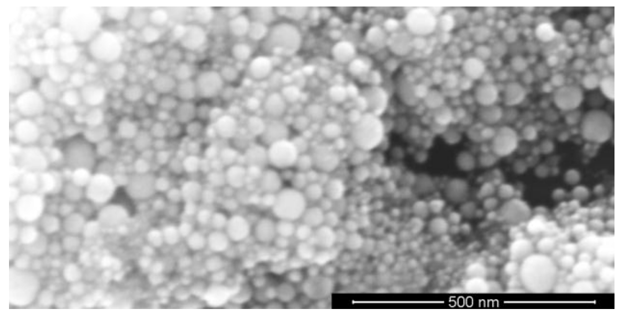


Figure 2: Hydrodynamic diameter distribution (top) and SEM (below) of laser-generated gold nanoparticles from picosecond laser ablation in water

3 APPLICATIONS

Three examples demonstrate the commercial benefits of laser ablation over chemically synthesized colloids: the labeling of functional biological molecules with nano-markers (gold conjugates), the embedding of antibacterial metal nanoparticles in polymer nanocomposites, and nanoparticle coatings of carrier substrates for catalysis.

3.1 Gold conjugates

The role of gold nanoparticles has been increasing significantly in biotechnology, as alternatives on the basis of fluorophores bleach out quickly and semiconducting particles are not applicable to an in-vivo use because of their toxicity. Major applications usually concern the detection and addressing of specific molecules, e.g. for in-vitro diagnostic, immunostaining or bio-imaging. The market volume of such gold conjugates meanwhile amounts to 100 million EUR and has already reached 50 % of the volume of metal colloids (200 million EUR) [11].

Conjugation of laser-generated gold particles with biomolecules leads to better results in therapeutic applications as well as medical technology, because they are more reactive and less toxic than chemically synthesized materials, meaning that they open up a larger

NSTI-Nanotech 2012, www.nsti.org, ISBN 978-1-4665-6274-5 Vol. 1, 2012

"therapeutic window" [14]. Nanoparticle surface coverage with bio-functional ligands is 5 times higher than for chemically synthesized nano-gold, which is advantageous for applications that benefit from a high specificity, such as antibody-, DNA-, or aptamer-targeting.

Custom combinations of nanoparticles and biomolecules can be provided with low development effort, using either a batch method or a patented continuous flow chamber. Chambers that we have developed allow processes in a highly pure environment and generate biomolecule conjugates with binding efficiencies of up to 95 %. This high efficiency is of special economical relevance for the conjugation of expensive biomolecules such as aptamers [6,12].

The purity of the colloids thus implies three advantages for biological applications: a more efficient binding to biomolecules (higher yield), a higher coverage rate (higher specificity in the application), and a smaller cleaning effort (no disturbing chemical rests).

3.2 Polymer nanocomposites

Laser-generated colloids can be used as a synthesis component or masterbatch to directly embed nanoparticles during polymer processing. Such materials release metal ions with antibacterial effects, while the nanoparticles stay safely embedded in the polymer matrix [14]. They remain active for long periods of time (months to years). Depending on the polymer, they can even be processed by extrusion or injection molding and can therefore be used for the production of polymer parts like implants or catheters, as has been demonstrated in our research partnerships.

The purity of laser-generated colloids allows attaching the particles to the polymer without additional so-called matrix binders that would impurify and influence an approved polymer. Direct laser ablation in a solvent of the final polymer utilizes this polymer as a "binder" for the nanoparticles.

3.3 Energy conversion / catalysis

In the field of energy conversion technology and catalysis, a technically simple process under mild conditions allows the deposition and immobilization of laser-generated nanoparticles on almost any carrier substrate in the liquid phase. This method can be integrated into a continuous process chain for the production of heterogeneous catalysts ("downstream processing") and allows a wide spectrum (metals, alloys) of catalytically active nanomaterials.

Due to surface defects, laser-generated particles exhibit an electrical charge which stabilizes them electrostatically without the use of ligands. The absence of a ligand layer has a positive effect on the affinity of nanoparticles to the carrier surface and increases long-term stability and activity of these materials, as no catalytic centers are blocked by ligands. In a direct comparison with chemically synthesized nanoparticles (containing rests of citrate), the deposition efficiency was 100 times higher.

The purity of the colloids thus implies two advantages: a significant increase of the particles' sorption efficiency and the reduction of costs due to the fact that heterogeneous catalysts do not need to be cleaned.

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