NOVEL LASER BASED PRODUCTION TECHNIQUE OF PURE NANOPARTICLE COLLOIDS BY LASER ABLATION IN LIQUIDS

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Introduction

There is a fast growing demand to a great variety of nanomaterials, multifunctional nanocomposites which affect many segments of our life. Even if a diversity of nanoparticle formulation does already exist, there is still a lack in providing customers with rapid design, prototyping and manufacturing of functional nanoparticles and nanocomposites. Using conventional nanoparticle synthesis methods like the gas phase hydrolysis and pyrolysis, milling, grinding or the wet chemical sol-gel process often restrict the range of applications due to available material, purity, agglomeration and re-dispersability problems involved. Laser ablation in liquids is a versatile, pure, full physical fabrication method of nanomaterials providing size and stability control offering novel opportunities to solve the agglomeration and impurity problems. Laser engineered nanoparticles can be utilized in opto-electronic purposes, nanocomposites and coatings for various biomedical application from antibacterial implants, catheters, modification of textiles to improvement of polymers, etc. The technique is based on the ablation of a target material by pulsed laser irradiation (from femtosecond to nanosecond), leading to plasma formation and the generation of nanoparticles/ nanostructures which are quenched and stabilized by the confining liquid environment. Using femtosecond lasers the effective thermal load is minimal to the material as this ultrashort irradiation occurs in a time regime shorter than the electron-photon coupling of the lattice, thus nanoparticles can be ablated stoichiometrically. It also allows rapid fabrication of nano-biomaterials and formation of in-situ bioconjugates. Using longer laser irradiations (picosecond to nanoseconds) allows the generation of higher amount of pure nanocolloids as higher laser powers are available, nevertheless at the expense of thermal load.

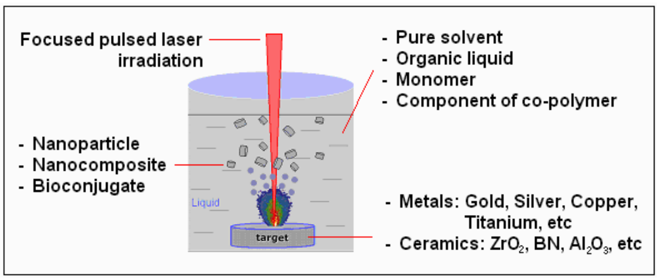


Fig. 1 General routes to rapid nanocomposite manufacturing by laser ablation in liquids

Experimental

Figure 1 demonstrates the schematic principle of nanoparticle manufacturing by laser ablation in liquids (solvent, monomer or resin component). Generation of various nanomaterials was carried out using a femtosecond laser system (Spectra Physics Spitfire PRO) emitting 120 fs laser pulses at 800 nm with 5 kHz repetition rate and an industrial nanosecond laser (Rofin Sinar Marker 100D) delivering 40 ns laser pulses with 3-60 kHz repetition rate at central wavelength of 1064 nm. Precise micromachining and pulse delivering were achieved by a four stage positioning unit (3D-Micromac) and by a laser scanner system (Scanlab, HurryScan II-14). The target material was placed at the bottom of an open glass vessel filled with the liquid solution, whereas all ablation experiments were performed at room temperature at atmospheric pressure.

Results and Discussion

Experiments have been carried out to manufacture nanocomposites with embedded nanoparticles of a wide range of metallic materials [1]. Examples of these nanocomposites are shown in the left image of Figure 2.

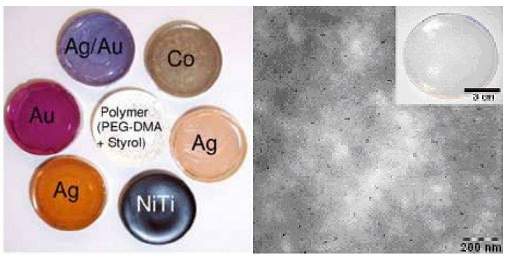
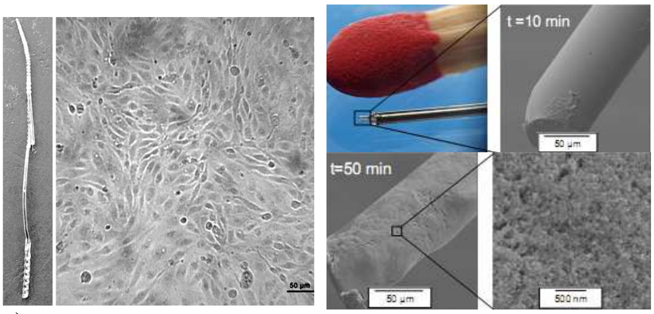


Fig 2 (Left) Examples of manufactured nanocomposites with embedded metallic nanoparticles. (Right) TEM image of gold nanoparticles embedded into acrylic polymer.

Additionally to the metallic nanoparticles also multimaterial colloids (Ag/Au) and nanoparticles of alloys (NiTi) are generated. Electron energy loss spectroscopy measurements revealed that NiTi alloy particles were ablated stoichiometrically opening a new page in the history of laser ablation in liquids [2]. The right image of

Figure 2 shows a transmission electron microscope (TEM) image of gold nanoparticles embedded in acrylic polymer. This demonstrates the homogeneous distribution of the nanoparticles in the polymeric matrix.

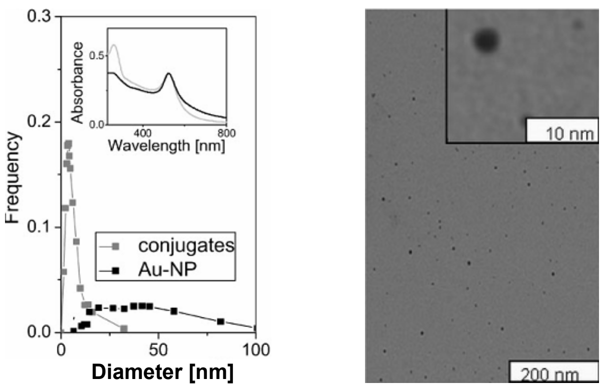
Functionalization of these nanomaterials for medical application is demonstrated at the example of silicone used as cochlear implant electrode carrier. Laser ablated silver nanoparticles are embedded into the silicone matrix using the above mentioned method shown in Figure 3a.



a) b)

Fig. 3 (a) Silicone electrode mantle of a cochlear implant and Endothelial cells grown on a silicone-silver nanoparticle composite. (b) Pt/Ir neural electrodes coated with fs-laser generated platinum iridium nanoparticles for improvement of neural contact using electrodeposition [3].

It is well-known that silver hydroxide ions are released from water permeable polymers with embedded nano-particles, resulting in antibacterial functionality. But care has to be taken in case of nanomaterial enhanced implant, in order to prove material biocompability.



a) b)

Fig. 4 (a) Size distribution and visible absorption spectrum gold-bioconjugate and unconjugated gold nanoparticles. (b) TEM micrograph of gold-bioconjugates.

In case of the cochlear implant electrode, spiral ganglia cells (responsible for signal transfer to the central nervous system) and endothelial cell (responsible for bio-compatibility) have to grow towards the silicone surface. First results of endothelial cells growth on the nano-composite material are shown in Figure 3a. Indicating the positive effect of nanoparticles, electro-deposition of Pt/Ir alloy nanoparticles were carried out on Pt/Ir neural electrodes to improve neural contact (see Figure 3b). Full coating of the neural electrode with Pt/Ir nanoparticles was achieved on the time scale faster than one hour.

Laser ablation of a target material in the presence of conjunctive agents allows in-situ generation of functional nanomaterials. Since laser generated gold nanoparticles show electron accepting properties owing to partial oxidation, gold nanoparticles have high affinity to bind to electron donor moieties like SH, S-S, COOH, NH_2, etc. Due to formation of strong dative bonds between the thiol group and gold surface, bioconjugates were prepared by laser ablation in an aqueous solution of thiolated oligo-nucleotides as a model antibody substance [4]. As expected, nanoparticle size is significantly reduced due to size quenching during the in-situ bioconjugation shown in Figure 4a. The maximum absorbance value does not show any noticeable shift in wavelength, however the band is significantly narrowed for gold-bioconjugates, indicating a reduced amount of agglomerates in bioconjugated colloids, confirmed by TEM analysis (see Figure 4b).

Besides properties and functions of laser generated metal nanopartciles (Au, Ag, Co, etc) we carried out productivity related investigations with various laser sources and laser pulse durations. Through the example of Al_2O_3 hard ceramic material we carried out the influence of cost-effective (pulse energy) and non cost-effective process parameters (thickness of liquid layer, liquid flow rate, repetition rate, interpulse distance) on nanoparticle productivity. Investigations revealed that besides high laser pulse energy, small height of liquid layer, specific interpulse distance and repetition rate combination are required for the generation of high amount of pure nanoparticles. Nanoparticle productivity of 1.3 g/h was achieved by 18 W focalized laser power using nanosecond laser irradiation. Since similar laser source of 720 W is now commercially available, we believe that laser ablation in liquids will become a powerful technique to nanomaterial fabrication in the multi gram scale.

References

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