

STEPHAN BARCIKOWSKI^{*)}, MICHAEL HUSTEDT, BORIS CHICHKOV

Laser Zentrum Hannover e.V., Hollerithallee 8, 30419 Hannover, Germany
e-mail: s.barcikowski@lzh.de

Nanocomposite manufacturing using ultrashort-pulsed laser ablation in solvents and monomers

Summary — On the basis of literature data on ablation was characterized as a method of nanoparticles preparation. The own research concerned the direct ultrafast laser ablation of solids used to produce the engineering nanoparticles with narrow size distributions. Without using any chemical precursors, stoichiometric nanoparticles are generated from different materials (silver, gold, NiTi alloy) and directly dispersed in a liquid, *e.g.* acrylic acid, acetone, water, or a monomer of polymeric material. The produced nanoparticle solutions may be used to fabricate nano-modified plastic materials with specially designed properties by polymerization directly subsequent to particles' production, without the necessity to re-disperse the particle aggregates. In order to control the size distribution and related properties, nanomaterial characterization using on-line measurements of the particle size is applied. The developed processes give access to new homogeneous nanomaterials such as multi-component nanosystems.

Key words: laser ablation, nanoparticles, nanocomposites, particle dispersion, femtosecond laser.

WYTWARZANIE NANOKOMPOZYTÓW Z ZASTOSOWANIEM ABLACJI WYMUSZANEJ LASEREM FEMTOSEKUNDOWYM W ŚRODOWISKU ROZPUSZCZALNIKÓW I MONOMERÓW

Streszczenie — Na podstawie literatury scharakteryzowano ablację laserową jako metodę otrzymywania nanocząstek (rys. 1). Opisane badania własne dotyczyły wytwarzania nanocząstek o wąskim rozkładzie wymiarów za pomocą bezpośredniej ultraszybkiej ablacji substancji stałych. W ten sposób z rozmaitych materiałów (srebra, złota, stopu NiTi) uzyskiwano — bez wprowadzania jakichkolwiek chemicznych prekursorów — nanocząstki bezpośrednio zdyspergowane w cieczy, którą stanowił rozpuszczalnik (aceton, woda) lub monomer (np. akrylanowy). Polimeryzacja tak uzyskanej dyspersji monomeru prowadziła do powstawania kompozytu polimerowego z nanocząstkami, np. srebra (rys. 7 i 8). Opisywane nanocząstki charakteryzowano metodami SEM, TEM, ESEM i spektroskopii VIS (rys. 2—6).

Słowa kluczowe: ablacja laserowa, laser femtosekundowy, nanocząstki, dyspergowanie, nanokompozyty.

LASER ABLATION AS NANOPARTICLES PREPARATION METHOD

Production of nanoparticles from different materials with well-controlled composition, size, and shape is a very important topic in nanotechnology. In 2002, nanoparticulate materials and composites had a remarkable nanoparticle market share of 23 % with a volume of 13 billion EUR [1]. About 28 % of the worldwide nanotechnology market is related to nanomaterials, of which nanocomposites played the major role with 15 billion EUR in 2004 [2].

Engineering nanoparticles are used in nanocomposites and coatings for biomedical applications such as antibacterial implants or catheters, modification of textiles, and refinement of polymers. Very often the desired range of applications is restricted due to a limited avail-

ability of nanoparticle materials, their purity, their re-dispersability and costs.

Nowadays, lasers are applied in a wide range of industrial applications, especially in polymer technology [3—5]. Laser ablation has shown itself as an alternative physical nanofabrication method, offering the novel opportunities to solve the problems of agglomeration and impurities. The method consists in ablation of a target (mostly solid) by an intense laser radiation, leading to an ejection of its constituents and the formation of nanoparticles/nanostructures. Such a method let do both nanostructuring of surfaces and the synthesis of nanostructures in the vapour state [6].

In particular, when the target is ablated in vacuum or in a residual gas, the vaporized nanoparticles can be deposited on a substrate, placed at some distance from the target, to form a thin nanostructured film [7]. It is known that the generation of nanoparticles and nanostructures is achieved due to a natural property of laser matter

^{*)} To whom correspondence should be addressed.

interaction to eject material in the form of atoms and nanoclusters [8–10]. Such nanocluster-based regime of ablation is typical for almost all parameters of pumping radiation, although larger microscale fragments or droplets can also be present in some cases due to melting and detachment of microspikes, formed on the target surface as a result of a multi-pulse illumination of the same spot [11, 12].

Nevertheless, the initial ablation process does not determine the final size of nanostructures, since the nanoclusters then experience a rapid cooling under laser plume expansion and interaction with the environment, giving rise to their progressive growth. In fact, in the first approximation the process can be described by the classical theory of condensation and nucleation in a vapour layer, which distinguishes several phases of the nanocluster growth [13, 14]: nucleation, kinetics-controlled growth, diffusion-controlled growth and finally Ostwald ripening related to the coalescence or fusion of two nanoparticles. In this case, the final size of nanoparticles is mainly determined by the competition of coalescence and agglomeration processes during the last phase, where the properties of the environment (vacuum, air, water, organic solvents) affect the rate of nanocluster cooling and may quench the nanoparticle growth rate. Hence, the ablation in a liquid environment (*e.g.* in aqueous solutions) causes a release of nanoclusters to the environment to form a colloidal nanoparticles solution. When performed in a clean, well-controlled environment such as deionized water or aqueous biocompatible solutions, laser ablation realizes the production of ultra-pure nanomaterials with novel surface chemistry, not reproducible by any other method [6, 7].

In contrast to the laser generation of nanoparticles using continuous wave CO₂ lasers (*e.g.* [15, 16]),

nanosecond pulsed Nd:YAG lasers [17], or UV-lasers [18, 19], the conversion of a bulk material into nanoparticles using ultrashort laser pulses is based on completely different material ablation processes [20]. This is due to the fact that laser pulses with the duration below 10 picoseconds cause a minimal thermal load to the material [21]. In Fig. 1, the nanosecond-pulsed and femtosecond-pulsed laser ablation is compared with respect to the thermal load of the material [22].

This ultrafast ablation process makes possible to produce very gentle material removal converting a bulk material into nanoparticles in gases and liquids [23] without changing its stoichiometry [24, 25]. If the nanoparticle generation is carried out by ablation in an infrared transparent liquid (such as water, ethanol, acetone, ethyl acetate, acrylates, etc.), an *in-situ* dispersion of the nanoparticles in these solvents and subsequent polymerization is possible, which is the aim of the investigation presented.

EXPERIMENTAL

The generation of nanoparticles was carried out using a femtosecond laser system by Spectra Physics (Spitfire PRO), emitting 120 femtosecond laser pulses at 800 nm. This laser produces femtosecond pulses with energies of up to 1 W and works with a frequency of 1 kHz. A 4-stage positioning unit for laser micromachining by 3D-Micromac was used. Femtosecond laser ablation in liquid media was carried out in an open glass vessel (diameter 2 cm) with the target material placed on the bottom. The vessel is filled with a liquid (water or organic solvent with low boiling temperature), optional with 2 to 10 ml. The thickness of the liquid layer above the target was 3.5 to 18 mm. The laser beam was focused by a lens on the surface of the target (silver, gold, NiTi alloy). Having moved the target, the laser beam is writing well-defined structures on the surface of the substrate. During the process in liquid media, generated particles are dispersed as colloids. The particle size was determined by tracking of the trajectories of the particles' laser Mie-scattering (at 650 nm). The instrument (LM10, NanoSight) was calibrated using latex particles of defined size (NanoSight). Moreover, the nanoparticles were characterized by SEM (CamScan, Series No. 2), ESEM (Jeol), TEM (Jeol, JEM-2100 F) and VIS spectra (Perkin-Elmer, Lambda 900).

RESULTS AND DISCUSSION

Femtosecond laser ablation in liquids

When target materials are placed at the bottom of a liquid reservoir, ultra-short pulsed laser radiation can be transmitted and focused through the liquid, such as water or dichloromethane, onto the target surface. By this method colloidal nanoparticles dispersed in the

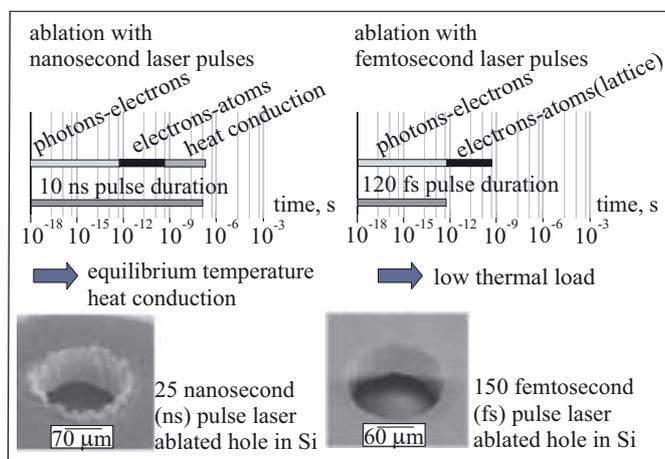


Fig. 1. Comparison of nanosecond- and femtosecond-pulsed laser ablation with respect to the time regime of photon-electron, electron-atom interaction, and heat conduction (top, see [22]) and influence of the different thermal load on the geometry of laser holes in silicon (bottom)

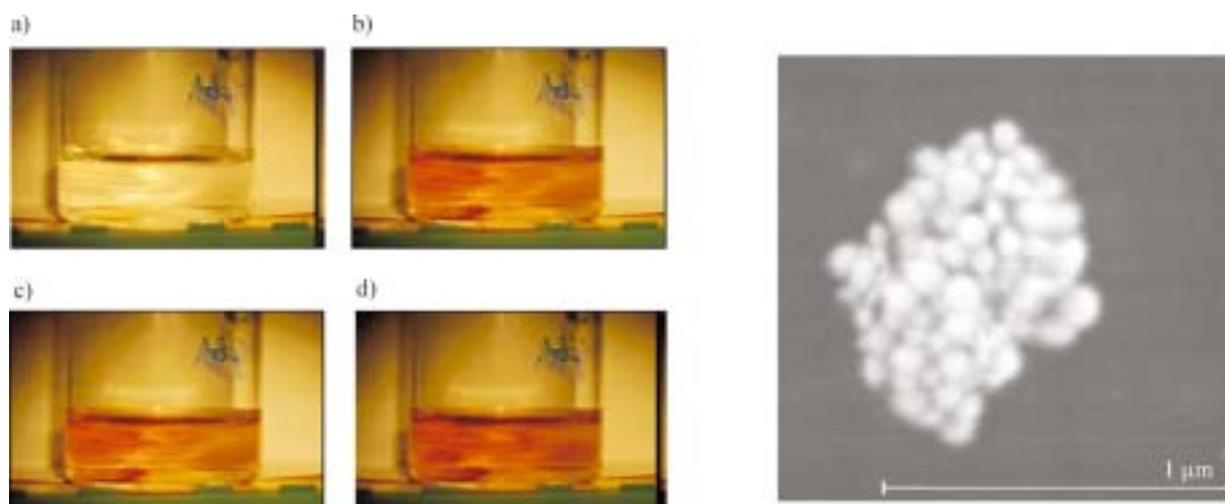


Fig. 2. Coloration of the liquid in the vessel at different time intervals of the ultrashort-pulsed laser ablation of gold in water (left): a) 0 s, b) 36 s, c) 108 s, d) 144 s, and SEM image of the particles (right, average diameter 70 nm)

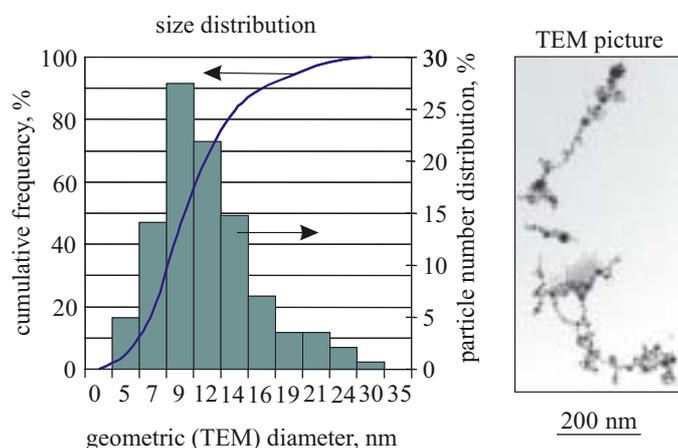


Fig. 3. Size distribution and TEM picture of gold nanoparticles obtained by femtosecond laser ablation of gold in water

liquid can be formed. For example, when ablating gold in distilled water with pulse energies of 50 to 500 μJ, there is a clear red coloration of the medium after a short processing time (Fig. 2). The VIS spectra of ablated gold in water show a plasmon resonance at 525 nm for several days, without addition of stabilizing agents. During femtosecond laser ablation in water, a linear log-normal correlation of the nanoparticle size with the value of laser fluence has been shown, so the size of particles may be decreased by using lower pulse energies at the irradiated spot [6, 7].

Using a pulse energy of 500 μJ during femtosecond laser ablation of gold in water, 90 % of nanoparticles are smaller than 14 nm (average diameter 10.5 nm). The TEM analysis of a droplet of this liquid reveals spherical particles with a Feret diameter of 4 to 20 nm (Fig. 3).

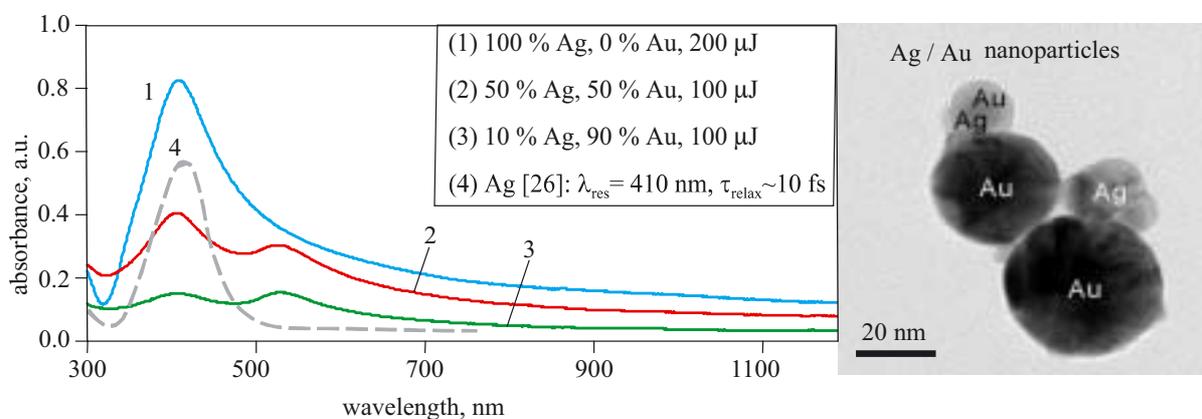


Fig. 4. Gold and silver nanoparticles produced by femtosecond laser ablation of solids in water. Left — absorption spectra and plasmon resonance at 410 nm (silver) and 524 nm (gold) of the generated colloids: 1 — 100 % Ag, 0 % Au, 200 μJ; 2 — 50 % Ag, 50 % Au, 100 μJ; 3 — 10 % Ag, 90 % Au, 100 μJ; 4 — Ag [26]: λ_{res} = 410 nm, T_{relax} ~ 10 fs. Right — TEM picture of silver and gold nanoparticles generated by sequential ablation of gold and silver targets in the same water sample (conditions — see text)

It has been shown that the optical characteristics of the colloid strongly depended on the pulse energy during ablation. When silver is used as the target material, the color of the solution becomes yellow with the corresponding absorption peak located around 410 nm (plasmon resonance of silver [1]). Placing a silver target and additionally a gold target within the water reservoir and processing these targets sequentially, a mixture of different particles could be produced (Fig. 4). The particle ratio was controlled by the processing time for the single targets, as can be clearly seen from the plasmon resonance spectra.

The TEM picture in Fig. 4 shows the gold and silver nanoparticles obtained by femtosecond laser ablation of gold (67 %) and silver (33 % of the total time duration of the ablation process) at 100 μ J laser pulse energy (100 mW). Correspondingly, properties of other nanoparticle mixtures may be tuned in small steps, which is of great interest for various applications in material engineering or medicine.

Apart from gold and silver, preliminary experiments on preparation of nanoparticles from Cu, Ti, Co, Fe₂O₃, TiO₂, ZrO₂, and even alloys such as FeCo, FeNi targets in several liquids have already been carried out at the Laser Zentrum Hannover using kHz femtosecond laser pulses. To produce nanoparticle dispersions continually at a higher rate (*e.g.* using high repetition rate femtosecond or picosecond laser pulses), comparable processes with continuous supply and drain of the liquid can be applied. Consequently, the question arises whether a coating of surfaces or nanocomposite generation is possible using these colloids.

Nanoparticle coating and embedding

Organic molecules with low molecular weight are reported to have a stabilizing effect during nanoparticle dispersion. In addition, low boiling point or high vapour pressure of the liquid are advantageous for a coating process.

The size of the nanoparticles generated in ethyl acetate was in the range of 90–110 nm, but mainly aggregates and only a few agglomerates were generated. In addition, the ablation process was carried out in acetone and dichloromethane. After the generation of the nanoparticles in acetone, the dispersion was placed in an open glass vessel to evaporate the solvent at room temperature. The SEM images of the glass surface coated with nanoparticles generated from ablation of NiTi alloy and gold in acetone are shown in Fig. 5.

For biomedical applications, the antimicrobial effects caused by silver ions released from silver nanoparticles is of increasing interest, so that the same procedure of surface coating was repeated with silicone (which is commonly used for biomedical devices) using a nanoparticle dispersion of silver in dichloromethane generated from ablation.

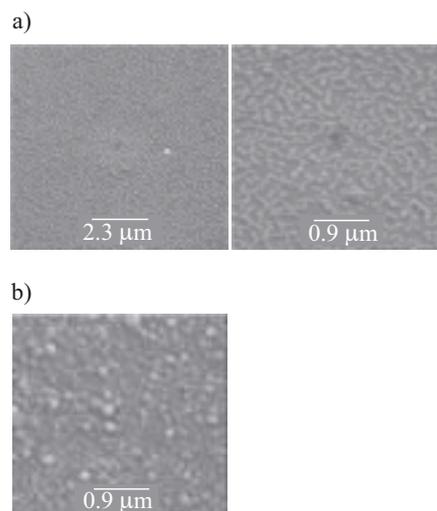


Fig. 5. SEM images of glass surface after coating with nanoparticles from dispersions generated using femtosecond laser ablation of NiTi (Nitinol — NiTi shape memory alloy) (a) and of gold in acetone (b)

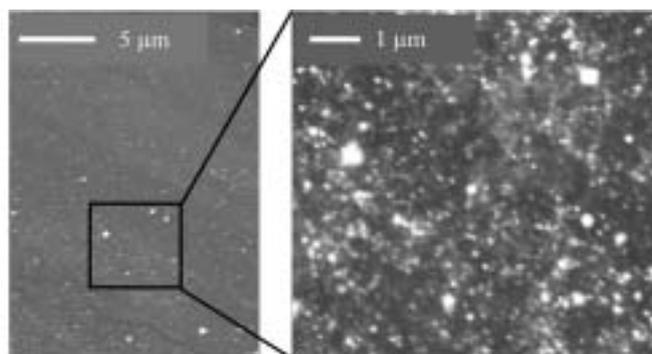


Fig. 6. ESEM images of silver nanoparticles produced by femtosecond laser ablation (pulse energy 150 μ J) in dichloromethane on a silicone sample

In Fig. 6, the ESEM picture of a representative section of the surface is shown, demonstrating the high surface density of the silver nanoparticles with sizes of 50 to 200 nm, but also some agglomerates with a size of several hundred nanometers.

Even if the release of silver ions is desired, a release of the nanoparticles from a medical device of implants should be avoided with regards to possible adverse health effects. Since the method of ablating a sample in a liquid can be carried out using solvents, monomers, or components of copolymers, the access to three different routes of nanocomposite manufacturing is given. Fig. 7 gives the scheme and process steps following these routes, with the simple steps: (i) laser generation within a liquid (solvent, monomer or resin component), (ii) preparation of mixture for polymerization, and (iii) polymerization by heating or applying of UV light.

As an example, femtosecond laser ablation of silver was carried out in ethyl acetate and the dispersion was

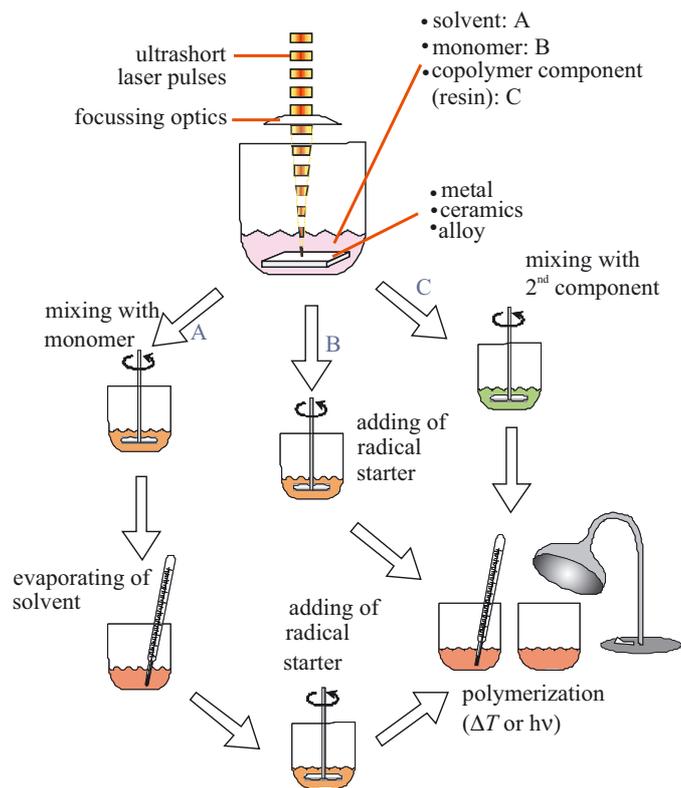


Fig. 7. Paths of to nanocomposites manufacturing based on laser ablation of solids in organic solvents (A), monomers (B), and components of copolymers (C)

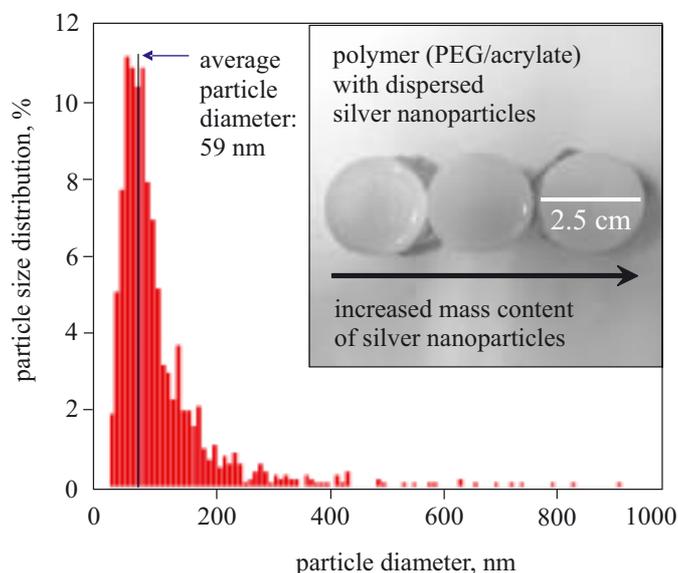


Fig. 8. Generation of silver nanoparticle polymer composites: particle size distribution of silver nanoparticles generated by femtosecond laser ablation in liquid. Insert: dispersion of silver nanoparticles generated by femtosecond laser ablation of silver in ethyl acetate and subsequent dispersion and polymerization into the volume of polymer samples (see text)

transferred into polyoxyethylene glycol (PEG) dimethacrylate following route A) of Fig. 7. In the silver colloid, an increased nanoparticle concentration leads to a more

intense plasmon resonance peak. Hence, an increase in the laser ablation interval (for the system silver/ethyl acetate) causes a higher intensity of the coloration of the polymer nanocomposite indicating a higher nanoparticle concentration in the polymer sample (Fig. 8).

Combination of the two methods initially studied in this investigation, namely the generation of nanoparticle mixtures by sequential femtosecond laser ablation of different targets in the same liquid, and its subsequent polymerization, may give a straight-forward access to multifunctional nanocomposites, meaning that they fulfil multiple requirements (such as being antiseptic, hydrophobic, antistatic, harder, biocompatible, or antireflective).

CONCLUSIONS

Even though many techniques of the dispersion of nanoparticles in polymers are available up to now, the enhancement of the material performance is still restricted due to inefficient homogenization and re-dispersion of available nanoparticle materials in the polymers or master batches. Moreover, improvements are still required in terms of their purity and costs. In this study, a novel route of nanocomposite manufacturing is presented, based on the *in-situ* dispersion of nanoparticles of solids in monomers and subsequent polymerization. The capability of a novel method of nanocomposite manufacturing is demonstrated of the examples specific to biomedical applications. Direct ultrafast laser ablation of solids is used to design and produce nanoparticle-based nanomaterials. Without using any chemical precursors, nanoparticles are generated from different materials (silver, gold, NiTi alloy) and directly dispersed in a liquid, such as acrylic acids, acetone or water. This direct (*in-situ*) dispersion of the nanoparticles in pre-polymers allows manufacturing of highly homogeneous nanocomposite materials.

REFERENCES

1. Ebenau A.: "Economic Perspectives of Nanotechnology: Enormous Markets for Tiny Particles", in: "Nanotechnology in Chemistry – Experience meets Vision" on Oct. 28th/29th 2002 in Mannheim, press release BASF Future Business GmbH, Ludwigshafen 2002.
2. Luther W., Malanowski N., Bachmann G., Hoffknecht A., Holtmannspötter D., Zweck A., Heimer T., Sanders H., Werner M., Mietke S., Köhler T.: "Nanotechnologie als wirtschaftlicher Wachstumsmarkt", Reihe "Innovations- und Technikanalyse", Vol. 53, VDI Technologiezentrum GmbH, Düsseldorf 2004.
3. Rytlewski P., Żenkiewicz M.: *Polimery* 2007, **52**, 243.
4. Wisniewski M., Sionkowska A., Kaczmarek H., Lazare S., Tokarev V.: *Polimery* 2007, **52**, 259.
5. Rytlewski P., Żenkiewicz M.: *Polimery* 2007, **52**, 403.

6. Kabashin V., Meunier M.: "Laser Ablation-Based Synthesis of Nanomaterials", in: "Recent Advances in Laser Processing of Materials" (Eds.: Perriere J., Millon E., Fogarassi E.), Elsevier, Oxford 2006, p. 1—36.
7. Kabashin A.V., Sylvestre J.-Ph., Patskovsky S., Meunier M.: *J. Appl. Phys.* 2002, **91**, 3248.
8. Muramoto J., Nakata Y., Okada T., Maeda M.: *Jpn. J. Appl. Phys., Part 2*, 1997, **36**, L563.
9. Geohegan D. B., Poretzky A. A., Duscher G., Pennycook S. J.: *Appl. Phys. Lett.* 1998, **73**, 438.
10. Geohegan D. B., Poretzky A. A., Duscher G., Pennycook S. J.: *Appl. Phys. Lett.* 1998, **72**, 2987.
11. Foltyn S. R.: "Surface Modification of Materials by Cumulative Laser Irradiation", Chap. 4 in: "Pulsed Laser Deposition of Thin Films" (Eds.: Chrisey D. B., Hubler G. K.), Wiley, New York 1994, p. 89—114, and references therein.
12. Krajinovich D. J., Vazquez J. E.: *J. Appl. Phys.* 1993, **73**, 3001.
13. Abraham F. F.: "Homogeneous nucleation theory: the pretransition theory of vapor condensation", Academic Press, New York 1974.
14. Kashchiev D.: "Nucleation: Basic Theory with Applications", Butterworth-Heinemann, Oxford 2000.
15. Barcikowski S., Goede M., Ostendorf A.: "High Power Macro Processing HPL2002", 1st International Symposium at LAMP 2002, Osaka, Japan, p. 459—462.
16. Staupendahl G., Michel G., Eberhardt G., Müller E., Oestreich C., Vogelsberger W., Schlegel J.: *J. Laser Appl.* 1998, **11**, 14.
17. Barcikowski S., Ostrowski R., Marczak J., Strzelec M., Walter J., Ostendorf A.: "Nanoparticles during laser cleaning of decoration samples of Sigismund's Chapel", in: 4th International Workshop on "Laser Cleaning & New Trends in Laser Cleaning", Mq Univ., Sydney, AU, Dec. 14th—17th 2004. Publ.: World Scientific Publishing Company, Singapore, as "Laser Cleaning II" (Ed. Kane D. M.).
18. Lee J., Becker M. F., Keto J. W.: *J. Appl. Phys.* 2001, **89**, 8146.
19. Nichols W. T., Malyavanatham G., Henneke D. E., Brock J. R., Becker M. F., Keto J. W., Glicksman H. D.: *J. Nanoparticle Res.* 2000, **2**, 141.
20. Bunte J., Barcikowski S., Puester T., Burmester T., Brose M., Ludwig T.: "Secondary Hazards: Particle and X-Ray Emission", Chapter 9.2 in: "Femtosecond Technology for Technical and Medical Applications" (Eds.: Dausinger F., Lichtner F., Lubatschowski H.), Springer Verlag "Topics in Applied Physics", Vol. 96, Berlin 2004, p. 309—320.
21. Korte F., Serbin J., Koch J., Egbert A., Fallnich C., Ostendorf A., Chichkov B. N.: *Appl. Phys. A* 2003, **77**, 229.
22. Bauer T.: "Abtragen von bioresorbierbaren Implantatwerkstoffen mittels ultrakurzer Laserpulse", Dissertation, Publ.: A. Ostendorf, LZH-Verlag, Hannover 2005.
23. Barcikowski S., Bärsch N., Hustedt M., Sattari R., Ostendorf A.: *Proc. ICALEO 2005*, **23**, 375.
24. Wu M. H., Mu R., Ueda A., Henderson D. O.: *Mat. Res. Soc. Symp. Proc.* 2003, **780**, Y3.2/1.
25. Koch J., von Bohlen A., Hergenröder R., Niemax K.: *J. Anal. At. Spectrom.* 2004, **19**, 267.
26. Kik P. G., Maier S. A., Atwater H. A.: *Mat. Res. Soc. Symp. Proc.* 2002, **705**, Y3.6.1.

Received 8 V 2007.