

Laser and Plasma Assisted Fabrication of Nanoparticles in Liquids

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In this paper capabilities of two plasma assisted methods based on a pulsed laser ablation and electrical discharges in liquid media for fabrication of metallic and composite nanoparticles are discussed.

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1. INTRODUCTION

We report about a development of the material and process technology which allows the fast and flexible production of metallic and composite nanoparticles (NPs) with controlled parameters. Preparation of nanosized particles with the well-defined morphology, structure and chemical composition are crucial for achieving their unique properties attractive for a variety of practical applications, including microelectronics, medicine, biophotonics, gas sensor technology, heterogeneous catalysis, etc. The developed technology is based on a pulsed laser ablation (LAL) and electrical discharges (EDL) in liquid media. Additional advantages was obtained by using optimal conditions of the joint effects of laser radiation and pulsed electric discharge plasma fluxes on the material to ensure efficient initiation of the discharge and modification of the size, structure and composition of the formed particles.

Laser ablation in liquid environment provides a simple method with the more effective collection of synthesized particles compared to the typical laser ablation experiments in gas or vacuum. In particular, the method of laser ablation in aqueous solutions can be developed to synthesize colloidal NPs with unique properties, including (a) variable size (down to 5 nm), (b) narrow size dispersion, (c) absence of toxicity that is important for biological sensing, imaging and therapeutics applications.

The electrical discharge in solution is a nanometer-scale engineering technique, which can also produce NPs with predictable composition and structure. Some characteristics of the technique: (i) high versatility and capability for the synthesis of nanostructures with different stoichiometry as a function of solution nature and electrode material composition; (ii) controlled particle size distribution and (iii) possibility to scale-up the process.

Both the developed synthesis techniques offer advantages eliminating the need in large-scale vacuum system (the laser ablation and discharges are performed at normal atmosphere) and they offer a good control over the synthesis process. In the frame of these techniques one can combine particle synthesis with functionalization, encapsulation and stabilization of products.

In this paper capabilities of the developed techniques for synthesis of metallic (Au, Ag, Cu, Gd, Co, Ni,

W), bimetallic (Ag-Cu, Ag-Au) as well as oxide (ZnO, CuO, Gd₂O₃:Tb³⁺), carbide (WC, TiC) and silicide (GdSi) nanoparticles as well as some examples of application of synthesized materials are demonstrated [1-3].

As examples, our results of the following activities are presented and discussed:

a) Preparation of functionalized magnetic nanoparticles on a base of nanoscale compounds and alloys of gadolinium for biomedical applications, for instance as agents in hyperthermia.

b) Fabrication of semiconductor CuInSe₂ (CIS) nanocrystals suitable for incorporating into functional photovoltaic devices as well as doped ZnO nanoparticles for applications in blue/UV light emitting diodes.

c) Laser induced modification of synthesized nanoparticles. Development of optical diagnostics for in situ monitoring of the formation of intermediates and final nanosized particles in solutions.

2. RESULTS AND DISCUSSION

2.1 Laser Ablation Experiments

Laser ablation experiments were carried out by focusing of radiation of a Nd:YAG laser (LOTIS TII, LS2134D), operating in a double-pulse mode at 1064 nm (energy 80 mJ/pulse, repetition rate 10 Hz, pulse duration 8 ns), on the surface of the relevant target placed in the cell filled with a liquid (water, ethanol, acetone etc.). Different optical techniques were applied to investigate the LAL process: the optical emission spectroscopy for plasma characterization; fast shadowgraph for cavitation bubble dynamics study; surface plasmon resonance (SPR) absorption spectroscopy for on-line characterization of NPs in colloidal solutions.

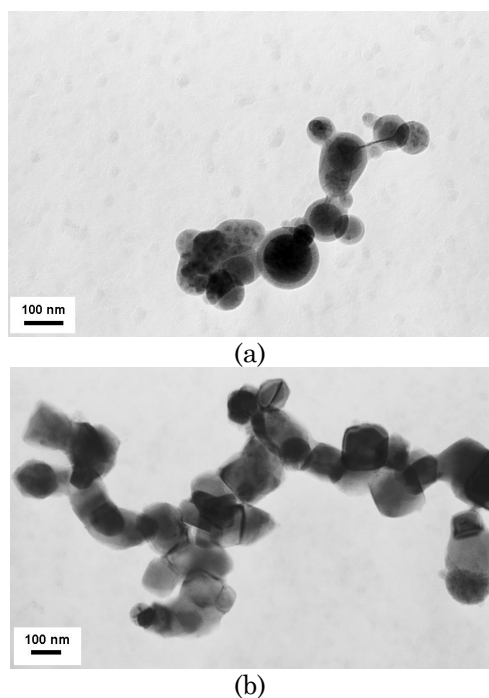
The as-prepared colloids were subjected to laser irradiation with the second harmonic of the Nd: YAG laser (wavelength 532 nm, pulse duration 10 ns) with fluences of 230 and 400 mJ/cm².

The synthesized NPs were characterized by TEM, SEM, EDS and XRD.

The LAL technique has been shown to be suitable for preparation of particles with various compositions and morphologies and with size in the nanometric range (of 5-30 nm diameters). Some examples of NPs produced by LAL are shown in Table 1 to demonstrate potentials of the technique. As examples, TEM images of particles produced by LA of tungsten target indicating

Table 1 – Parameters of NPs synthesized by LAL

Target	Solution	Composition of NPs	Average size, nm
Ag	acetone	Ag	10±5
Au	water	Au	2-4
Au	glucose aqueous solution	Au	5±2
Cu	acetone	Cu	10±2
Cu	SDS	Cu	7-10
Zn	water	ZnO	30-40
ZnO	water	ZnO	15-20
Gd-Si	ethanol	Gd ₅ Si ₄ , (Gd ₅ Si ₃ , GdSi)	10-20
Gd-Si-Ge	ethanol	Gd ₅ Si ₂ Ge ₂	10-40

**Fig. 1** – TEM images of the tungsten NPs produced by LAL in water (a) and octane (b).

different shapes of NPs produced in water and octane are presented in Fig. 1.

A control of stability, size, stoichiometry, crystallinity and chemical composition of the formed particles was shown to be achieved by a proper selection of several experimental parameters such as laser fluence, interpulse delay, a sort of liquid used and post irradiation conditions.

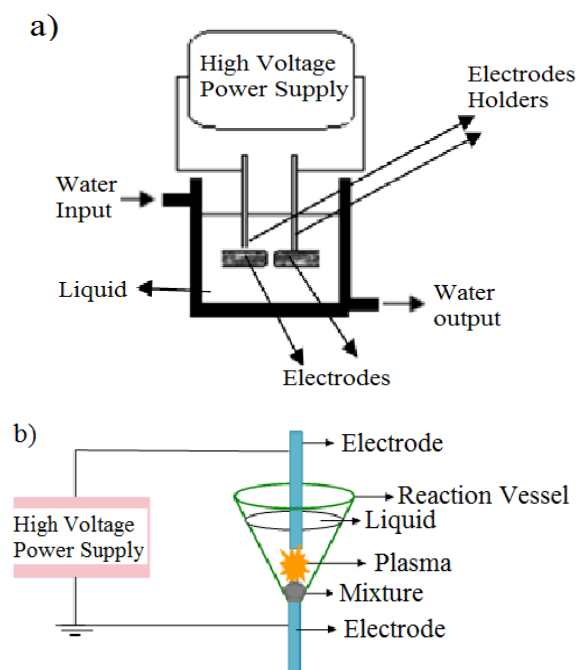
It is interesting to note a capability of the LAL technique in combination with a post-ablation irradiation for formation of composite NPs. In particular, the gadolinium silicides and germano-silicides compound NPs were synthesized by four step process which involved a sequential ablation of silicon, gadolinium and germanium targets followed by additional laser irradiation of the

mixture of the formed colloids. The synthesized particles exhibited the superparamagnetic magnetic behavior promising for their potential application in the method of magnetic hyperthermia treatment. [4, 5].

For a synthesis of doped ZnO NPs we used two step process which involved a sequential ablation of Zn and Ag targets in the 0.01M ammonium nitrate solution followed by the additional laser irradiation of the formed colloid with the second harmonic of the Nd:YAG laser (532 nm, 90 mJ). The analysis of SAED patterns of the as-prepared sample showed that it was composed of the ZnO NPs in zincite structure and of cubic Ag. Laser irradiation of NPs resulted in the distortion of the lattice and disappearing of Ag reflections that might be the consequence of doping of ZnO or alloying of Ag and Zn NPs.

2.2 Preparation of NPs by Electrical Discharges

Three types of electrical discharges were used for synthesis of NPs. First a high-voltage discharge between two electrodes submerged into liquid was used for generation of tungsten and titanium carbide, copper and copper oxide, zinc oxide and gadolinium silicide as well as silicon NPs. (Fig. 2a). The power supply provided an alternating current (ac) spark or arc discharges with a repetition rate of 100 Hz. The discharge was initiated by applying a high-frequency voltage of 8.5 kV.

**Fig. 2** – Schematic diagrams of the discharge chambers: *a* – for synthesis of NPs by a pulsed high-voltage discharge, *b* –for a plasma processing of micropowders.

The optimal distance between the electrodes was 0.3-0.5 mm. The peak current of the pulsed spark discharge was 60 A with a pulse duration of 30 μ s. The peak current and pulse duration of arc discharge were 10 A and 4 ms, respectively.

Second, a funnel-shaped plastic cell with two coaxial vertically orientated electrodes made of a refractory metal (Fig. 2b) was used for the synthesis of CuInSe₂

nanoparticles from the stoichiometrical mixture of copper, indium and selenium powders. Conical shape of the cell prevented removal of the particles from the discharge zone. The similar power supply (as in the first case) was used for a discharge ignition. A presence of suspended particle allowed discharge burning at the expanded inter-electrode distances (15-20 mm).

Third, a gas-liquid interface discharge (plasma in contact with liquid) was used for the synthesis of nanosized metallic NPs. A principle of synthetic process is clear from the Fig.3. In this type of discharge an anodic dissolution of metallic (Ag, Cu, Zn) electrodes occurs followed by reduction of aqueous metal cations with charged, energetic species directed from a microplasma. Metal electrodes are placed inside a solution consisting of 1 mM HNO₃ with 10 mM glucose (fructose) solution or without it. The acid is necessary to make the solution conductive; the glucose (fructose) is a stabilizer that prevents uncontrolled particle growth and agglomeration. A stainless steel capillary tube that served as a cathode (500 μm inside diameter, 5 cm length) was located 3 cm away from the metal electrode with distance of 1-3 mm between the tube end and the liquid surface. Argon gas flow (approximately 60 sccm) was directed through the capillary tube. The discharge was ignited by applying of high voltage of 3.6 kV using a dc power supply. The discharge current could be kept constant in the range 1 - 4 mA during the synthesis process.

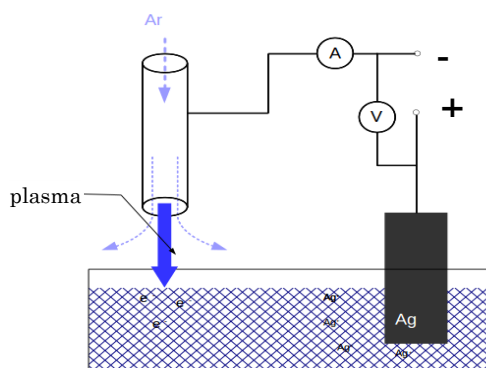


Fig. 3– Schematic diagram of the gas-liquid interface discharge used for NPs synthesis.

Using the first type of discharges it was demonstrated that the pulsed spark discharge between the bulk silicon electrodes immersed in the liquid (water, ethanol), provides the effective method for the synthesis of silicon NPs in result of the nucleation of the evaporated atoms from the electrodes in the decaying plasma channel and a growth of the embryonic particles, limited by the rate of cooling in the surrounding liquid [6]. The experimental results showed that the morphology and phase composition of the resulting particles are determined by the discharge regime and the composition of the liquids in which the discharge is initiated. In particular, it was shown that in the pulsed electrical discharge between the silicon electrodes in water isolated spherical NPs with the average diameter of about 5 nm were formed. For the NPs synthesized in the spark discharge in ethanol, the characteristic dimensions of the particles were larger and could reach up to 50 nm, probably in result of aggregation.

Analysis of the phase composition of the powders showed that NPs with the cubic silicon structure are major in the samples produced by the spark discharge both in water (90 vol.%) and ethanol (95 vol.%) with a small impurity of the oxide phase (SiO₂) in the samples synthesized in water and carbide phase (SiC) in the powder obtained in ethanol. Absorption and Raman scattering features of synthesized particles confirmed their polycrystalline nature.

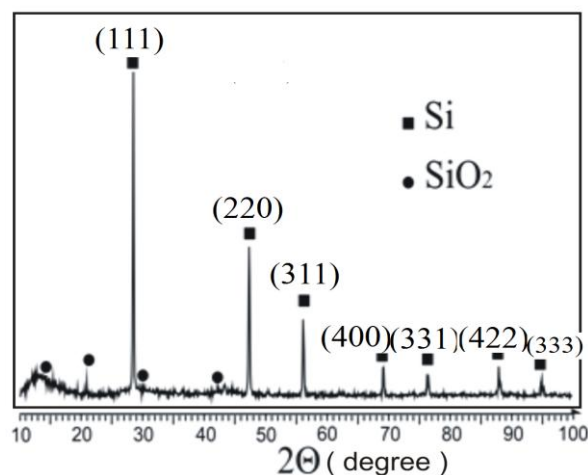


Fig. 2 – XRD pattern of Si NPs produced by spark discharge in water.

The Si-NPs synthesized exhibited a violet-blue photoluminescence at the room temperature through the mechanism of the radiative recombination via the defect centers formed in the surface oxide layer and can be used in light-emitting optoelectronic devices [6].

Processing of suspended powder mixture of copper, indium, and selenium, taken in the stoichiometrical proportions, in ethanol by pulsed electrical discharge (Fig. 2b) initiated chemical reactions between powder components resulting in generation of compound chalcopyrite CuInSe₂ (CIS) nanocrystals with an average size of about 25 nm and a band gap of 1.2 eV [7]. Since the properties of CuInSe₂ NPs crucially depend on the stoichiometric composition, structural defects, surface conditions, particle size and shape, a special attention was paid to the investigation of the impact of the discharge regime on the parameters of the synthesized particles.

As demonstrated by the TEM studies the synthesized CIS NPs had a spherical shape and size about 20-30 nm (Fig.3).

The composition of the prepared NPs was controlled by XRD analysis and Raman spectroscopy. Three peaks at $2\theta = 26.7^\circ$; 44.4° and 52.4° corresponding to the crystallographic planes (112), (204/220) and (116/312) of CIS with tetragonal chalcopyrite structure, that is the stable phase of bulk CIS crystals at room temperature, dominated in the XRD pattern of the as-prepared samples. Annealing of the synthesized powder for 1.5 h at 700 °C in vacuum resulted in the disappearing of weak diffraction peaks corresponding to the intermediate CuSe₂ and In₄Se₃ phases and pure phases of indium and selenium unreacted.

The Raman spectrum of the synthesized NPs had a peak at 172 cm⁻¹, which is usually observed in the Raman spectrum of I-III-VI₂ compounds with chalcopyrite

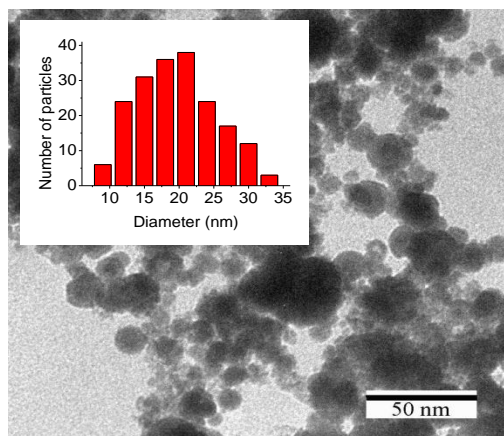


Fig. 3 – TEM image and size distribution (inset) of the CIS NPs produced by the treatment of copper, indium and selenium powders in the spark discharge in ethanol.

structure. Weak peaks at 208 and 258 cm^{-1} were assigned to In_4Se_3 and Cu_xSe compounds, respectively.

From the viewpoint of thermodynamics, the formation of new compounds should occur as a result of the reactive collisions between the species in relatively high energy states, while the particles of complex composition are formed in result of clusterization of the formed compounds. During the discharge treatment of the suspended powder in liquid the powder particles are heated, melted and vaporized in the region of the discharge generated. Heating in the gap of discharge streamers, melting and the subsequent fragmentation of particles can be favorable for chemical interactions between powder components and to the generation of compounds.

Semiconductor nanomaterials including the ternary compound CuInSe_2 (CIS) and its solid solutions $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS) are considered as the most promising for use in photovoltaic devices, due to the high absorption coefficient in a wide spectral range, low toxicity, high photostability and sufficiently low cost. The optimal conditions for the CuInSe_2 nanocrystals formation are determined by the plasma temperature and particles concentrations, that opens up new possibilities for creating absorbing layers for photovoltaic converters.

Typical absorption spectra of the colloidal solutions prepared by the gas–liquid interfacial discharge (Fig.3) with a silver anode and a TEM photograph of the prepared silver NPs are shown in Fig 4. For silver nanoparticles the spectrum exhibited the characteristic

plasmon absorption band with a peak located at 400 nm. This band characteristic for spherical Ag nanoparticles appeared and grew in intensity with increasing discharge burning time.

TEM analysis of the as-grown NPs confirms that the particles are slightly agglomerated, quasi spherical with a mean size of about 15-20 nm. We found that varying the process time or other parameters such as the discharge current did not alter significantly the particle size distribution, but increased the particle density and led to the particle agglomeration. While further experiments may be necessary to fully understand the mechanism for particle nucleation and growth, we consider that the particle size is controlled by the reaction volume, which can be defined as a small region near the microplasma-liquid interface. Our experimental observations suggest that the particle nucleation is driven by the electromigration of metallic cations to this region and subsequent electrochemical reduction by the microplasma. A growth then occurs until the particles are carried out of the reaction volume by convective or diffusive flow back into the bulk solution. Thus, it can be inferred that the size distribution of the as-grown particles is slightly affected by the process time.

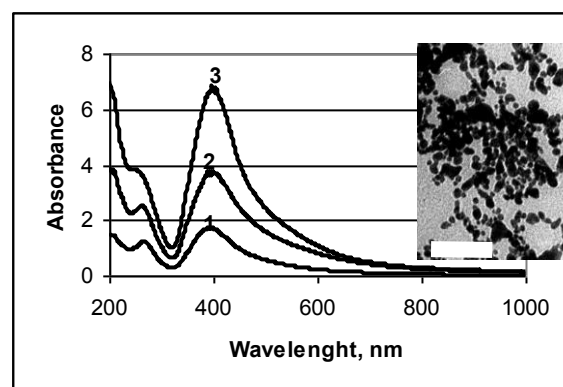


Fig. 4 –Absorption spectra and TEM image of Ag nanoparticles prepared by the gas–liquid interfacial discharge. The scale bar is 100 nm. Curves 1, 2, 3 correspond to the discharge burning time of 1, 2 and 3 min, respectively)

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