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Laser ablation of gadolinium targets in liquids for nanoparticle preparation

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Abstract Synthesis and preliminary characterization of gadolinium colloids prepared by pulsed laser ablation in different solutions was performed to clarify the capabilities of the laser ablation technique for preparation of stable nanoscale particles suitable for further bio(chemical) functionalization. Experiments were made by using a 10 Hz pulsed Nd:YAG laser, operating at 1064 nm. The formed colloids were examined by UV/VIS absorption spectroscopy, TEM and XRD. The developed technique was shown to be suitable for the preparation of particles of various compositions (oxides and carbides) with sizes in the nanometric range (of 5–12 nm diameters) by proper selection of both laser experimental parameters and the type of the liquid used (distilled water, ethanol and acetone).

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1 Introduction

In the last decade, lanthanide metals and their alloys have attracted much attention as suitable magnetic materials for a wide range of technological and biomedical applications [1–3]. For example, Gd and its compounds are of current interest as magnetic resonance contrast media, therapeutic agents in tumor treatment and drug delivery. Gadolinium is a ferromagnetic metal with a large magnetic moment. Gadolinium and its compounds exhibit the largest magnetocaloric effect known near room temperature [4] and therefore they are particularly promising as magnetic particles for hyperthermia treatment [5]. Gadolinium oxides doped with Tb, Eu, Dy, etc. ions are promising luminescent labels in bioanalysis, because of their optical properties (sharp emission spectra, large Stokes shifts and long luminescence lifetimes), as well as photostability and low-cost synthesis [6].

It should be noted that each potential application requires the nanoparticles to have different properties [7]. For instance, biomedical applications require the magnetic particles to be stable in water and in physiological solutions as well as to be coated with a biocompatible polymer [8].

Some advantages of using nanosized particles are expected because of size-dependent modifications of structural and magnetic properties at nanoscale level [9]. In addition, nanosized particles have higher effective surface areas (easier attachment of ligands), lower sedimentation rates (higher stability) and improved tissular movement. For example, the use of nanometer-sized (subdomain) particles for magnetic hyperthermia is preferred instead of the micron-sized (multidomain) particles because of higher heating efficiency at tolerable magnetic fields [10].

As for gadolinium nanoparticles, the studies are very few mainly because of the extreme sensitivity of Gd to oxidation. To our knowledge, to date there have been only several reports on gadolinium nanoparticles, prepared by gas-phase methods or synthesized by chemical means [10–13]. More papers are devoted to the synthesis of rare-earth-element-doped gadolinium oxide (RE:Gd_2O_3) nanoparticles and their applications in biotechnology [14, 15].

Since polycrystalline or bulk Gd is easily oxidized on exposure to air, most of the reported properties of Gd have been studied under vacuum conditions or in the presence of protective coatings of palladium (Pd) or graphite. But, recently, Gd nanoparticles with improved stability towards oxidation were synthesized via an inert gas evaporation method [16]. The improved stability of the prepared Gd

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nanoparticles was explained by the formation of a protective oxide shell around the particles and by the structural compatibility between the cubic oxide shell and the fcc structure of Gd in the nanoparticle core.

Since the properties of nanoparticles are strongly dependent on their morphology, particular attention should be paid to the choice of a preparation method. The method of nanoparticle preparation determines the size and shape of particles, their size distributions, the degree of structural defects and impurities in the particles. The chemical method is one of the most frequently used for preparing metal colloidal solutions. But, colloids produced by the chemical methods are usually contaminated with the residual by-products such as ions and reducing agents. The problem of colloid purification from the by-products is especially important for biological application of nanoparticles.

Recently, a laser ablation method has been developed to prepare noble-metal nanoparticles in solutions by the use of lasers having various performances [17–24]. Advantages of this method include the relative simplicity of the procedure and the absence of chemical reagents in the final preparation. However, synthesis of gadolinium nanoparticles is challenging due to their extremely reactive nature as nanoscale materials and, to our knowledge, there have been no reports of gadolinium nanoparticles synthesized by the laser ablation method.

In the present paper, characterization of gadolinium nanoparticles prepared by pulsed laser ablation in liquids was performed in order to elucidate the capabilities of this technique for preparation of stable nanoscale particles suitable for further bio(chemical) functionalization. The formed colloids were examined by UV–visible (UV/VIS) absorption spectroscopy and transmission electron microscopy (TEM) and energy-dispersive X-ray (EDX) analysis. The composition, structure and optical properties of synthesized particles were investigated. Particles of various compositions (oxides and carbides) with sizes in the nanometric range (of 5–12 nm diameters) were produced by proper selection of both laser experimental parameters and the type of the liquid used.

2 Experimental

The experiments were carried out by focusing of radiation of a Nd:YAG laser (LOTIS TII, LS2134), operating at 1064 nm (energy 50 mJ/pulse, repetition rate 25 Hz, pulse duration 15 ns), on the surface of a gadolinium target placed in a cell filled with liquid (ethanol, water and acetone). The sample was placed on a movable holder. The laser beam was focused by a lens with the focal distance of 7.5 cm onto the target surface and into a 0.4-mm spot. The depth of the liquid layer above the target was about 20 mm. The laser fluence at the target surface was 40 J/cm^2. The laser beam was employed for ablation of the gadolinium plate for 5 min. Freshly prepared colloidal solutions were used.

The laser ablation of a Gd target in liquid was accompanied by the presence of a small plasma plume above the target surface. The plasma plume intensity depended on the laser energy and light focusing conditions. We observed a visible coloration of the solution indicating nanoparticle formation after several minutes of the beginning of the ablation experiment. The transparency of the liquid decreased with time during the laser ablation of the target. The synthesized particles were obtained as a colloidal solution. After solvent evaporation white powders in the case of ablation in water and taupe powders in the case of ablation in ethanol and acetone were obtained.

Immediately after the ablation experiment, the optical absorption spectra of the formed colloids were measured by a UV–visible spectrophotometer (CARY 500). A 0.5-cm-path-length quartz cell was used for the absorption measurements. Along with the absorption spectroscopy, transmission electron microscopy (TEM) was used for studying the size and shape distributions of the resultant nanoparticles. The average diameters of the particles formed in solution were estimated from the TEM micrographs, which were obtained on a LEO 906E (LEO, UK, Germany) transmission electron microscope operated at 120 keV. Samples for TEM were dispersed by sonication and deposited on the copper grids covered by Formvar films. Normally, 100 or more particles are counted to determine the size distribution of each sample.

To determine the chemical composition of the produced nanoparticles a drop of colloidal solution was transferred to a single-crystal silicon substrate and dried at room temperature. The composition of the sample deposited on the substrate was detected using an energy-dispersive X-ray (EDX) spectrometer attached to a scanning electron microscope (SUPRA 55WDS, Carl Zeiss, Germany).

The powder formed after the drying of colloidal solutions was examined by X-ray diffraction analysis (XRD). Powder phase composition, its crystalline structure, lattice parameters and grain size were determined using X-ray diffraction at Cu K_α (0.154 nm). A D8-Advance X-ray diffractometer (Bruker, Germany) was used.

3 Results and discussion

Several experimental conditions were tested. By varying the experimental parameters, in particular the sort of the liquid used (distilled water, ethanol and acetone), the composition and morphology of nanoparticles could be changed.

The micrographs of the nanoparticles produced by pulsed laser ablation of Gd targets in water and ethanol are shown in Fig. 1. From TEM images and histograms, it can be seen that

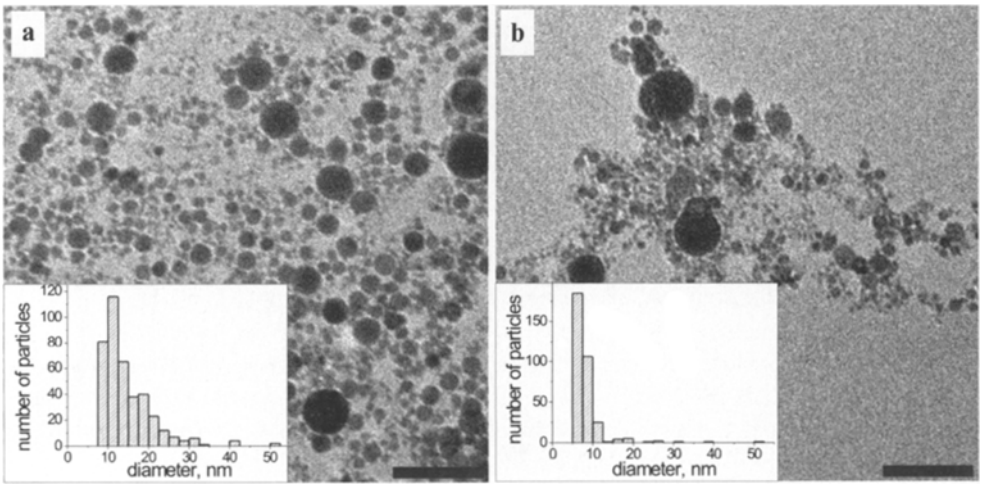

Fig. 1 Electron micrographs of gadolinium nanoparticles produced by laser ablation (1064 nm) of a gadolinium plate in distilled water (**a**) and in ethanol (**b**). The *black bars* in both images correspond to 100 nm. The particle size distributions are shown as *insets*

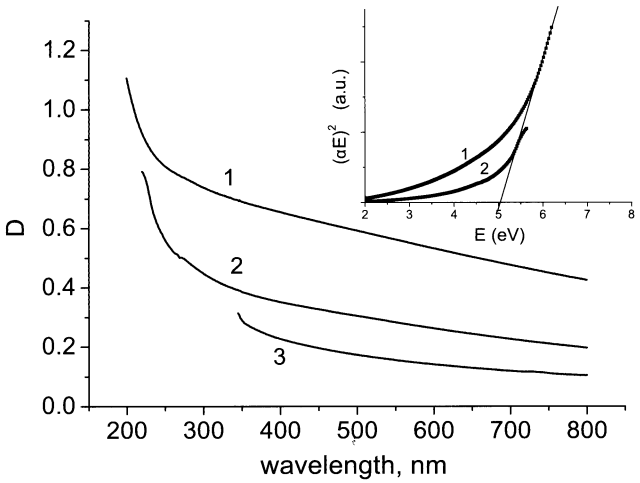

Fig. 2 Optical absorption spectra of colloidal solutions produced by laser ablation of gadolinium in water (1), ethanol (2) and acetone (3). The *inset* shows the dependence of the optical absorption coefficient $(\alpha E)^2$ on the photon energy, E

the as-synthesized product is mainly composed of spherical nanoparticles with average diameters of about 10–12 nm in water and of 6–10 nm in ethanol. The nanoparticles formed in ethanol show a relatively narrower size distribution.

The difference in color of the prepared colloids could be indicative of different compositions of the formed nanoparticles, for example residual carbon in the case of laser ablation in ethanol and acetone.

Figure 2 presents the typical absorption spectra of as-prepared colloidal solutions. Optical absorption spectra of the colloids are rather featureless. The spectrum of the aqueous suspension exhibits a broad absorption band edge in the UV spectral range, while spectral features of colloidal solutions prepared by laser ablation in ethanol (as well as in acetone) were masked by the strong absorption of solvents in this spectral region.

Since as a result of laser ablation of a Gd target in water the most probable product was expected to be gadolinium oxide having a semiconducting nature, we tried to estimate the optical band gap from the absorption spectrum of the formed nanoparticles. The optical absorption coefficient, k, was evaluated from the absorbance D, reflectance and thickness l data, according to the relation $k = D/0.43l$. The band-gap energy was evaluated from a straight-line plot of $(kh\nu)^2$ against photon energy $h\nu$ extrapolated to $k = 0$. The optical band gap was estimated to be approximately 5.0 eV for nanoparticles produced in water, which is rather close to the reported value of the band gap for Gd_2O_3 [25]. This indicated that nanoparticles produced by laser ablation of Gd in water were most likely oxide nanoparticles.

To further confirm the composition of the formed nanoparticles, energy-dispersive X-ray (EDX) analysis was applied. The EDX spectra of samples prepared by laser ablation in ethanol showed the presence of carbon and they could be suggested to consist of carbon-coated Gd nanocapsules or GdC_2 nanoparticles, similarly to the results in [11]. It was not the case when nanoparticles were produced in water. In this case the result revealed that only gadolinium, oxygen and silicon of a substrate material were detected. The ratio of atomic contents Gd:O determined from the EDX spectrum was rather close to the stoichiometric ratio of the Gd_2O_3 phase.

The phase composition and crystalline structure of the powders were determined from XRD spectra. A typical X-ray diffraction (XRD) pattern of the powder produced in water is shown in Fig. 3a. As follows from the XRD pattern, the synthesized product is composed of monoclinic Gd_2O_3 phase with lattice constants $a = 14.095$ nm, $b = 3.576$ nm and $c = 8.769$ nm, which are in agreement with the JCPDS card for Gd_2O_3. No obvious impurity phases were detected.

The XRD line broadening technique was used for crystallite size determination. The average particle size was estimated from the full width at half maximum (FWHM) of

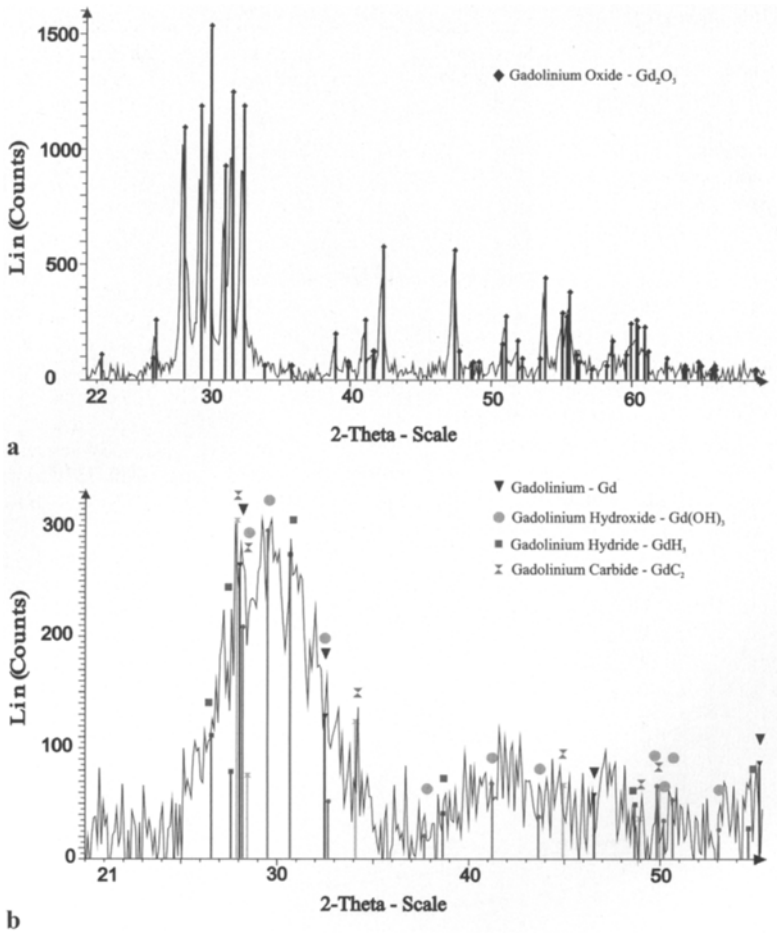

Fig. 3 X-ray diffraction patterns of sample produced by laser ablation of Gd target in water (**a**) and in ethanol (**b**)

the XRD peaks using the Scherrer equation. The average crystallite size was calculated to be around 56 nm, which is almost five times higher that obtained from the TEM results. Most probably, it indicates that solvent removal has caused agglomeration of the nanoparticles.

Similar XRD diagrams (Fig. 3b) for the powder produced in ethanol exhibited a more complex phase composition. The powder was composed of a mixture of gadolinium carbide GdC_2, gadolinium hydride GdH_3 and gadolinium hydroxide $Gd(OH)_3$ phases; the peaks of metallic Gd were also identified. The respective positions of all peaks were in agreement with the JCPDS standard data. Some peaks against a broad diffuse background (probably from a non-crystalline amorphous phase) in the X-ray diffraction diagram were not identified. It should be noted that these unidentified peaks could not be ascribed to the gadolinium oxide phases even though metallic gadolinium, especially at the nanoscale, is highly sensitive to oxidation. Most likely some other carbide phases as well as carbon-coated Gd/GdC_2 nanoparticles were formed in this case, but further confirmation is required by using high-resolution TEM investigations for clear observation of the core–shell structure of the nanoparticles formed in ethanol.

4 Conclusions

So, laser ablation of gadolinium targets in water and ethanol can be a very simple and efficient route to prepare metallic and composite Gd particles with sizes in the nanometric range (of 5–15 nm diameters). Highly crystalline nanooxide particles 10–12 nm in size with a spherical shape were formed during laser ablation in distilled water. In the nanopowder prepared by laser ablation in ethanol the presence of GdC_2 and metallic Gd was detected by X-ray diffraction. The EDX analysis confirmed the presence of Gd metal in the synthesized product. Nanoparticles produced by laser ablation in ethanol showed improved stability towards oxidation. It can be connected with the formation of carbon-coated nanoparticles composed of the metallic core and the graphite shell. The carbon coating protects the core against oxidation, preserving its specific properties. The coating also isolates nanoparticles from each other and will provide a biocompatibility and stability of them in many organic and inorganic solutions. The presence of metallic Gd in the nanoparticles will result in the enhancement of their magnetization compared with the gadolinium carbide nanoparticles without the metallic Gd core. The magnetic property measurements of prepared nanoparticles are in progress.

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