

Formation of nanoparticles during laser ablation of an iron target in a liquid

I.A. Sukhov, A.V. Simakin, G.A. Shafeev, G. Viau, C. Garcia

Abstract. Formation of nanoparticles during laser ablation of a bulk iron target in water and isopropyl alcohol by pulsed near-IR laser radiation has been experimentally investigated. The experiments were performed using a 3-ns neodymium laser and a 100-ns ytterbium fibre laser. A size distribution function is obtained for the nanoparticles, which is peaking near 15 nm. The diffraction patterns of the nanoparticles exhibit pronounced peaks of metallic iron. An analysis of the nanoparticles by transmission electron microscopy shows that in some cases they have a core–shell structure. The nanoparticles formed by laser ablation have pronounced magnetic properties. The absorption spectra of colloids with iron nanoparticles contain peaks, which presumably correspond to the electron plasmon resonance in these particles.

Keywords: magnetic nanoparticles, lasers, ablation, liquid, iron.

1. Introduction

Formation of chemically pure and biocompatible nanoparticles is an urgent problem of modern science, because the range of application of nanoparticles in medicine and biology constantly increases [1, 2]. These particles can be formed by laser ablation of solids in liquids [3]. When a solid placed in a liquid is exposed to a sufficiently high-power laser pulse, particles are transferred from the solid target into the environment. This process is characterised by high temperatures and a pressure of several hundreds of atmospheres in the region of laser action on the target. Under these conditions spherical nanoparticles are generally composed of the material of an irradiated solid; their sphericity is due to the effect of surface tension forces of the melt. The nanoparticle size depends on the type of liquid, target material, and experimental conditions (the radiation power and wavelength, the pulse width, and the diameter of the laser spot in the focal plane) [4].

In contrast to the chemical ways for synthesising nanoparticles, the colloids obtained by laser ablation contain no stabilising ions and surfactants. The particles formed consist of

only the target material and the liquid. The interaction between the material of nanoparticles and the liquid during laser ablation is often inevitable; however, this effect can be minimised by choosing proper liquid characteristics and experimental conditions. The technique of laser ablation is universal, because a solid target can be made of different materials: metals, insulators, or semiconductors. When nanoparticles are formed in a vacuum or in a gas, it is rather difficult to collect them because of their absorption on the substrate or chamber walls. At the same time, in the case of ablation in a liquid, nanoparticles remain in the colloid formed.

To date, experiments on the laser ablation of various elements (gold, silver, copper, titanium, tin, etc.) in liquids have been performed [5]. Laser synthesis of alloyed gold and silver nanoparticles has been investigated in [3]. Both organic (ethanol, acetone, isopropyl alcohol) and inorganic (for example, water) liquids have been used.

Magnetic nanoparticles of iron and magnetite Fe_3O_4 are widely applied in medicine and biology for diagnostics, drug transport, destruction of tumours by heating (hyperthermia), etc. Magnetite nanoparticles are generally used in biomedicine [1]. A decrease in the size of magnetic particles to several nanometres leads to the formation of a high magnetic moment and the so-called superparamagnetism. These properties of iron oxide particles have been studied well [6, 7]. An advantage of magnetic nanoparticles is the possibility of controlling their motion in biological tissues with the aid of an external magnetic field.

Formation of iron nanoparticles by laser ablation is hindered by the high chemical activity of this element, especially at high temperatures characteristic of the irradiated region of the target. One might expect the composition of nanoparticles formed by laser ablation of iron target in liquids to depend on the type of the liquid. At the same time, production of magnetic nanoparticles by laser ablation allows one to implement in full measure the advantage of this method over chemical synthesis. In particular, iron nanoparticles were formed by laser ablation in organic liquids in [8]. The possibility of obtaining iron nanoparticles in aqueous media should facilitate their wider application in medicine.

2. Experimental

The experiments were performed using two diode-pumped lasers: a pulsed ytterbium fibre laser LDesigner and a neodymium laser. The former had the following characteristics: average power 20 W, spectral range from 1060 to 1070 nm, energy per pulse 0.5 mJ, pulse width 100 ns, and pulse repetition rate 20 kHz.

I.A. Sukhov, A.V. Simakin, G.A. Shafeev A.M. Prokhorov General Physics Institute, Russian Academy of Sciences, ul. Vavilova 38, 119991 Moscow, Russia;
e-mail: wrc@kapella.gpi.ru, shafeev@kapella.gpi.ru;
G. Viau, C. Garcia Université de Toulouse, INSA-LPCNO, CNRS UMR 5215, IRSAMC, 135, av. de Rangueil, F-31077 Toulouse, Cedex 4, France

Received 24 October 2011; revision received 21 February 2012
Kvantovaya Elektronika 42 (5) 453–456 (2012)
Translated by Yu.P. Sin'kov

To decrease the absorption of laser radiation by colloid during ablation of iron by ytterbium laser radiation, we used a continuous-flow cell, which allowed us to form a liquid flow above the target surface and reduce the probability for nanoparticles to be exposed again to the laser beam. The target was a 1–2-mm-thick iron (99.9%) plate. The thickness of the liquid (water or isopropyl alcohol) layer above the plate surface was 1 mm and the flow velocity was 1–2 cm s⁻¹. A focused high-power beam moved over the target surface with a step of 1/35 mm and a velocity of 50 mm s⁻¹. The beam diameter on the target was 35 μm. In some experiments gaseous hydrogen (obtained using an electrolyser) was passed through the working liquid to suppress possible oxidation of the nanoparticles formed. Hydrogen was introduced into the circulating liquid 15 min before the ablation onset and continued to be supplied during the formation of nanoparticles.

The second radiation source (neodymium laser) had a pulse repetition rate of 10 kHz and a pulse width of 3 ns at an average power of 6 W. Ablation by the neodymium laser was performed in a cell without liquid flow; the laser radiation was introduced into the cell through a transparent wall.

The nanoparticles obtained by laser ablation were investigated using a CPS DC2400 disk centrifuge, which makes it possible to measure the size distribution function of nanoparticles (in the range from 10 to 200 nm). The absorption spectra of the colloids in the wavelength range of 200–800 nm were recorded with an OceanOptics fibre spectrometer. In view of the limited dynamic range of this instrument, we studied colloids with different concentrations. To reduce the sample concentration, a liquid (in which ablation was performed) was added to the colloid. Powder diffraction patterns of the nanoparticles formed by evaporation of colloidal solutions were recorded with a PANalytical Empyrean X-ray diffractometer (Co K_α radiation).

Transmission electron microscopy (TEM) images of nanoparticles were recorded on a JEOL microscope. To this end, colloidal solutions were deposited on a special carbon membrane and evaporated.

3. Results

The optical density of a colloidal solution formed increases with increasing target exposure time. In the visible spectral range the solution is almost transparent; characteristic absorption peaks are observed in the UV region. The absorption spectrum of the colloid obtained during laser ablation of iron in hydrogen-saturated isopropyl alcohol is characterised by a peak at $\lambda = 340$ nm, which is observed at the initial colloid concentration (Fig. 1a). The spectrum of a tenfold diluted colloid exhibits a second peak at $\lambda = 280$ nm (Fig. 1a). The absorption spectra for the target ablated with and without passing hydrogen through isopropyl alcohol do not differ radically. The absorption spectrum of the nanoparticles obtained by iron ablation in water exhibits a peak at $\lambda = 270$ nm (Fig. 1b).

The size distribution function of the nanoparticles formed by iron ablation in isopropyl alcohol has two peaks, which correspond to nanoparticles with sizes of 15 and 95 nm (Fig. 2a). The distribution function for the nanoparticles obtained by ablation of iron in water has one peak at 10 nm (Fig. 2b).

The X-ray study showed that both the nanoparticles formed in isopropyl alcohol and those obtained in water have a crystalline structure. The diffraction pattern of the powder

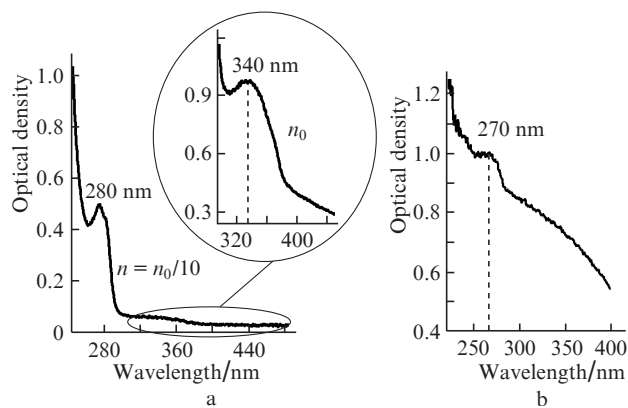


Figure 1. Absorption spectra of the colloids obtained by ablation of iron in (a) hydrogen-saturated isopropyl alcohol and (b) water using an ytterbium laser; n_0 is the colloid concentration.

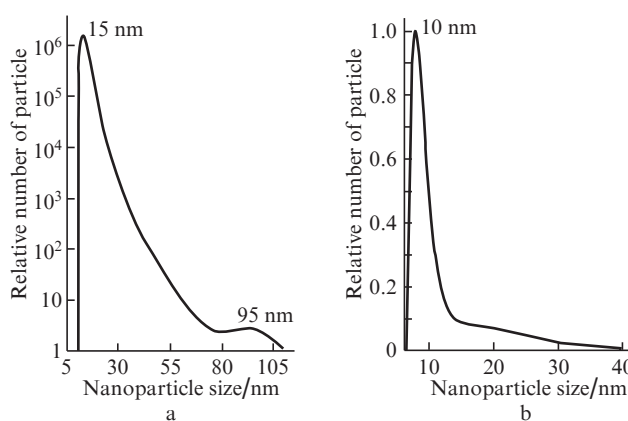


Figure 2. Size distribution functions for the nanoparticles obtained by ablation of iron in (a) hydrogen-saturated isopropyl alcohol and (b) water using an ytterbium laser.

obtained by evaporation of colloids of nanoparticles in isopropyl alcohol (Fig. 3) exhibits reflections corresponding to the strongest peaks of metallic iron with an fcc lattice. These

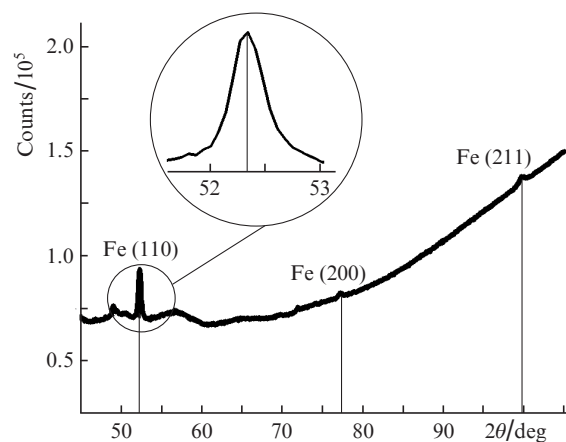


Figure 3. Diffraction pattern of the sample obtained by ablation of iron in hydrogen-saturated isopropyl alcohol using an ytterbium laser. The inset shows a fragment of the diffraction pattern with pronounced broadening of the Fe(110) peak; 2θ is the diffraction angle.

peaks are significantly broadened, which is indicative of small coherent-scattering regions.

The diffraction pattern of the nanoparticles formed by laser ablation of iron in water contains peaks corresponding not only to compounds of iron with oxygen but also to metallic iron (Fig. 4).

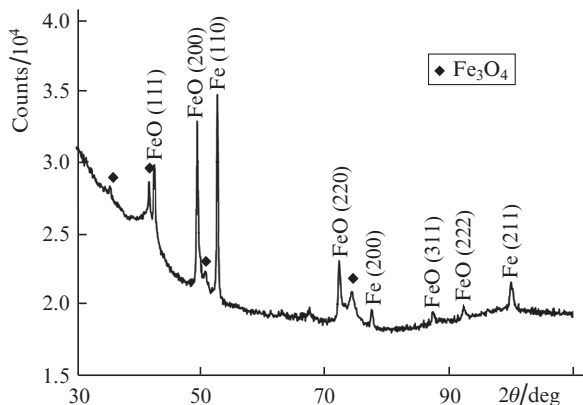


Figure 4. Diffraction pattern of the nanoparticles obtained by ablation of iron in water using an ytterbium laser.

Figures 5–7 present the TEM images of the samples. One can see that most particles are less than 50 nm in size; this is in good agreement with the size distribution function obtained by centrifugation. The particles have a core–shell structure.

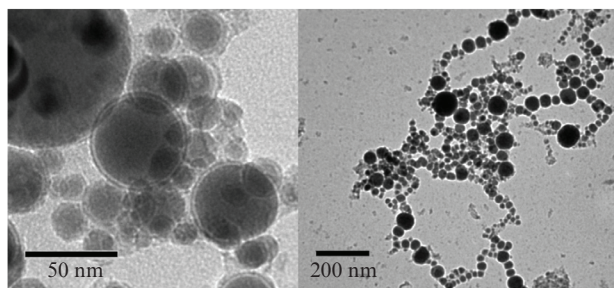


Figure 5. TEM images of the nanoparticles obtained by ablation of iron in isopropyl alcohol using an ytterbium laser.

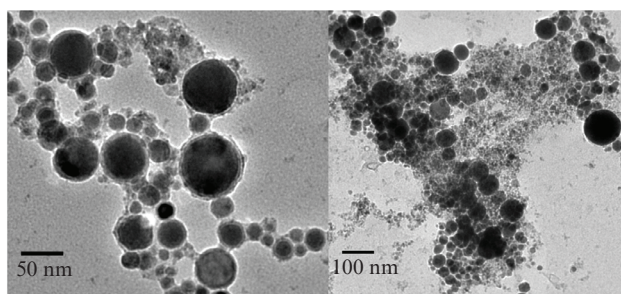


Figure 6. TEM images of the nanoparticles obtained by ablation of iron in isopropyl alcohol using a neodymium laser.

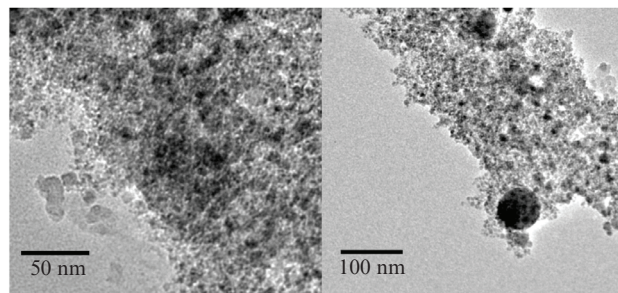


Figure 7. TEM images of the nanoparticles obtained by ablation of iron in water using an ytterbium laser.

Irrespective of the type of the liquid in which the iron target was ablated, all nanoparticles exhibited pronounced magnetic properties. In particular, an inhomogeneous external magnetic field applied to a vessel with colloids leads to extraction of all nanoparticles from the solution bulk to the field-application region.

4. Discussion

Our X-ray data (Figs 3, 4) suggest that laser ablation of iron in a liquid (isopropyl alcohol or water) leads to the formation of nanoparticles of iron and its oxides (FeO, Fe₃O₄). The photographs in Figs 5 and 6 show that the particles are coated by a shell, which has a lower contrast in comparison with the core; i.e., the electron density in the nanoparticle shell is lower than in the core material. Based on the X-ray data, it is reasonable to suggest that the nanoparticle shell consists of iron oxide. Note that, despite the high chemical activity, many nanoparticles (even among those obtained by ablation in water) have a metal core.

The peak at a wavelength of 340 nm in the absorption spectrum of colloid (Fig. 1a) can be attributed to metal nanoparticles. The shape and height of this peak, as well as the colloid concentration at which it was observed, indicate its relationship with the plasmon resonance in iron nanoparticles, which becomes blue-shifted with a decrease in the particle size to several nanometres [9]. A similar peak is observed in the absorption spectrum of the nanoparticles formed by laser ablation of iron in acetonitrile [8]. The absorption spectrum of the colloid obtained by laser ablation of iron in isopropyl alcohol (Fig. 1a) also contains a peak at $\lambda = 280$ nm, which is presumably due to the products of isopropyl alcohol decomposition. The absorption spectrum of the colloid formed by laser ablation of iron in water exhibits a peak at $\lambda = 270$ nm (see Fig. 1b). A similar peak was observed in [10], where the absorption of nanoparticles produced by explosion of a fine iron wire in water was investigated. According to the theoretical estimates, the plasmon resonance peak of 10-nm iron nanoparticles in water is at $\lambda = 220$ nm [9]. The difference between the peak position in the absorption curves of the colloids formed and the theoretical estimate can be caused by the presence of oxide shells on particles. The refractive index of iron oxide in the UV region exceeds significantly the refractive index of water, as a result of which the plasmon resonance becomes red-shifted.

The size distribution functions of the nanoparticles (Fig. 2) indicate that the colloid obtained by laser ablation of iron in isopropyl alcohol contains mainly 15-nm particles. The peak corresponding to the 95-nm nanoparticles can be

due to the presence of both aggregates and large nanoparticles. The analytical methods used in this study do not make it possible to draw an unambiguous conclusion. The TEM data suggest that saturation of the liquids used for iron ablation with hydrogen does not lead to the formation of cavities in nanoparticles, which were observed in the previous studies on laser ablation of an aluminium target in hydrogen-saturated ethanol [11].

5. Conclusions

Nanoparticles have been formed in experiments on laser ablation of an iron target in water and isopropyl alcohol. The X-ray data on the chemical composition and crystal structure of these nanoparticles indicate that they contain both metallic iron and iron oxides. The average sizes of particles are 15 and 10 nm for the laser ablation in isopropyl alcohol and water, respectively. The absorption spectra of the colloidal solutions exhibit peaks that are presumably due to the plasmon resonance in iron nanoparticles. However, the position of these peaks does not coincide with the results of theoretical calculations. The TEM study of the nanoparticles obtained suggests that their morphology and average size barely depend on the IR pulse duration and that the particles have a core-shell structure. The core and shell consist of metallic iron and iron oxide, respectively. The particles exhibit magnetic properties. This study will be continued in order to test the nanoparticles obtained on samples of biological tissues and compare their properties with the characteristics of magnetic nanoparticles produced by chemical methods.

Acknowledgements. We are grateful to P.G. Kuzmin for his help in the experiment. This study was supported in part by the Russian Foundation for Basic Research (Grant Nos 10-02-90044-a and 11-08-00574-a) and Grant NSh-214.2012.2 of the President of the Russian Federation for Support of Leading Scientific Schools.

References

1. Anisimov S.V., Belostotskaya G.B., et al. *Nanotekhnologii v biologii i meditsine* (Nanotechnologies in Biology and Medicine) (St. Petersburg: Lyubavich, 2009).
2. Chornya M., Fishbeina I., Yellenb B.B., et al. *Proc. Nat. Acad. Sci. USA*, **107** (18), 8346 (2010).
3. Shafeev G.A., in *Lasers in Chemistry* (Wienheim: Wiley VCH Verlag GmbH&Co, 2008) Vol. 2, pp 713 – 741.
4. Anisimov S.I., Luk'yanchuk B.S. *Usp. Fiz. Nauk*, **172** (3), 301 (2002).
5. Shafeev G.A., in *Encyclopedia of Nanotechnology* (New York: Nova Sci. Publ. Inc., 2009) p. 991.
6. Jacobs I.S., Bean C.P., in *Magnetism* (New York: Acad. Press, 1963) Vol. 3, p. 271.
7. Gubin S.P., Koksharov Yu.A., Khomutov G.B., Yurkov G.Yu. *Usp. Khim.*, **74** (6), 539 (2005).
8. Amendola V., Riello P., Meneghetti M. *J. Phys. Chem. C*, **115**, 5140 (2011).
9. Creighton J.A., Eadon D.G. *Chem. J., Soc. Faraday Trans.*, **87** (24), 3881 (1991).
10. Alqudami A., Annapoorni S. *Plasmonics*, **25**, 13 (2007).
11. Viau G., Collière V., Lacroix L.-M., Shafeev G.A. *Chem. Phys. Lett.*, **501**, 419 (2011).