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Femtosecond laser synthesis of hybrid magnetic nanoparticles based on iron and gold with photothermal response

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The paper presents the results of femtosecond laser ablation synthesis of magnetite nanoparticles, hybrid nanoparticles based on iron and gold in deionized water. The average size of the resulting hybrid nanoparticles was 60 nm with inclusions of gold nanoparticles no larger than 10 nm on the surface. The results of scanning electron microscopy of the obtained nanoparticles, optical density curves and dependences of photothermal activity of solutions under irradiation with continuous laser radiation at 805 nm are presented.

Keywords: laser ablation, synthesis of iron nanoparticles, magnetic nanoparticles, hybrid nanoparticles, ultrashort lasers.

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1. Introduction

Currently hybrid nanoparticles (HPs) with magnetic and plasmon properties command great interest [1]. The main methods for synthesis of hybrid magnetic-plasmon materials are chemical methods. HPs synthesized in this manner may have various shape and structure, for example, nucleus-shell structure, nucleus-satellites, „Janus" HPs; HP configuration features in their turn provide substantial effect on magnetic and optical properties [2]. Combination of magnetic and plasmon properties makes it possible to consider such HPs as multifunctional materials, which may be used in various fields of biomedicine [2,3], used for magnetic spectroscopy of giant Raman scattering [4]. The common alternative for HP synthesis are the methods of femtosecond laser ablation and fragmentation in liquid medium [5,6], making it possible to also produce magnetic and photosensitized HPs, and their hybrid forms by simple and pure method [7–9]. Besides, by changing the medium and conditions of the experiment, it is possible to control the structure and properties of HPs.

2. Experiment

Nanomaterial synthesis experiments were carried out in a femtosecond laser system Yb:KGW (Avesta Ltd.), generating pulses with duration of 280 fs with repetition rate of 10 kHz at wavelength 1030 nm. The specimens used were volume targets from pure iron ($6 \times 10 \times 3$ mm, 99.99%) and gold ($8 \times 13 \times 0.7$ mm, 99.99%). The synthesis was carried out in several stages. For gold HP synthesis, a target was located in a tray filled with 10 ml of the prepared 1-mmol NaCl solution. Laser beam scanning on the target surface was carried out with the help of a Galvano scanner with pulse energy 30 μJ (energy flux density 3.055 J/cm^2), process duration 50 min. The solution was mixed in process of synthesis with the help of a magnetic mixer and anchor, the concentration of the produced colloidal solution was 0.125 mg/ml. Measurement of optical density of solutions was carried out in quartz trays with optical path length of 10 mm in the measurement range from 400 to 1000 nm using spectrophotometer SF-2000, spectral resolution 1 nm.

To select particles of the required size, the produced colloidal solutions of gold NPs were centrifuged at the relative centrifugal force of 9660 for 15 min. Upon completion of the process, the supernatant fluid was sampled, which was used in further experiments, with the total concentration of around 0.055 mg/ml.

For synthesis of hybrid nanomaterials, the laser ablation of the iron target was carried out directly in the colloidal solution of gold HPs produced in 1-mmol NaCl solution after the centrifuging stage. The process duration was 15 min with pulse energy 50 μJ (energy flux density 5.092 J/cm^2). No mixing was done in process of ablation. Separation into magnet and non-magnet HPs was carried out by the method of magnetic separation using a permanent magnet

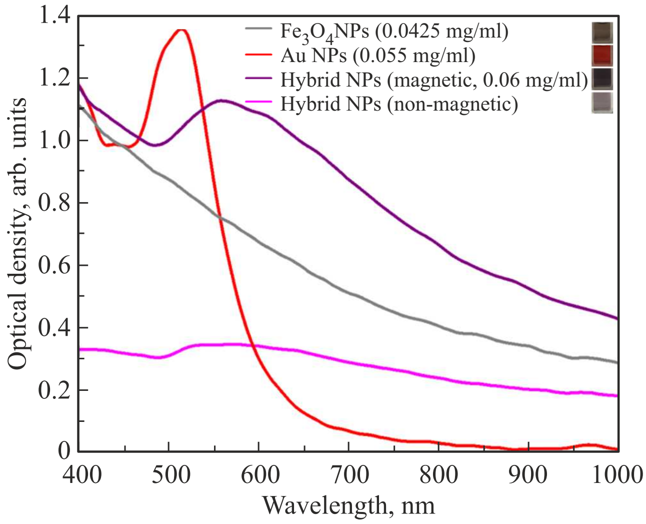

Figure 1. Curves of optical density of gold HP, magnetite HP solutions, and also solutions of hybrid HPs based on iron and gold.

with maximum magnetic field of 5000 G. In 5 min the supernatant fluid was sampled, and the HPs left on the bottom were resuspended in 10 ml 1-mmol NaCl solution, the process was repeated three times.

3. Results

In case of ablation of the iron target in the fluid medium not containing the gold HPs, synthesized NPs, further sampled using magnetic separation, were preferably magnetite (Fe_3O_4). Optical density curves of gold HP, magnetite HP solutions and also hybrid HPs based on iron and gold are presented in Figure 1, where the inserts show the photographs of these solutions (the concentration is shown in the figure).

In case of hybrid HPs based on iron and gold (concentration ~ 0.06 mg/ml) the red shift of the plasmon resonance position and its broadening compared to the curve of the optical density of magnetic HPs received as a result of laser ablation of iron in deionized water is observed. Due to configuration effects related to the surface plasmonic resonances, in the Au–Fe system, the amplification of the optical density of iron oxide is observed and, therefore, the increase of the optical density of the solution of hybrid HPs in the visible and infrared regions of the spectrum compared to the solution of magnetite HPs with concentration ~ 0.0425 mg/ml [10–12].

Morphology of synthesized NPs was studied by method of scanning electron microscopy (SEM) using microscope FEI Helios NanoLab 650; measurements were carried out with accelerating voltage of electron beam 5 kV. SEM-images of gold NPs produced by laser ablation method in deionized water with content of 1 mmol NaCl after the centrifuging stage, and also SEM-images of hybrid NPs based on iron and gold selected by means of magnetic separation are presented in Figure 2, *a* and *b* accordingly (inserts shown histograms of particle distribution by size).

The average size of gold NPs after the centrifuging stage is ~ 8 nm. Hybrid NPs based on iron and gold that were produced as a result of two-stage process of laser ablation and subsequent magnetic separation, are iron oxide NPs decorated with gold, which have magnetic and plasmon properties. The average size of hybrid NPs is ~ 60 nm, with presence of gold NPs (with specific size, not exceeding 10 nm) directly on the surface of larger NPs of iron oxide, the NP shape is spherical.

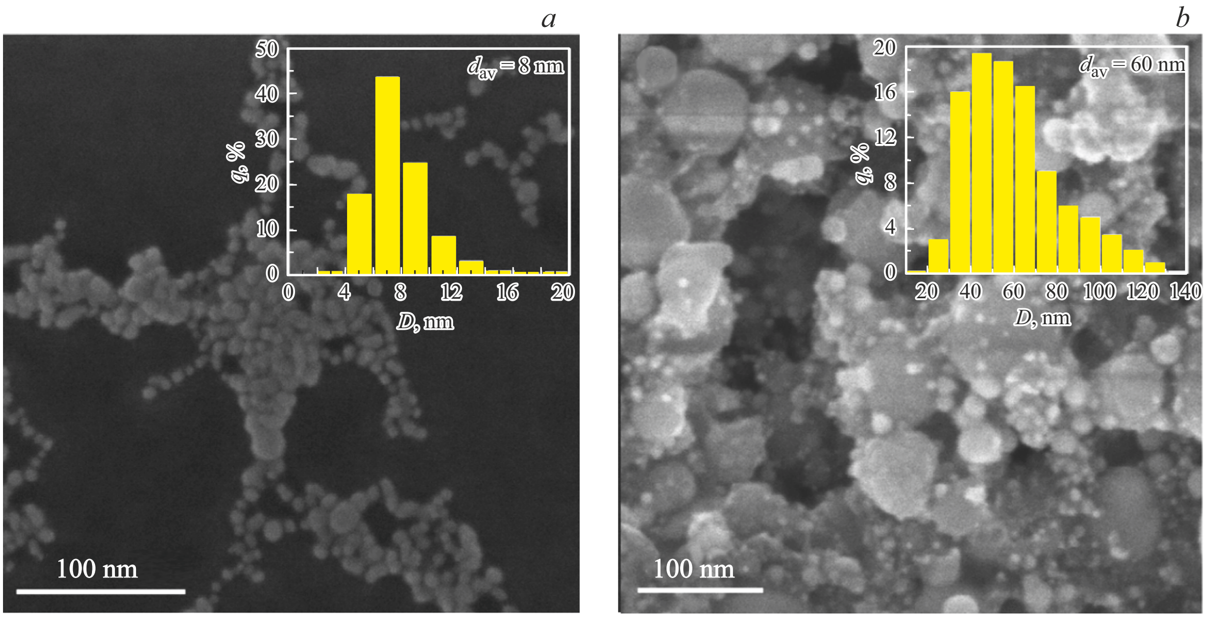

Figure 2. SEM-images: *a*) gold HPs; *b*) hybrid HPs based on iron and gold samples by magnetic separation.

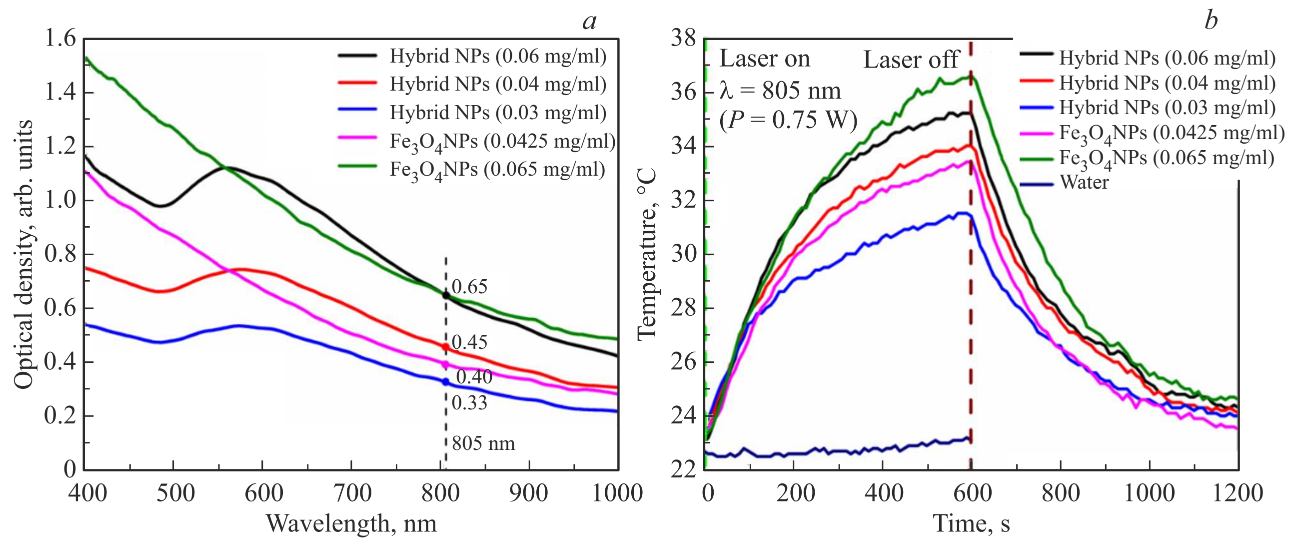

Figure 3. *a*) Curves of optical density of solutions with different concentration of magnetite NPs and hybrid NPs based on iron and gold; *b*) curves of temperature change dependence on irradiation time.

To study photothermal activity of synthesized NPs, a scheme was assembled, which includes continuous laser (wavelength 805 nm, maximum capacity 0.75 W, laser beam of rectangular shape, with dimensions $2 \cdot 6$ mm), thermal camera, and detector and meter. Duration of irradiation is 10 min, with subsequent cooling for 10 min. Measurements were performed every 10 s. Specimen temperature was measured under irradiation with the help of a thermal camera, besides, weakened laser beam capacity parameters were also recorded. Figure 3, *a* presents curves of optical density for two types of colloidal solutions of NPs (solutions of magnetic NPs of iron oxide (green and pink curve, concentration 0.065 and 0.0425 mg/ml accordingly) and solutions of hybrid NPs based on iron and gold oxide (black, red and blue curve, concentration 0.06, 0.04 and 0.03 mg/ml accordingly). Curves of temperature variation dependence on irradiation time in Figure 3, *b*, where the blue curve specifies the curve of temperature variation dependence on time for 1-mmol NaCl solution.

When the solution of hybrid NPs based on iron and gold with concentration of 0.06 mg/ml was irradiated, the temperature increased from 23 to 35.2°C (increase by 12.2°C), in case of concentration of 0.04 and 0.03 mg/ml, the temperature change was 10.6 and 7.9°C accordingly. Irradiation of magnetite NP solutions with concentration of 0.0425 and 0.065 mg/ml caused temperature increase by 10 and 13.4°C accordingly. At the same values of optical density (0.65) at wavelength 805 nm, the higher temperature value for the solution of hybrid NPs and solution of magnetite NPs with concentration 0.065 mg/ml was achieved in the second case.

4. Conclusion

As a result of a two-stage femtosecond laser synthesis, hybrid NPs based on iron and gold were produced that represent iron oxide nanoparticles decorated with gold, which have magnetic and plasmon properties. The used approach does not require chemical reagents, but provides for good reproducibility and high purity of NPs without ligands. The advantage of the produced NPs configuration is provision of the high specific area of gold and the possibility of further functionalization of the uncoated nucleus surface. Colloidal solutions of hybrid NPs demonstrated high photothermal response, and the paper conducted the comparison to the photothermal activity of magnetite NP solutions.

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Conflict of interest

The authors declare that they have no conflict of interest.

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