Pulsed laser co-deposition in air: a way of fabricating composite nanostructures

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Abstract. This work presents results of applying a method based on pulses laser co-deposition of a noble metal and a magnetic iron oxide for fabrication of ordered composite nanostructures. The experimental scheme includes two nanosecond laser beams with a wavelength of 1064 nm that ablate simultaneously two targets – Au and Fe3O4. The process is implemented in air – a condition that leads to a fast condensation of the ablated material into nanoparticles. By choosing different positioning of the ablation plumes and the substrate, composites of iron oxide nanoparticles decorated by noble metal ones can be fabricated. An external magnetic field applied close to the substrate orients and aligns the nanoparticles into chains. The effects of the processing parameters that define the geometry of the experiment are studied and presented. The method can be optimized for fabrication of complex composite nanostructures with applications in sensorics, optics and magneto-optics.

1. Introduction

The interest in structures with nanosized dimensions continues growing due to the unique properties that matter at this size domain expresses. These properties are related to both intrinsic effects – size-related changes in the volume and surface material properties, such as ionization potential, binding energies, chemical reactivity, structure, melting temperature, and discrete electron-energy levels structure – and to extrinsic effects, where size-dependent responses to external field (plasmon excitation, surface-phonon oscillations, phase retardation) can occur. From an application point of view, the high surface-to-volume ratio of the nanostructures results in specific properties that can be used in areas as sensor device fabrication and catalysis. The initial milestones of the nanotechnology were focused on the fabrication and properties characterization of passive nanostructures that includes nanosized coatings, nanoparticles, and nanostructured materials. The recent trends in the field are oriented to the study of more complex system of nanostructures – 3D networks and architectures [1]. Since the properties of nanostructured systems strongly depend on their geometry, orientation, internal inter-structures distances, environment and material characteristics, by controlling these characteristics one may obtain novel properties. It is shown, for example, for noble metal nanoparticle ensembles that the plasmon resonance, and respectively the optical properties, can be drastically influenced by the particle size, the interparticle distance, and the cluster orientation with respect to the incident electromagnetic field polarization [2, 3]. If, in addition, these ensembles have internal structural anisotropy, for example,
oriented non-spherical particles or oriented chains of particles, one may expect also anisotropic optical, magnetic and electrical properties that may lead to higher efficiency in their applications [4-7]. Although such structures may offer novel properties and improved performance, their study and applications are still hampered due to the lack of reliable fabrication methods. The physical and chemical ones developed so far [7] usually suffer from low productivity, use of costly systems and precursors, application of several steps, and inclusion of hazardous chemicals. Fabrication of oriented non-spherical nanoparticle ensembles can be achieved via bottom-up technologies that use different growth mechanisms [8-11], the use of patterned substrates as seeds, and complex deposition geometry. These structures are usually monolayer, while complex geometries can be produced [12]. The fabrication of ordered architectures of nanoparticles includes self-assembly methods and/or presence of external forces that control the particles ordering. Usually, the techniques for preparing such structures require a step where the nanoparticles are formed followed by additional interaction that leads to controlled particle aggregation. Among the developed methods, those based on laser ablation have shown promising results. Due to the specific features of the laser-matter interaction, the ablation process may lead to direct ejection of nanoparticles (as in the use of ultrashort laser pulses [13]) or their formation due to condensation of the plume in a surrounding gas [8]. It has been shown that the latter could be achieved in air at atmospheric pressure [14], which makes the technology easy to implement and can reduce the fabrication costs. The ablation in a gas phase at atmospheric pressure results in formation of nanoparticles and a rapid decrease in the velocity of expansion of the ablated material. This is an important condition when external manipulation of the formed particles is applied. Due to this effect, well oriented chains composed of magnetic nanoparticles can be formed when the ablation takes place in an external magnetic field [15].

In this work, we propose a further step toward fabrication of complex nanostructured materials using the process of laser ablation in air and in a magnetic field. In the method proposed, simultaneous ablation from two targets and a specific design of the experimental setup allow the fabrication of oriented chains of magnetic nanoparticles decorated with noble metal ones. As it is shown, the structures produced exhibit specific optical properties due to the plasmon resonance in the noble metal nanoparticles in the structure; on this basis, they can be used in the development of magneto-plasmonic devices.

2. Experimental
The method developed for fabrication of oriented chains of magnetic nanoparticles decorated with noble metal ones makes use of simultaneous laser ablation of two targets. Figure 1 presents the scheme of the experimental setup. The laser beam delivered from a nanosecond Nd:YAG laser system (LOTIS TII) operated at 1064 nm is equally split by a 50-% mirror; the two resulting beams are focused on two deferent targets. The estimated laser fluence on the targets is 4 J/cm² and is fixed in all experiments. The target used is made of Fe₂O₃ powder pressed and sintered at 900 °C. Our previous works demonstrated that the ablation of hematite in air leads to efficient production of nanoparticles composed mainly of magnetite [15]. A glass substrate and a permanent magnet behind it are placed in front of the hematite target at distance of 15 mm. The magnetic flux density at the target surface is 0.2 T. This part of the experimental setup is capable of producing nanoparticle chains due to ablation and condensation in the air environment followed by their orientation and deposition on the glass substrate [15]. At a certain distance from the hematite target, a Au (99.99 Sigma Aldrich) target is ablated. We introduced several parameters in this setup that affect the characteristics of the structure deposited on the surface. These are the height of the iron oxide ablation area with respect to the gold target surface (a), the distance between the ablation spots on the hematite and gold targets (b), and the distance between the hematite target and the substrate (c). All experiments were performed in air at atmospheric pressure.
3. Results and discussion

The ablation in air at atmospheric pressure ensures efficient ablation plume condensation and formation of nanoparticles. As an initial step of the experimental work, iron oxide nanoparticles were deposited in magnetic field without gold ablation in order to estimate the efficiency of oriented nanoparticle chains formation. Figure 2 is a SEM image of the structure deposited on the glass substrate for $a = 5$ mm and $c = 15$ mm for deposition time of 5 min and laser fluence of 4 J/cm$^2$. The deposited material consists of chains oriented parallel to the magnetic field lines and composed of nanoparticles with an average diameter of less than 50 nm. Since a fraction of the formed nanoparticles are ferromagnetic (magnetite), the external magnetic field induces a magnetic moment. The magnetic force action on the nanoparticles during their flight to the substrate results in their ordering into chains. These are further oriented by the external magnet in the direction of the magnetic field lines.

The crucial parameter for deposition of such structures is the distance between the target and the substrate (parameter $c$). As it is increased, the density of the deposited material decreases due to the decrease of the magnetic field intensity and, respectively, the attraction force that directs the ablated material to the substrate. On the other hand, in the configuration used, lower values of $c$ will cause a worsening of the structures due to the deposition of large droplets ejected in the ablation process and the direct deposition of Au, when experiments with the two targets are conducted. Since our goal here is to produce oriented chains of nanoparticles decorated by Au nanoparticles, the latter is also an undesirable effect.

In the configuration proposed, the simultaneous ablation of the two targets results in the formation of magnetic nanoparticle chains that, when passing through the Au ablation plume, are decorated by gold nanoparticles. A crucial parameter affecting the efficient mixing of the two plumes is the parameter $a$, since the air drastically confines the ablated material close to the target. Its role was estimated by depositing gold nanoparticles while varying this distance without ablating iron oxide. Figure 3 shows a SEM image of the nanoparticles deposited on a glass substrate placed parallel to the gold surface at a distance $a = 5$ mm. Their density gradually decreases with the increase of $a$, and at a distance of about 10 mm no deposition is observed with the available SEM resolution. A lower distance $a$ will ensure the appearance of big droplets into the plume that may collect the iron oxide material directed to the substrate or scatter it. On the basis of these estimates, the values of $a = 5$ mm and $c = 15$ mm were considered optimal for the experimental conditions used.
Figure 2. SEM image of the structure deposited on glass substrate for $a = 5$ mm, $c = 15$ mm, deposition time of 5 min and laser fluence of 4 J/cm$^2$.

Figure 3. SEM image of the material deposited on glass substrate placed parallel to the gold target at a distance $a = 5$ mm for deposition time of 5 min and laser fluence of 4 J/cm$^2$.

With these parameters, experiments were performed on the simultaneous ablation of the iron oxide and gold targets. Figure 4 presents transmission spectra of the structures obtained at different values of the parameter $b$. In the following discussion, it is assumed that the transmission value gives an approximate quantitative estimation of the amount of material deposited. The results indicate that at low values of $b$, namely 3 mm and 5 mm, the transmission of the sample is close to that of the bare substrate. The transmission is higher compared to the case when only iron oxide is ablated at $b = 5$ mm. These results indicate that at these values of the parameter $b$, the ablation of gold results in a lower amount of material deposited on the substrate. At a distance of 6 mm, the transmission values indicate deposition of more material and an appearance of a dip centered at about 570 nm, which can be attributed to the presence of Au nanoparticles in the deposited material. As is known, due to the efficient plasmon excitation in spherical gold nanoparticles, an increase of the absorption is observed with a center position in the spectral range of 520 – 600 nm depending on the particles size, their environment, and the inter-particle distance. Figure 5 shows a SEM image of the material deposited on the substrate under these deposition conditions. It consists of chains of nanoparticles with a certain orientation in the direction of the magnetic field. The degree of orientation, defined as the number of chains oriented in the direction of the magnetic force at angles lower than 20º, is smaller compared to the case of ablation of iron oxide only (figure 2).

Figure 4. Transmission spectra of structures obtained at different values of the parameter $b$. The other parameters are: $a = 5$ mm, $c = 15$ mm, deposition time of 5 min and laser fluence of 4 J/cm$^2$.

Figure 5. SEM image of a structure obtained at $a = 5$ mm, $b = 6$ mm, $c = 15$ mm, deposition time of 5 min and laser fluence of 4 J/cm$^2$. 
Figure 6 presents TEM images of material deposited under the same conditions, but on a Cu grid for direct analysis. The image in (a) indicates the presence of two components in the deposited material defined by the different contrast. The high-resolution images, (b) and (c) confirm that these phases are iron oxide (magnetite in this case) and gold, the gold being predominantly on the iron oxide particles. The SAED analysis performed shows that the ablation process also results in the formation of different phases of iron oxide – FeO, Fe$_2$O$_3$ – in addition to Fe$_3$O$_4$. Only the last one is ferromagnetic and contributes to the arrangement of chains and their orientation due to the external magnetic field.

Figure 6. TEM images of a structure obtained at $a = 5$ mm, $b = 6$ mm, $c = 15$ mm, deposition time of 5 min and laser fluence of 4 J/cm$^2$. (b) and (c) show high resolution images where the Au and Fe$_3$O$_4$ inter-plane distances can be recognized.

The effects observed need a more detailed study: however, one can assume that the expansion of the plume created by the ablation of gold distorts the flight dynamics of the iron oxide components. This can be related to the generation of a shock wave due to the explosive ejection of material in the ablation process [16, 17]. Furthermore, the motion of the ablated material in the air leads to development of vortices in the plume. These effects may induce efficient scattering of the material ablated from the iron oxide target and expel it from the area of strong magnetic field attraction.

It should be mentioned that a further increase of the parameter $b$ results in the direct deposition of Au on the substrate with the gold nanoparticles distributed randomly on the substrate surface rather than decorating the iron oxide ones, as seen in the case shown in figure 6.

The technique proposed can be optimized further by varying the laser processing parameters, namely, laser wavelength, laser fluence, deposition time, and by applying different fluences to the different targets. Such experiments are already under way.

4. Conclusions
We present a technique for fabrication of chains composed of magnetite nanoparticles decorated with gold nanoparticles. It is based on laser ablation in air in the presence of an external magnetic field and mixing the plumes from simultaneous ablation of two targets. Different parameters are found to influence the structure of the material deposited on the substrate. The optimal distance of the iron oxide target to the substrate and the relative position of the two plumes are defined. These conditions results in fabrication of a structure composed of chains of magnetite nanoparticles decorated with gold nanoparticles. The chains deposited on the substrate are oriented parallel to a certain degree to the magnetic force lines. The structures also express specific optical properties defined by the plasmon resonance in the gold nanoparticles. The process could be further optimized by varying the processing parameters with regard to forming more homogeneous structures. The structures thus fabricated could find applications in magneto-optical devices.

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