Nanosecond laser ablation of composite thin films in liquid

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Abstract. We present a study on nanosecond laser ablation of thin composite films immersed in
liquids. The composite films are obtained using a classical on-axis pulsed laser deposition
technology, where the target consists of two sectors with different composition. Multicomponent
films containing ZnO, TiO₂, and Ag, are thus deposited on a substrate. The as-prepared
composite films are then immersed in double distilled water and irradiated by nanosecond laser
pulses. This results in the production of colloids composed by multicomponent nanoparticles.
The optical properties of the colloids are evaluated by optical transmittance measurements in the
UV-VIS spectral range. Transmission electron microscopy is used to visualize the nanostructures
formed in the solution, as well as to evaluate their size distribution. The phase composition of
the samples is determined by selected area electron diffraction.

1. Introduction
Over the past two decades, the attention of researchers and technologists has been focused on the
synthesis of multicomponent nanomaterials with specific physicochemical and structural properties.
Among the various multicomponent nanomaterials, composite nanostructures based on metal oxides
stand out with their attractive properties allowing their use in many applications, for example:
photocatalysis, electrochemistry, biotechnology etc. [1-4]. Two of the most widely used metal oxides in
the nanotechnology are ZnO and TiO₂. Both metal-oxide semiconductors possess chemical stability,
efficient photocatalytic, optical, antibacterial, and gas sensing properties making them excellent
candidates for applications in environmental pollutant elimination, solar cells, gas sensors, electronic
and medical devices [5-8]. In addition to the composite nanostructures based on oxides, complex
multicomponent systems of the noble metal-semiconductor type showed great potential for use in
photocatalysis due to the special interface interaction. In turn, Ag is one of the most widely explored
nanomaterials, which stands out from other noble metals such as Pt, Pd and Au with its low cost, high
efficiency and easy preparation [9, 10]. Therefore, it is expected that combining the properties of Ag
NPs and those of a semiconductor such as ZnO would lead to a Ag-ZnO nanosystem with novel optical
electrical properties [11, 12].

So far, many techniques, such as sol-gel process [13], hydrothermal method [2], photo-reduction
[14], and thermal reduction [15], have been used for fabrication of composite NPs. An alternative to the
above methods is the nanosecond laser ablation in a liquid (LAL), a physical method that offers contamination-free nanomaterials, and inexpensive, fast and easy implementation [16, 17]. One of the biggest disadvantages of the LAL method is that in the process of ablation, in addition to NPs, submicron and even micron particles are ejected from the solid target [18]. This drawback can be overcome by using a thin film instead of a bulk target [19]. In this paper, we propose and apply a modified LAL method in a configuration that allows easy fabrication of colloidal multicomponent NPs. For this purpose, thin Ag-ZnO and TiO₂-ZnO composite films were previously deposited on glass substrates by the classical pulsed laser deposition (PLD) technique. Thus, the ablation of the deposited composite film in double distilled water would allow us to obtain chemically pure multicomponent colloidal NPs with potential use in biomedicine and sensorics.

2. Experimental
The synthesis of multicomponent colloidal nanostructures is performed in two successive steps which are shown schematically in figure 1. In the first one, composite thin films are deposited by the standard on-axis PLD technique. The third harmonic (355 nm) of a Q-switched Nd:YAG laser (pulse duration 15 ns, repetition rate 10 Hz) at a laser fluence of 2.5 J/cm² was used in the deposition process. The targets in the PLD experiments consist of two sections (with approximately the same area) of different materials. In this way, the rotation of the two-sector target leads to repeated successive deposition of layers of the two materials. Three different materials – Ag (polished plate, purity 99.99%), and sintered targets of ZnO and TiO₂ are used in the PLD experiments. Thus, Ag-ZnO and TiO₂-ZnO films were deposited on glass substrates in oxygen atmosphere at a pressure of 5 Pa for deposition time of 15 min and 20 min, respectively.

The second step consists of LAL of the deposited composite films. The as-prepared Ag-ZnO and TiO₂-ZnO films are immersed in double distilled water and exposed to irradiation by focused laser pulses of the same Nd: YAG laser. The third harmonic is used in the case of ablation of the Ag-ZnO film; and the fourth harmonic (266 nm), for ablation of the TiO₂-ZnO film. The laser fluence is fixed at 5.5 J/cm² in both cases. The duration of the ablation process is 8 min and the scanning of the surface of the sample is carried out by means of an XY translation stage. The nanostructures in the dried colloids were visualized by a transmission electron microscope (JEOL JEM 2100, accelerating voltage of 200 kV). In order to identify the phase composition of the colloidal nanostructures, selected area electron diffraction (SAED) measurements were performed. The optical properties of the obtained colloidal nanostructures were investigated by absorbance spectra measurements performed by a UV–Vis spectrometer (Ocean Optics HR 4000). The crystalline structure and phase composition of the multicomponent thin films were explored by an Empyrean diffractometer (PANalytical) by glancing (3°) incidence X-ray
diffraction (GIXRD) using CuKα radiation. The crystalline phases were identified using the PAN-ICSD and COD databases cards.

3. Results and discussion
An XRD pattern of the film deposited by successive ablation of ZnO and Ag targets is presented in figure 2 (a). As seen, the pattern could be indexed to a cubic structure of bulk Ag (ICSD 98-004-4387). The presence of ZnO in the film’s crystal structure is not evident. It is not surprising, since the experimental conditions used for film deposition—substrate at room temperature and a large amount of doping element (Ag), favour the deposition of ZnO in amorphous stage. Thus, the film structure represents an amorphous ZnO medium with a distributed crystalline phase of Ag.

![Figure 2](image2.png)

**Figure 2.** XRD spectra of Ag-ZnO (a) and TiO$_2$-ZnO (b) multicomponent thin films deposited on a glass substrate by PLD.

An XRD pattern of the film deposited by alternative ablation of ZnO and TiO$_2$ targets is shown in figure 2 (b). As seen, the film structure is amorphous. Again, given the experimental conditions chosen, one should not expect the growth of a crystalline film.

Figure 3 presents the TEM image and the corresponding size-distribution histogram of the NPs produced by laser ablation ($\lambda = 355$ nm, $F = 5.5$ J/cm$^2$, $t_{abl} = 8$ min) of Ag-ZnO film in water.

![Figure 3](image3.png)

**Figure 3.** TEM image and SAED pattern of nanostructures produced by laser ablation of Ag-ZnO thin film in water using laser wavelength of 355 nm and fluence of 5.5 J/cm$^2$. The size distribution of the formed nanostructures is also presented.

An XRD pattern of the film deposited by alternative ablation of ZnO and Ag targets is presented in figure 2 (a). As seen, the pattern could be indexed to a cubic structure of bulk Ag (ICSD 98-004-4387). The presence of ZnO in the film’s crystal structure is not evident. It is not surprising, since the experimental conditions used for film deposition—substrate at room temperature and a large amount of doping element (Ag), favour the deposition of ZnO in amorphous stage. Thus, the film structure represents an amorphous ZnO medium with a distributed crystalline phase of Ag.

formation of spherical and spherical-like shaped NPs with a relatively narrow size distribution is observed. The histogram of the particle size distribution reveals a mean particles size of 5.5 nm and a standard deviation of 2.6 nm. The inset in figure 3 next to the TEM image presents the corresponding
SAED pattern to reveal the composition of the nanostructures produced. The diffraction rings in the SAED pattern in figure 3 can be assigned to the (1 1 1), (2 0 0), (2 2 0), and (3 1 1) crystal planes of cubic Ag with lattice parameter \( a = 4.077 \) Å, PDF 87-0720, to the (1 0 1) and (1 0 3) crystal planes of the hexagonal ZnO \( (a = 3.253 \) Å, \( c = 5.213 \) Å, PDF 89-1397), and to the (2 1 1), (2 2 0), (0 2 2), and (0 4 0) crystal planes of the orthorhombic Zn(HO)\(_2\) \( (a = 5.160 \) Å, \( b = 8.530 \) Å, \( c = 4.920 \) Å, PDF 76-1778). The TEM image and size distribution of the NPs prepared by LAL of the TiO\(_2\)-ZnO film are shown in figure 4. The ablation parameters (laser fluence and duration of ablation) are the same as in the above case, except for the laser wavelength, which is 266 nm.

![Figure 4](image_url)

**Figure 4.** TEM image of nanostructures produced by laser ablation of TiO\(_2\)-ZnO thin film in water using laser wavelength of 266 nm and fluence of 5.5 J/cm\(^2\). The size distribution of the formed nanostructures is also presented.

The reason for using this wavelength is that the absorption of laser radiation by the composite TiO\(_2\)-ZnO film is more efficient compared to the absorption at 355 nm. Spherical NPs with a relatively wide size distribution (standard deviation of 6.5 nm) are visible (figure 4). The histogram of the size distribution reveals the presence of NPs with sizes up to 55 nm and a mean size of 11.5 nm. It should be noted that an SAED analysis was also performed on the nanostructures obtained by LAL of the TiO\(_2\)-ZnO film.

![Figure 5](image_url)

**Figure 5.** Optical absorption spectra of colloids produced by laser ablation of Ag-ZnO and TiO\(_2\)-ZnO composite films in water.

A characteristic halo ring pattern was observed in this case suggesting an amorphous material formation in the colloid. The corresponding SAED pattern is not shown here because it does not provide information about the phase composition of the formed NPs.

In what concerns the optical properties of the obtained colloids, we studied their optical absorbance spectra. Figure 5 shows absorbance spectra of the colloids produced by laser ablation of the Ag-ZnO and TiO\(_2\)-ZnO films in water. An absorbance peak with position at 400 nm is observed in the optical spectrum of the colloid obtained by ablation of the Ag-ZnO film. It is well known that pure Ag NPs exhibits surface plasmon resonance absorption around 400 nm [20]. In turn, the LAL of a thin TiO\(_2\)-ZnO film results in a transparent colloid in the visible spectral range. A strong
increase in the absorbance in the UV region (below 350 nm) is probably due to a superposition of characteristic band gap absorption of ZnO NPs [21] and of TiO$_2$ [22].

4. Conclusion
In this work, we present the basic characteristics of a method for synthesizing complex nanostructures in liquid media. The method is based on laser ablation in double distilled water of a multicomponent thin film, which is previously prepared by consecutive PLD of Ag-ZnO and TiO$_2$-ZnO layers on a glass substrate. The TEM analysis reveals that the ablation of the Ag-ZnO film leads to the formation of spherical and spherical-like NPs with sizes up to 20 nm (mean size of 5.5 nm). In turn, the ablation of the TiO$_2$-ZnO film in water leads to the formation of larger particles (up to 55 nm) with a mean size of 11.5 nm. The SAED analysis reveals the formation of Ag, ZnO and Zn(OH)$_2$ phases in the case of ablation of Ag-ZnO film in water. The SAED analysis indicated that amorphous nanostructures were formed in the case of ablation of the TiO$_2$-ZnO film in liquid.

Combining the capabilities of the PLD technique of producing samples of complex composition and structure with the flexibility of the LAL method in terms of choice of liquid medium, stabilizing agents and control of the laser parameters opens a new direction in the synthesis of new nanomaterials.

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