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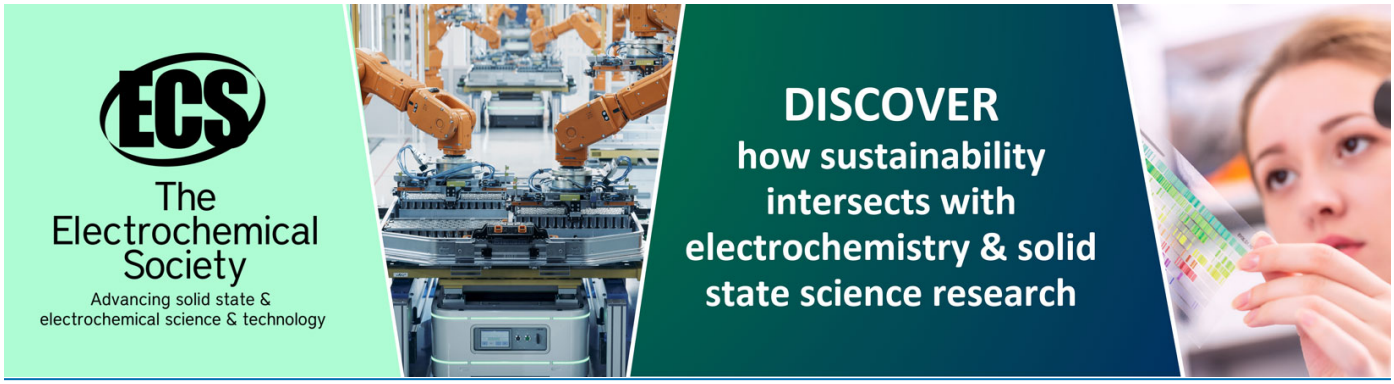

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Synthesis of bimetallic nanostructures by nanosecond laser ablation of multicomponent thin films in water

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Abstract. The paper presents results on nanosecond laser ablation of thin films immersed in a liquid. The thin films were prepared by consecutive deposition of layers of different metals by thermal evaporation (first layer) and classical on-axis pulsed laser deposition (second layer); Ni/Au, Ag/Au and Ni/Ag thin films were thus deposited on glass substrates. The as-prepared films were then placed at the bottom of a glass vessel filled with double distilled water and irradiated by nanosecond laser pulses delivered by a Nd:YAG laser system at $\lambda = 355$ nm. This resulted in the formation of colloids of the thin films' material. We also compared the processes of ablation of a bulk target and a thin film in the liquid by irradiating a Au target and a Au thin film by the same laser wavelength and fluence ($\lambda = 355$ nm, $F = 5$ J/cm^2). The optical properties of the colloids were evaluated by optical transmittance measurements in the UV–VIS spectral range. Transmission electron microscopy was employed to estimate the particles' size distribution.

1. Introduction

The synthesis of metallic and bimetallic nanoparticles (NPs) with controlled size, morphology, and composition attracts considerable interest from both the scientific community and the industry because of their unique physical and chemical properties [1–4]. A special interest has been devoted to the fabrication of multicomponent NPs consisting of noble and ferromagnetic metals with potential applications in catalysis, biophotonics and magneto-optics [5–7]. Ag/Co, Ag/Ni, and Au/Ni particles show well-expressed plasmon effects combined with magnetic properties [8]. In particular, the bimetallic NPs of Ag and Ni can be used as catalysts, electrical contacts, switches, electromagnetic wave absorbers, and in plating of conducting materials [9, 10]. Functionalized magnetic particles, such as Ni, Fe or magnetite can also be incorporated in Au-based NPs to enhance the efficiency and flexibility of drug treatment by applying an external magnetic field [11]. The position of the surface plasmon resonance (SPR) of NPs of Au/Ag alloys can be precisely tuned in a wide spectral range by varying the Au/Ag ratio. In [12], a linear dependence was reported of the position of the plasmon absorption maximum on the amount of one of the metals included. This effect can help in increasing the efficiency of the surface-enhanced Raman spectroscopy, the photothermal cell therapy, and the bio-imaging based on such nanostructures.

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The preparation of bimetallic NPs is based on different techniques; the most popular among them were reported in [13]: wet chemical synthesis, photochemical synthesis, sputter deposition, sonochemical synthesis, electroless plating, and electrochemical synthesis. However, these synthesis techniques usually involve several steps and require toxic reagents.

The method known as pulsed laser ablation of a target in liquid (PLAL) has emerged as one of the most interesting techniques of preparing nanostructures in a wide variety of liquids, since it is a simple, environmentally friendly, inexpensive and clean procedure [14-16]. Its most important advantage is the fact that the resulting colloidal NPs are chemically pure, containing elements of the target and the liquid only. A disadvantage of the PLAL method is the relatively broad size distribution of the NPs obtained compared to the NPs synthesized via chemical methods. However, it has been reported [17] that laser ablation of thin metal films could result in the formation of NPs with a narrow size distribution; i.e., this drawback can be overcome.

In the work presented, we applied laser ablation in a liquid in a configuration that allows easy fabrication of colloidal bimetal NPs. For this purpose, thin films were previously deposited on a glass substrate by consecutive deposition of two layers of different metals (Au, Ag and Ni). The first layer was deposited by thermal evaporation, a method characterized by fast and relatively easy implementation, allowing deposition of large surfaces. The second layer was deposited by the classical pulsed laser deposition (PLD) technique. It allows one to deposit films with different thickness by controlling the laser radiation parameters – number of pulses, laser fluence and wavelength. The multicomponent films produced were then immersed in double distilled water and irradiated by ь nanosecond Nd: YAG laser. In another experiment, we followed the influence of the film thickness on the morphology and size distribution of the NPs formed in the solution. For this purpose, laser ablation of a thin Au film and a Au target in water was performed under identical experimental conditions. The morphology, composition and optical properties of the colloidal NPs prepared were studied and discussed.

2. Experimental

The preparation of the colloidal metal and bimetallic NPs was carried out in two steps. In the first one, we prepared thin Au, Ni/Ag, Ni/Au, and Ag/Au films. The second step consisted in ablation of thin films in double distilled water, which resulted in the production of colloidal NPs. The multicomponent films preparation involved a consecutive deposition of two layers of different metals on glass substrates. The first layer was formed by thermal evaporation, and the second, by the classical on-axis PLD technique, using the third harmonic (355 nm) of a Nd:YAG laser (pulse duration 15 ns, repetition rate 10 Hz, fluence 1.5 J/cm^2. Both films were deposited in vacuum at an ambient pressure of about 10^{-3} Pa for six minutes. The thickness of the multicomponent films thus produced was measured by optical profilometer to be in the range of 160 ÷ 200 nm.

The thin-film samples were placed at the bottom of a glass vessel under 5 mm of double distilled water and ablated by the same Nd:YAG laser, whose third harmonic was focused on the metal film surface by a fused quartz lens and scanned by an XY stage for 5 min. The laser fluence was chosen to be 5 J/cm^2 to avoid optical breakdown in the liquid, which would drastically change the laser-target interaction and reduce the efficiency of the ablation process. The absorbance spectra of the colloids were recorded immediately by a UV–Vis spectrometer (Ocean Optics HR 4000) in the 300 – 900 nm range. The nanostructures in the dried colloids were visualized by a transmission electron microscope (JEOL JEM 2100, accelerating voltage of 200 kV).

3. Results and discussion

3.1. Laser ablation of bulk target and thin film

We first studied the influence of the film thickness on the size distribution of the NPs formed during laser ablation in water. We ablated a Au bulk target (purity of 99.99 %, thickness of ~1 mm) and a Au thin film (deposited by thermal evaporation, thickness of 120 nm) under the conditions described

above. The TEM images of the dried colloids are presented in figure 1, (a) and (b), with the particles size distribution histograms shown on the right-hand side. The predominantly spherical or spherical-like shape of the NPs is evident in both TEM images, which is typical of particles formed in a liquid environment [18]. The histogram of the size distribution of the particles obtained by ablation of the bulk target revealed a mean particles size of 7.2 nm, with a relatively high standard deviation of 5.7 nm. In the case of the thin Au film (figure 1-b), the mean size of the formed Au NPs was 4.1 nm and the standard deviation, 1.5 nm. Moreover, in the case of bulk target ablation, large particles with dimensions over 500 nm were also observed (*inset* in figure 1-a). Generally, the ablation of the thin film yielded NPs with a smaller mean size and a more uniform (narrower) size distribution compared to the NPs produced by ablation of a bulk target.

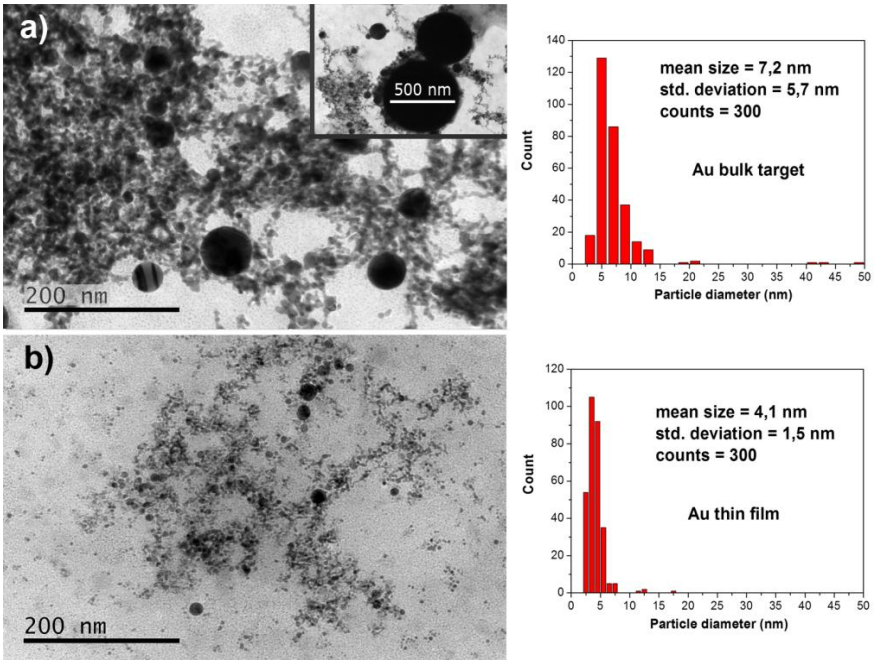

Figure 1. TEM images and corresponding histograms of the particles size distribution of Au nanoparticles produced by laser ablation of Au bulk target (a) and Au thin film (b) in water.

The optical absorption spectra of the colloids produced by ablation of the bulk target and the thin film are presented in figure 2. A single SPR band in the 500 – 600 nm range, characteristic of the presence of nanosized Au particles, is seen in both spectra. The slight red-shift and the higher intensity

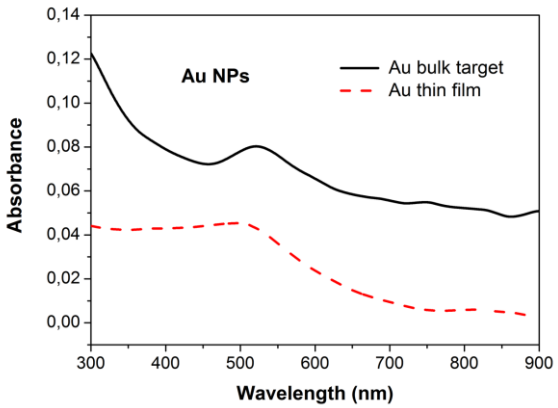

Figure 2. Optical absorption spectra of colloids produced by laser ablation of Au bulk target and Au thin film in water at laser wavelength of 355 nm and laser fluence of 5 J/cm^2.

of the SPR maximum in the spectrum of the colloid fabricated by ablation of the bulk target, compared to the thin-film case, could be attributed to the larger mean size of the NPs in the former case [19].

3.2. Laser ablation of multicomponent thin films

In this section we consider the laser ablation of multicomponent thin films of different metals. Figure 3 shows the TEM images and the corresponding size-distribution histograms of the NPs produced by laser ablation of Ni/Au (a), Ag/Au (b) and Ni/Ag (c) thin films in water. Formation of separated spherical and spheroidal shaped NPs with a relatively narrow size distribution is observed in the case of ablation of Ni/Au (top layer/bottom layer) thin film (figure 3-a). The histogram of the particle size distribution indicates a mean particles diameter of 3.8 nm and a standard deviation of 1.4 nm. In the case of Ag/Au thin-film ablation, besides spherical NPs, nanostructures with a chain-like shape (nanowires) are also observed (figure 3-b). The mean size of the spherical NPs and the particles forming the nanowires is 5.2 nm and the standard deviation is 2.1 nm. These elongated nanostructures are probably formed by joining of particles already created in the colloid. The laser wavelength used (355 nm) falls within the absorption band of the Ag and Au NPs. Thus, the absorption of laser radiation by the NPs may lead to partial melting of the particles' surface, whose melting temperature is significantly lower than that of the bulk material [20]. The shape of the particles in the case of ablation of the Ni/Ag thin film is predominantly spherical or spheroidal (figure 3-c). However, it should be noted that the larger particles have a rounded and asymmetrical shape, which is probably due to aggregation of smaller particles at a later stage, after the condensation of the plasma plume. According to the histograms, the mean particle size and the standard deviation are 19.4 nm and 16.1 nm, respectively.

The specific properties of the colloidal nanostructures prepared were explored by optical transmission measurements. Figure 4 shows the optical absorption spectra of the colloids produced by ablation of Ni/Au, Ag/Au and Ni/Ag thin films in water. It should be mentioned that the concentration of the particles in the colloidal solution is relatively low in all cases considered. A single plasmon band with a maximum located at 450 nm is observed in the spectrum of the NPs produced by ablation of the Ag/Au film. One should also bear in mind that the position of this SPR band falls in between those related to pure Au and Ag NPs [19]. This fact confirms the fabrication of bimetallic NPs [21] and the absence of monometallic Au and Ag NPs. Further, it is well known that the Ag/Au alloy phase is stable and can exist in a solid or liquid state. Therefore, Au-Ag alloy NPs are formed as a result of ablation of the bimetallic Ag/Au films. Two absorbance peaks with positions at 416 nm and 574 nm are observed in the optical spectrum of the colloid obtained by ablation of the Ni/Ag film. It is known that pure Ag NPs exhibits SPR absorption around 400 nm [19], while there is some controversy about the optical absorption of pure Ni NPs. Creighton et al. [22] have calculated the spectrum of Ni NPs and found a single SPR between 300 nm and 400 nm. In what concerns experimental works, Lee et al. have not reported any absorption band for Ni NPs [9]. However, Xiang et al. [23] and Carja et al. [24] have found absorption bands around 370 nm related to oxidized nickel nanoparticles, as well as a broad absorption band at 550–700 nm related to absorptions of nanostructures containing Ni^{2+} ions.

Nevertheless, the main reason for the appearance of an absorption band at 416 nm is excitation of SPR of Ag-containing NPs. The position of this band corresponds to the presence of NPs with sizes up to 60 nm in the solution [19]. The histogram in figure 3-c confirms that most of the NPs formed have such dimensions. The appearance of a second peak at 574 nm could be due to two factors: the presence of NPs with significantly larger sizes (over 80 nm) and particles with a shape deviating from spherical. Both statements are confirmed by the TEM image in figure 3-c. It thus appears that additional studies are necessary to clarify the nature and composition of the nanostructures obtained in the case of ablation of Ni/Ag thin films. In the optical absorption spectrum of the NPs produced by ablation of the Ni/Au thin film, a wide absorbance band with a maximum at 467 nm is seen. The position of this band is blue-shifted with respect to the SPR band of pure Au NPs. Similar shifting of

the SPR band of Au-containing NPs has already been seen in the spectrum of the nanostructures obtained by ablation of the Ag/Au film. The reason for this behavior could be the same, namely, formation of alloyed NPs, in this case Ni-Au. However, further research is necessary to confirm this statement.

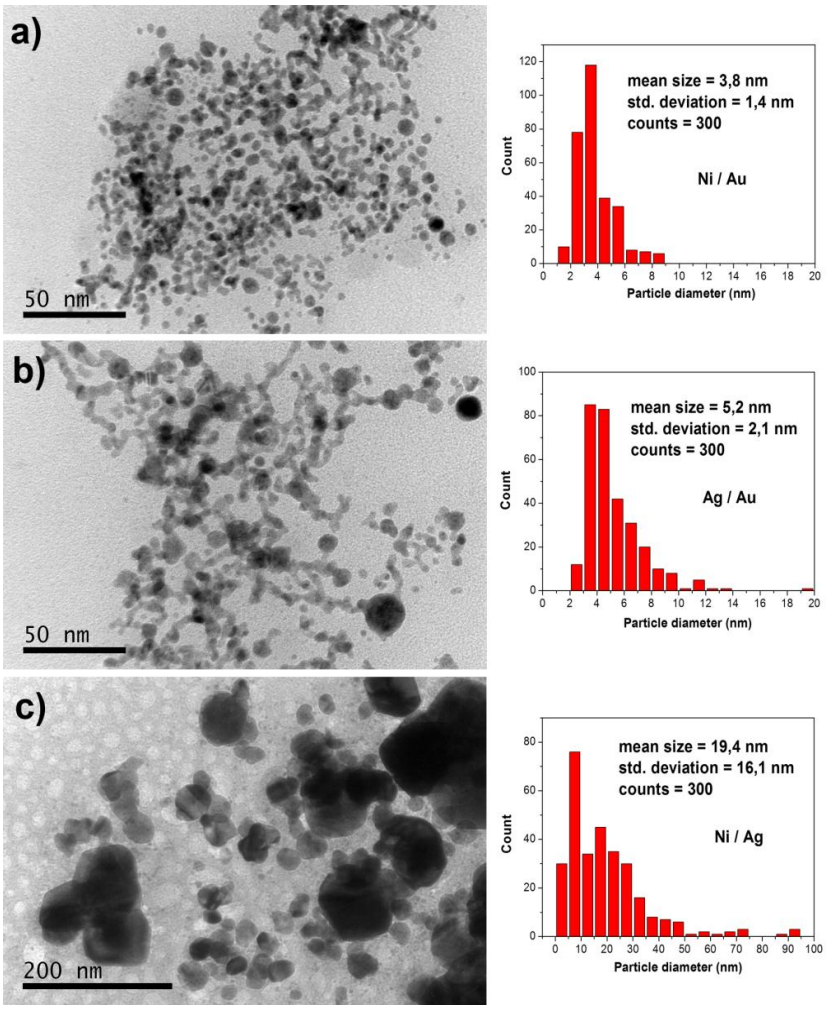

Figure 3. TEM images and corresponding size distribution histograms of nanoparticles produced by laser ablation in water of multicomponent thin films: Ni/Au (a), Ag/Au (b) and Ni/Ag (c). The ablation is performed by using laser wavelength of 355 nm and laser fluence of 5 J/cm^2.

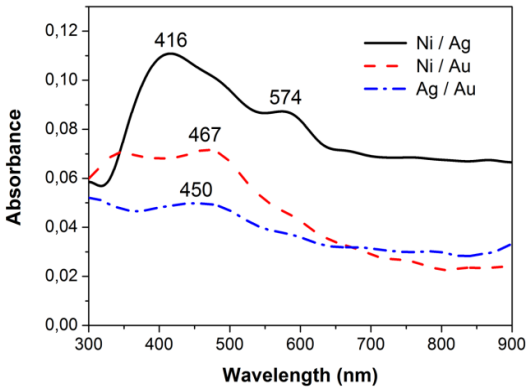

Figure 4. Optical absorption spectra of colloids produced by laser ablation of multicomponent (Ni/Ag, Ni/Au, and Ag/Au) thin films in water at the laser wavelength of 355 nm and laser fluence of 5 J/cm^2.

4. Conclusions

We presented the basic characteristics of a method for synthesizing multicomponent colloidal nanostructures. The method is based on laser ablation in double distilled water of a bimetallic thin film prepared by a consecutive deposition of layers from different metals by thermal evaporation and PLD on a glass substrate. TEM analysis reveals that the ablation of the Ag/Au film leads to the formation of both nanowires and spherical NPs, with their size ranging from 2 nm to 20 nm. The optical absorption spectrum of the colloid produced by ablation of the Ag/Au film reveals that the SPR maximum of the resulting NPs lies between the resonance maxima of pure Ag and Au NPs. This demonstrates that the NPs obtained are composed of both Au and Ag. In the case of Ni/Au thin-film ablation, spherical NPs with a relatively small size (up to 10 nm) are predominantly observed. In contrast, the ablation of the Ni/Ag film results in the formation of larger NPs with a broad size distribution and asymmetrical shape. Also, the Au thin-film ablation results in producing NPs with a more uniform size distribution compared to that of NPs formed by ablation of the corresponding bulk target. The method proposed appears to be an efficient alternative to the known methods of fabrication of bimetal NPs in solutions.

Acknowledgments

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