Abstract

Laser irradiation of a mixture of single element micro/nanomaterials may lead to their alloying and fabrication of multielement structures. In addition to the laser induced alloying of particulates in the form of micro/nanopowders in ambient atmosphere which forms the basis of the field of additive manufacturing technology another interesting problem is the laser induced alloying of a mixture of single element nanoparticles in liquids since this process may lead to the direct fabrication of alloyed nanoparticles colloidal solutions. In this work Ag and Pd bare, surface ligand-free nanoparticles in solution were prepared by laser ablation of the corresponding
bulk target materials separately in water, the two solutions were mixed and the mixed solution was laser irradiated for different time durations in order to investigate the laser induced nanoparticles alloying in liquid. Nanoparticles alloying and formation of AgPd alloyed nanoparticles takes place with the decrease of the intensity of the surface plasmon resonance peak of the Ag nanoparticles (at ~405 nm) with the irradiation time while the low wavelength interband absorption peaks of either Ag or Pd nanoparticles remain unaffected by the irradiation for times even as long as 30 mins. The alloyed nanoparticles have lattice constants with values between those of the pure metals which indicates that they consist of Ag and Pd in approximately 1:1 ratio similar to the atomic composition of the starting mixed nanoparticles solution. Formation of nanoparticle networks consisting of bimetallic alloyed nanoparticles and nanoparticles which remain as single elements even after the end of the irradiation, joining together, are also formed. The binding energies of the 3d core electrons of both Ag and Pd nanoparticles shift to lower energies with the irradiation time also a typical characteristic of AgPd alloyed nanoparticles.

*Keywords*: laser ablation; nanoparticles; nanoalloying

*PACS*: 78.67.Bf - Nanocrystals and nanoparticles; 79.20.Eb - Laser ablation; 81.05.Bx - Metals, semimetals, and alloys.

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1. Introduction.

Bimetallic nanoparticles, i.e. nanoparticles composed of two different metals are of wide scientific and research interest mainly because they exhibit properties which is a combination of the properties which nanoparticles of each metal exhibit separately and/or have better and unique properties not found in nanoparticles of each of the two metals [1]. These properties arise from both the structural and the electronic effects of the bimetallic nanoparticles through the alteration of the lattice constant of the individual metals and the vacancies in the valence orbitals of the electronic structure of the binary alloy nanoparticles, respectively. Throughout the years, bimetallic nanoparticles consisted of a number of different element combinations have been investigated.

An interesting system which finds wide applications in practice involves Ag-Pd bimetallic nanoparticles. This system combines Pd nanoparticles which are very important nanomaterials for utilization mainly as catalysts in different reactions [2] and in hydrogen storage and sensing applications [3], with Ag nanoparticles which are used as antimicrobial agents [4], plasmonic nanomaterials [5], in biosensing [6], catalysis [7] and other applications. Ag and Pd are completely miscible and Ag-Pd bimetallic nanoparticles are interesting for SERS, electrochemical biosensors [8], catalysts for the hydrogen production from formic acid decomposition and the fabrication of micro polymer electrolyte membrane fuel cells [9], electrodes in multilayer ceramic capacitors (MLCC) [10], widely tunable over the entire visible spectrum plasmonic nanostructures which also remain SERS active [11], as selective hydrogenation catalysts [12], as smart drug delivery systems in photothermal therapy and chemotherapy [13] and other applications.

Ag-Pd alloy nanoparticles in solution are traditionally synthesized by chemical methods involving the simultaneous reduction of Ag and Pd salts such as for instance AgNO₃ and K₂PdCl₆ using TritonX-100 as reducing agent and stabilizing ligand on the nanoparticles [14],
AgNO₃ and Pd(NO₃)₂ using PVP as stabilizing ligand and synthesizing Ag-Pd core-shell nanoparticles [15], AgNO₃ and PdCl₂ using aminosilane (N'-[3-(Trimethoxysilyl)propyl]diethylene triamine (TPDT)) as a supporting matrix and stabilizing ligand (the amino group (-NH₂)) of the nanoparticles [16] or palladium acetate and silver acetate using sodium dodecyl sulfate (SDS) as reducing agent and stabilizing ligand of the nanoparticles [17]. Addition of Na₂PdCl₄ in aqueous solution of Ag nanocubes resulted to their conversion to Ag-Pd nanoboxes due to the reduction of the salt onto the nanocubes' surfaces caused by the dissolution of Ag from their interior and AgCl reaction by-product (precipitate) was produced [18]. Ag-Pd nanoparticles were formed on substrates by the e-beam co-evaporation of the metals [19] while more recently Pd-rich Ag-Pd alloy nanoparticles were synthesized on substrates by the reduction of PdCl₂ and AgNO₃ salts in the micellar core of monolayer films of the diblock copolymer poly(styrene)-block-poly(4-vinylpyridine) (PS-b-P4VP) [20].

The method of laser ablation of a bulk single metal target material in liquid has been used so far in the investigation of nanoparticles alloying in liquids and synthesis of bimetallic alloy nanoparticles, on several occasions. This methodology usually involves three strategies [21]: (i) mixing nanoparticles colloidal solutions from each of the two metals which were initially prepared by laser ablating each target separately in liquid and subsequently laser irradiating the mixed solution. Examples include nanostructures which were prepared consisting of Au-Pt nanoparticles joined together (nanowebs) [22] or Au-Co nanoparticles [23], (ii) ablating one target material in the colloidal solution of nanoparticles of the other target which was previously prepared by ablating it separately in the liquid. Examples include bimetallic Ag-Au or Ag-Cu nanoparticles [24], or (iii) combining nanoparticles of one metal synthesized by laser ablation with a chemical precursor of the other metal. Examples include Ag-Pd core-shell nanoparticles which were synthesized by adding PdCl₂ precursor into the solution of Ag nanoparticles which were initially prepared by laser ablating the Ag bulk target in water [25]. The precursor was
reduced via galvanic displacement onto the surface of the Ag nanoparticles because of their negative surface charge induced by the laser ablation synthesis. PtCo alloy nanoparticles impeded in CoO\textsubscript{x} matrix were synthesized by laser ablating a Co target in potassium tetrachloroplatinate(II) (K\textsubscript{2}PtCl\textsubscript{4}) precursor solution [26]. Part of the Co seeding nanoparticles which were generated from the bulk target laser ablation reacted with Pt-based ionic species in the solution from the chemical precursor forming PtCo alloys while the seeding nanoparticles which are in excess were oxidized to CoO\textsubscript{x} finally forming PtCo/CoO\textsubscript{x} nanocomposites. For just the preparation of bimetallic alloy nanoparticles (excluding investigation of nanoparticles alloying in liquids), laser ablation of a bulk target material which is either a bimetallic alloy or a sintered mixture of powders of the two elements, has also been used [27,28].

The purpose of this paper is to investigate laser induced Ag and Pd nanoparticles alloying in liquid. In addition to the interesting physicochemical properties which bimetallic alloy nanoparticles of these two elements exhibit, outlined above, other reasons for investigating this system are that Pd and Ag are completely miscible elements over the entire composition range [29], they are in subsequent columns in the periodic table and have the same crystal structure (fcc) differing only in the value of the lattice constants and also Pd exhibits only an intraband transition in the UV range of the spectrum while Ag exhibits an intraband transition in the UV but also a Surface Plasmon Resonance (SPR) absorption in the visible range thus it would be interesting to investigate the effect of the alloying on the SPR absorption peak. Also the literature lacks data on the laser induced alloying in liquids of nanoparticles of this combination of elements.

2. Experimental Details.

Nanoparticles synthesis was performed by using a picosecond pulsed laser source (10 ps, 1064 nm, 100 kHz, 15 W (150 µJ, 40 J/cm\textsuperscript{2} assuming a beam diameter equal to ~22 µm)) and
Ag and Pd bulk targets (purity 99.9 %). Each target was first ablated for ~5 mins separately in 40 ml DI water in a steering liquid flow cell resulting to ~2 and ~18 mg of Ag and Pd nanoparticles respectively in the volume of the liquid. Then the Pd solution was diluted to the same atomic concentration with the Ag solution and equal amounts from each solution were mixed and irradiated in a cuvette by using the same laser parameters, under magnetic stirring, for different time durations between 0 and 30 mins. An experimental configuration for the irradiation of the mixed nanoparticles colloidal solution was used, similar to the ones in ref. [30] and [22] but using a rectangular cuvette (flat walls) with the beam incident horizontally, irradiating the solution from the side of the cuvette and focused at the middle of the liquid volume. The UV-vis absorption spectrum of the mixed solution was measured after each irradiation. In order to investigate the effect of the irradiation in the nanoparticles of each metal separately, colloidal solutions from each metal were irradiated for the same time durations and the UV-vis absorption spectra were measured. The nanoparticles sizes/size distribution, morphology of the bimetallic structures and crystal lattice were imaged by TEM/HRTEM from solution droplets dried out on carbon coated copper grids immediately after irradiation. The effect of the formation of the bimetallic alloyed nanoparticles in the crystal structure was investigated by X-Ray Diffraction (XRD) using a diffractometer with a Cu K$_\alpha$ source ($\lambda=1.5406$ Å) and in the band structure by X-Ray Photoelectron Spectroscopy (XPS) using a spectrometer with Al K$_\alpha$ primary radiation (1486.6 eV) at a pass energy of 40 eV for high resolution scans and 160 eV for survey scans, from solution droplets dried out onto clean glass substrates. Crystal structures were determined from the XRD patterns using the software of the instrument (DiffracPlus EVA).

3. Results and Discussion.
The UV-vis absorption spectrum from pure Pd nanoparticles (Fig. 1(a)) is characterized by a broad band peaked at ~218 nm which is due to superposition of interband transitions rather than to any SPR transition [31]. The absorption spectrum from pure Ag nanoparticles (Fig. 1(b)) is characterized by a SPR absorption peak at ~405 nm and a broad interband transition band peaked at ~270 nm [32,31]. Upon laser irradiation of the mixed nanoparticles colloidal solution, it is observed that the SPR absorption peak from Ag decreases in intensity and shifts slightly to smaller wavelengths while the interband absorption peaks from both metals remain almost unaffected by the irradiation (Fig. 1(c)). This effect has been observed previously during the synthesis of bimetallic nanoparticles consisting of Pd and of a plasmonic metal such as Ag or Au and it was attributed to the blocking of the SPR absorption of the plasmonic metal by the Pd atoms which are added on its surface (adatoms) and to the gradual increase of the surface coverage of Ag nanoparticles by the Pd adatoms as the irradiation time increases. Examples include the case of Au nanoparticles decorated by Pd atoms by a chemically epitaxial seeded growth method in which the SPR absorption peak of Au nanoparticles (at 509 nm) was decreasing in intensity with the increase of the Pd: Au ratio [33] and the synthesis of Ag-Pd bimetallic nanoparticles by the reduction by a galvanic replacement reaction of PdCl₂ precursor on the surface of laser ablation generated Ag nanoparticles where the intensity of the Ag SPR absorption peak was reduced with the amount of precursor in the solution [25]. At the present experiment, formation of bimetallic alloy nanoparticles takes place (as it will also be shown below from other measurements) and the decrease of the SPR of the Ag nanoparticles is due to the surface Pd atoms on the bimetallic AgPd nanoparticles (which it will be shown that they also contain inclusions of pure Ag or Ag-oxides) while the decrease of the intensity of the SPR peak with the irradiation time is due to gradual increase of the number of Ag nanoparticles which have formed alloy with Pd. Fig. 1 (b) shows the absorption spectra from the pure Ag nanoparticles solution, irradiated for different time durations up to 20 mins. Initially for irradiation times up to
5 mins the SPR peak becomes stronger in intensity and narrower due to the fragmentation by the laser beam of large nanoparticles and aggregates which results to the narrowing of the nanoparticles size distribution [30]. As the irradiation time becomes longer the SPR peak decreases in intensity due to the starting of the decomposition of the silver nanoparticles and conversion to silver ions but for times even as long as 20 mins the SPR peak is still observed which indicates that even such a long irradiation time does not lead to the complete decomposition of the nanoparticles. It is also seen that the interband transition peak of Pd nanoparticles of the pure solution remains unaffected by the irradiation for the same length of time of 20 mins (Fig.1(a)). These both observations confirm that the decrease with the irradiation time of the SPR peak from Ag nanoparticles in the mixed solution and its almost complete disappearance for the longest time duration used (of 4 mins) is not due to the decomposition of the nanoparticles of either element by the laser beam but rather to their alloying.

XRD patterns from pure Pd (Fig. 2(a)) or Ag (Fig. 2(b)) nanoparticles show all peaks corresponding to Pd or Ag metal, respectively [34]. In the pattern from the Ag nanoparticles another peak at 32.231° appears which corresponds to AgO [34]. In a previous work involving also the synthesis of nanoparticles of Ag by laser ablation of the bulk target material in DI water [35], Ag2O3 was observed in the nanoparticles ensemble in addition to pure Ag. Formation of silver oxide nanoparticles is due to the interaction of the silver plasma plume ablation products (silver atoms or ions) with the oxygen atoms or radicals from the water decomposition and the type of oxide which is formed depends mainly on the oxygen partial pressure and the plume temperature [36]. AgO is formed at low oxygen partial pressures and it is stable at a wider temperature range while at higher pressures Ag3O4 is formed followed by Ag2O3. The absence from the ablation products here of higher valency silver oxides (Ag3O4 or Ag2O3), might indicate that the plasma plume pressure during material's ablation was lower at the present case as in the previous experiments because of the different experimental parameters and conditions such as
laser beam fluence (one order of magnitude higher than previously), pulse overlap, ablation time duration, level of liquid above the target surface, liquid temperature or by carrying out the ablation in a moving than in a stationary liquid (liquid volumetric flow rate), all of which critically determine the pressure and temperature conditions of the ablation plume [37,38]. The XRD pattern from the as mixed (un-irradiated) sample (Fig. 2(c)) shows the peaks from Pd and Ag pure metal. Peaks from any silver oxide are not distinguished in the pattern most probably because of the low material quantity and lower count rate (maximum of ~3000) as compared to the pattern for the pure Ag sample (maximum of ~10000) (Fig. 2(b)). Indeed from the intensity of the AgO peak in the pattern from the pure Ag nanoparticles sample it seems that the percentage concentration of the silver oxides in the original sample is quite small and this percentage becomes even smaller in the as mixed sample due to the lower quantity of the original Ag solution in the mixture. The XRD patterns from the irradiated samples are shown in Fig. 2 (d) (4 mins) and 2 (e) (20 mins). It is readily seen that peaks from pure Pd metal are not observed in the patterns but instead strong peaks appear at angles between the angles corresponding to peaks from pure Ag or pure Pd nanoparticles and their relative intensities ratio is approximately the same as the intensities ratio of the peaks from the pure metals. These peaks correspond to Ag-Pd bimetallic alloy nanoparticles with lattice constants between the constants of the pure metals (Table 1) [39,40]. According to Vegard's law [41], the lattice constant \( d_{Ag_1-xPd_x} \) of the dilute alloy \( Ag_{1-x}Pd_x \) is given by the relation: 

\[
(1 - x) \cdot d_{Ag} + x \cdot d_{Pd},
\]

where \( d_{Ag} \) and \( d_{Pd} \) are the lattice constants of the pure metals and \( x \) is the molar fraction of Pd in the alloy. From the measured values of the lattice constants (for the (111) reflection) for the pure metal and alloy nanoparticles (Fig. 2(a)-(e)) according to the above relation, the molar fraction of the two elements in the binary alloy nanoparticles are determined as: \( Ag_{0.46}Pd_{0.54} \) and \( Ag_{0.44}Pd_{0.56} \) for the 4 and 20 mins (irradiated) samples, respectively. Weak peaks appear from pure Ag nanoparticles corresponding to nanoparticles which remained as pure even after the end of the
irradiation - have not formed alloy with Pd (Fig. 2(d) and (e)). Peaks corresponding to silver oxides are also distinguished in the patterns most probably due to the secondary ablation of the Ag or AgO nanoparticles in the original solution (which takes place at the high fluence used), formation of plasma plumes and interaction again of the plume species with the oxygen species from the water thermolysis [42]. Due to the large variation of nanoparticles diameters, ablation of the nanoparticles themselves contrary to ablation of a bulk material results in a large range of values for the pressure and temperature of the formed plasma plumes mainly due to the dependence of the absorbed laser energy by the nanoparticle's diameter [43] and thus to the formation of different oxides in the same nanoparticles ensemble, ranging from the AgO for low pressures to the Ag$_3$O$_4$ and Ag$_2$O$_3$ for higher pressures.

Low magnification TEM images of the original Pd and Ag nanoparticles are shown in Fig. 3 (a) and (b) (and also in Fig. S1) and of the AgPd as mixed and irradiated for 2, 4 and 30 mins nanoparticles in Fig. 4 (a)-(d) (and also in Fig. S2). It is seen that the original nanoparticles are almost perfectly spherical. The size distribution histograms of the nanoparticles by counting approximately 400 nanoparticles in images of nanoparticles ensembles obtained on different areas on each grid, are shown in Fig. 3 (c), (d) and Fig. 4 (e)-(h). The histograms are described quite well by log-normal functions with median diameters of $<d_0>$=3.8 and 3.5 nm and standard deviations of $\sigma$=0.61 and 0.45 for the Pd and Ag nanoparticles, respectively and $<d_0>$= 3.9, 7, 7 and 5 nm and standard deviations of $\sigma$=0.74, 0.53, 0.49 and 0.55 for the AgPd as mixed, 2, 4 and 30 mins irradiated, respectively.

Formation of the bimetallic alloy nanoparticles upon irradiation of the mixed solution is confirmed by elemental mapping TEM images shown in Figs. 5 and 6 (and also in Figs. S3 and S4). In the images of the as mixed un-irradiated nanoparticles (Fig. 5) it is seen that each nanoparticle consists of only one of the two elements, either Pd or Ag. In the irradiated solutions (Fig. 6 and Fig. S3, S4) it is seen that most of the nanoparticles consist of both elements Ag and Pd.
and thus they are bimetallic but there are also a few nanoparticles in the ensemble which are one of the two elements-rich or they consist of only of that element, for every irradiation time duration used. In the bimetallic nanoparticles both elements appear to be distributed quite uniformly over the whole nanoparticle. Furthermore, EDX analysis on a number of nanoparticles also with different diameters (Fig. S5 and Table S1) provides with average values of the atomic percentage composition for the two elements, Pd and Ag in the nanoparticles ensemble very close to the ones determined from the analysis of the XRD patterns using Vegard's law. There is no dependence of the ratio of the composition of the two elements on the nanoparticle's diameter but it rather varies randomly (plot near Table S1). While in the uniradiated sample the nanoparticles appear isolated to each other (Fig. 4 (a) and S2), in the irradiated samples there is a large number of single element or bimetallic nanoparticles which appear joining together (Fig. 4(b), 7, S6-S9) (examples are marked with arrows in the figures). On a few occasions more than two nanoparticles are joining together forming large globes which sometimes have irregular shape (Fig. S8 (b)).

HRTEM images are shown in Fig. 8 (and also in Fig. S10 and S11). The images show a few typical combinations of joined together nanoparticles such as for instance AgPd nanoparticles joined with other AgPd and Ag-oxide nanoparticles (example are the four nanoparticles at the bottom left hand side of the image in Fig. 8), nanoparticles which consist of AgPd, Ag and Ag-oxides but also from pure Pd joined with Ag nanoparticles (example is the two large diameter nanoparticles at the bottom right hand side of the image in Fig. 8) or other material combinations. Occasionally but very rarely, nanoparticles which are of pure Pd are distinguished in the images and these are nanoparticles which remain as pure Pd even after the end of irradiation. They are at a very low percentage (estimated to ~1 %) and do not produce any signal in the XRD patterns because their concentration in the nanoparticles ensemble is below the detection limit of the instrument.
Initial studies on laser irradiation induced alloying of nanoparticles in water conducted many years ago [22,23], suggested that formation of joined together nanoparticles results from the melting by the laser beam of the original nanoparticles in solution and sticking together which occurs at the same time as the irradiation of the solution takes place. However recently, based on laser induced nanoparticles fragmentation experiments in liquids, it was suggested that laser irradiation of the original nanoparticles solution results only to the photo-fragmentation of the nanoparticles and conversion to a large number of smaller size nanoparticles while formation of structures consisted of nanoparticles joining together takes place after the end of the irradiation in a process of unidirectional coalescence and reorganization of the fragments [44]. This conclusion was based on the fact that nanoparticles networks were not observed, but only smaller size nanoparticles, upon laser irradiation of the nanoparticles in solution in the presence of thiolated polyethylene glycol (PEG) in excess [44]. A similar observation was also made in the case of nanoparticles in sodium dodecyl sulfate (SDS) surfactant solution with concentration above the critical SDS concentration for micelle formation while nanoparticles "wires" were formed in less concentrated solution [45]. However in that work the band at high wavelengths characteristic of the formation of nanoparticles "wires" was also observed to increase in intensity with the number of laser "shots", an observation which supports the mechanism of the formation of the "wires" during laser irradiation, instead. According to the well studied mechanisms of the laser induced nanoparticle fragmentation in liquids [42], laser irradiation of the mixed single elements nanoparticles solution at such a high fluence used at the present experiments leads to the surface vaporization and Coulomb explosion of the nanoparticles with both mechanisms taking place at the same time. Surface vaporization causes ablation of the nanoparticles with the formation of plasma plume, mixing of the plasma plumes from each element, alloying in the vapour phase and formation of bimetallic alloy nanoparticles. Coulomb explosion results to the fission of the nanoparticles and formation of smaller nanoparticles either of the original single
element nanoparticles or of the already formed bimetallic alloy nanoparticles because of the secondary irradiation by the laser beam after their formation. Then nanoparticles joining together and formation of aggregates takes place. The effect of the irradiation on each nanoparticle may largely varies due also to their relatively wide size distribution and the scattering of the beam by the nanoparticles resulting to all mechanisms taking place at the same time and to all type of nanoparticles, single element or bimetallic alloy ones participating in the process.

XPS spectra from the nanoparticles on the glass substrates are shown in Fig. 9 and 10. All spectra are referenced to the C 1s line at 285 eV. The Ag 3d peaks in the as mixed sample appear at the same energies as in the Ag pure original sample (Fig. 9 (a1)) (368.1 and 374.1 eV for the Ag 3d$_{5/2}$ and Ag 3d$_{3/2}$ orbitals, respectively). However in the irradiated samples these peaks shift to lower binding energies and appear at: 367.6, 373.6 eV and 367.9, 374 eV for the 4 and 20 mins irradiated sample, respectively (Fig. 9 (a2)). A shift of ~0.4 eV for the Ag 3d$_{5/2}$ line is consistent with measurements of core level binding energy shifts in dilute PdAg alloys reported previously [46]. Similarly the Pd 3d peaks in the as mixed sample appear at the same energies as in the Pd pure original sample (Fig. 10 (a1)) (335.2 and 340.6 eV for the Pd 3d$_{5/2}$ and Pd 3d$_{3/2}$ orbitals, respectively) while in the irradiated samples these peaks shift to lower binding energies and appear at: 334.7, 340 eV and 335.1, 340.5 eV for the 4 and 20 mins irradiated sample, respectively (Fig. 10 (a2)) [47]. The smaller energy shift which is observed for the longer time (20 mins) irradiated sample as compared to the 4 mins one, might be because of the smaller size of the nanoparticles of this sample (histograms in Fig. 4 (e)-(h)) due to the dependence of the binding energy on the nanoparticle's size. It has been observed that the 3d core level peaks shift to higher binding energies in nanoparticles compared to the bulk material with an amount which increases with the decrease of the nanoparticles size [48,49]. Thus the shift to lower binding energies of the peaks of the longer time irradiated sample due to alloying effect might be compensated by a shift to higher energies because of the smaller size of the nanoparticles for this
sample resulting to a total shift by an amount smaller than for the shorter time irradiated sample. The shifts of the Ag 3d and Pd 3d peaks to lower binding energies in the irradiated samples is due to the interaction of the two metals in the AgPd alloy in which a charge transfer occurs and both elements gain d electrons and lose non-d electrons a phenomenon which was explained by Abrikosov et al. in terms of an intra-atomic charge re-distribution due to valence electron hybridization [50]. It is typical of the formation of a AgPd alloy and it confirms here once again the formation of AgPd bimetallic alloys nanoparticles [39,51,52]. Note that the band at 345 eV is characteristic of the absence of hydrogen in the lattice of Pd and it indicates the formation of pure Pd nanoparticles upon ablation of the bulk target material in DI water rather than PdHx, in consistency with what has been observed previously [53].


Laser irradiation of mixed single element nanoparticles colloidal solutions offers an alternative method for the synthesis of bimetallic alloy nanoparticles which have the same properties with similar nanoparticles which are synthesized by other methodologies such as for instance laser ablation of bimetallic targets in liquids [21]. In addition, it might be a preferred method for the synthesis of bimetallic nanoparticles for which the bimetallic bulk target is expensive and difficult to be manufactured. The original single element nanoparticles were also produced by laser ablation of the corresponding bulk targets in water and thus the nanoparticles have bare, ligand-free surfaces which is advantageous for the investigation of the laser induced bimetallic nanoalloys formation in liquids and the method can also be used for the fabrication of higher order structures such as nanowires (by joined together nanoparticles) which may find application in different fields in nanotechnology or nanosciences. In this work laser induced alloying of nanoparticles of an important plasmonic metal such as Ag with nanoparticles of a non-plasmonic metal such as Pd, was demonstrated and investigated. Alloy formation clearly
manifests itself with the decrease of the intensity of the SPR absorption peak of Ag with the irradiation time, a lattice constant of the irradiated nanoparticles which has a value in between those of the pure metals and a red shift of the binding energy of the Ag and Pd 3d electrons.
References


[34] JCPDS No. 089-4897 (Pd); JPCDS No. 4-783 (Ag); JCPDS No. 89-3081 (AgO); JCPDS No. 40-1054 (Ag₂O₄); JCPDS No. 40-909 (Ag₂O₃).


Table 1. Lattice constants of the original Ag and Pd and of the alloyed Ag-Pd nanoparticles determined from the XRD patterns (Fig. 2).

<table>
<thead>
<tr>
<th>sample</th>
<th>d (Å)</th>
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<tr>
<td></td>
<td>(111)</td>
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<tr>
<td>Ag</td>
<td>2.359</td>
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<tr>
<td>Pd</td>
<td>2.241</td>
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<td>Ag-Pd (4 mins)</td>
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<tr>
<td>Ag-Pd (20 mins)</td>
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FIGURE CAPTIONS

FIG. 1. UV-vis absorption spectra measured from the nanoparticles colloidal solutions for different irradiation times (in minutes). Pd (a) and Ag (b) original nanoparticles solutions and Ag/Pd (c) mixed nanoparticles solution.

FIG. 2. XRD patterns of the nanoparticles.

FIG. 3. TEM images and corresponding size distribution histograms of the original Pd (a) and (c) and Ag (b) and (d) nanoparticles.

FIG. 4. TEM images and corresponding size distribution histograms of the nanoparticles in the as mixed (unirradiated) solution (a) and (e) and in the solutions irradiated for 2 (b) and (f), 4 (c) and (g), and 30 (d) and (h) mins.

FIG. 5. Elemental mapping images of the as mixed (unirradiated) nanoparticles.

FIG. 6. Elemental mapping images of the irradiated nanoparticles (2 mins).

FIG. 7. TEM image showing examples of joined together nanoparticles (2 mins irradiated).

FIG. 8. HRTEM image of irradiated nanoparticles (4 mins).

FIG. 9. XPS spectra from the nanoparticles in the Ag 3d region.

FIG. 10. XPS spectra from the nanoparticles in the Pd 3d region.
Fig. 1
Fig. 2
Fig. 3

- **Pd**
  - \( \langle d \rangle = 3.8 \text{ nm} \)
  - \( \sigma = 0.61 \)

- **Ag**
  - \( \langle d \rangle = 3.5 \text{ nm} \)
  - \( \sigma = 0.45 \)
AgPd as mixed
\(<d>=3.9\ \text{nm}\)
\(\sigma=0.74\)

AgPd 2 mins
\(<d>=7\ \text{nm}\)
\(\sigma=0.53\)

AgPd 4 mins
\(<d>=7\ \text{nm}\)
\(\sigma=0.49\)

AgPd 30 mins
\(<d>=5\ \text{nm}\)
\(\sigma=0.55\)
Fig. 5
Fig. 6
Fig. 8
Fig. 9
Fig. 10

![Graph showing intensity (cps) vs. binding energy (eV) for different samples: AgPd, as mixed, Pd, AgPd, 4 mins, AgPd, 20 mins.](image)
Supplementary Material

NANOPARTICLES ALLOYING IN LIQUIDS: LASER ABLATION
GENERATED Ag OR Pd NANOPARTICLES AND LASER IRRADIATION
INDUCED Ag-Pd NANOPARTICLES ALLOYING

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FIG. S1. TEM images of the original Pd (a) and Ag (b) nanoparticles.
FIG. S2. TEM images of the as mixed (unirradiated) nanoparticles.
FIG. S3. Elemental mapping images of the irradiated nanoparticles (4 mins).
FIG. S4. Elemental mapping images of the irradiated nanoparticles (30 mins).
FIG. S5. EDX analysis of the nanoparticles (2 mins irradiated).
FIG. S6. TEM image showing examples of joined together nanoparticles (2 mins irradiated).
FIG. S7. TEM image showing examples of joined together nanoparticles (2 mins irradiated).

The black arrows mark the regions where atom clusters are observed.
FIG. S8. TEM images showing examples of joined together nanoparticles (4 mins irradiated).
FIG. S9. TEM image showing examples of joined together nanoparticles (30 mins irradiated).
FIG. S10. HRTEM image of irradiated nanoparticles (4 mins) showing AgPd bimetallic alloy nanoparticles joined together and also with a Ag₂O₃ nanoparticle.
FIG. S11. HRTEM image of irradiated nanoparticles (4 mins) showing a small AgPd bimetallic alloy nanoparticle joined together with an irregular shape globe consisting of Ag/Ag-oxides.
Table S1. EDX elemental analysis on individual nanoparticles (Fig. S5).

<table>
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<th>Pd (at.%)</th>
<th>Ag (at.%)</th>
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