# LASER-GENERATED NANOPARTICLES TO CHANGE PHYSICAL PROPERTIES OF SOLIDS, LIQUIDS AND GASES

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**Abstract**

Synthesis of nanoparticles was possible employing a Nd:YAG pulsed laser at fundamental harmonic. The production of nanoparticles in water depends mainly on the laser parameters (pulse duration, energy, wavelength), the irradiation conditions (focal spot, repetition rate, irradiation time) and the medium where the ablation occurs (solid target, water, solution concentration). The nanoparticles can be introduced in solids, liquids or gases to change many physical characteristics. The optical properties of polymers and solutions, the wetting ability of liquids, the electron density of laser-generated plasma, represent some examples that can be controlled by the concentration of metallic nanoparticles (Au, Ag, Ti, Cu). Some bio-medical applications will be presented and discussed.

**Keywords:** Nanoparticles, laser, plasma, bio-medical applications

## 1. INTRODUCTION

Laser interaction with solid targets in liquids represents a promising physical method to produce nanoparticles (NPs) without chemical agents. This technique allows to control the size, structure, concentration and morphology of the NPs by monitoring of the laser parameters (i.e., wavelength, fluence, spot size, pulse width, repetition rate and irradiation time), the irradiation conditions (focus, incidence angle, ...) and the target properties (composition, thickness, ...) [1]. Laser ablation induces physical modification of matter, due to photo-thermal and photo-chemical effects, and molecular fragmentation from solid into nano-particulates when the irradiation occurs in liquids instead in vacuum [2,3].

The pulsed laser ablation (PLA) process [4] in liquids involves different steps [5,6]: the laser beam is focused on the surface of the target, which is plunged into the liquid, and it is partially absorbed producing a direct photoionization on the target surface. A detachment of the material from the target occurs by thermal and Coulomb mechanisms with a consequent cavitation bubble effect, due to the energy released by the plasma plume to the surrounding liquids at the plume-liquid interface, ending with the bubble collapse. In the end, the plasma plume formation and its confinement at the metal-liquid interface induce the enhancement of temperature and pressure, a localised emission of atoms and electrons occurs and their strong interaction, due to the not possible expansion in the dense liquid, induces NPs production and a liquid solution generation [7].

The solutions, containing metallic nanoparticles at different concentrations, significantly modify the original physical and chemical properties of the liquid, such as the surface tension, density, viscosity, thermal and electric conduction [8,9]. The localised laser pulse induces target heating and the water causes fast cooling resulting in preferential crystallisation and grain growth of NPs [10].

The produced NPs generally have a spherical shape, a composition depending on the irradiated target and a size distribution depending on the used laser parameters and irradiation conditions. A special attention is given to metallic NPs of Au, Ti, Ag and C. The produced NPs in water can be employed to be inserted in solids, liquids and gases to modify their physical and chemical properties.

Surface Plasmon Resonance (SPR) absorption of the incident light, producing high absorption bands at particular wavelengths, is one of the main optical properties of metallic nanoparticles. It consists of collective oscillations of the conduction electrons excited by the electromagnetic field of the incident light. Thus, a metallic nanoparticle can be described as quasi-free sphere conduction electrons, moving on its surface. The light of the electromagnetic field exerts a force on moving conduction electrons of the surface, which induces an electric dipole when a nanoparticle is illuminated [11]. This dipole, in turn, generates an electric field opposite to that of the incident light, which forces electrons to return to their equilibrium position. After removing the external electric field, the electrons oscillate with a so-called "plasmon frequency", which is proportional to the square root of their density [11]. The surface plasmon oscillations are affected by various factors such as the composition, the size and shape of the nanoparticles. Its role plays also the surrounding medium and the electric field of the other close nanoparticles. Thanks to their peculiar properties, the Au nanoparticles are finding many potential applications for different scientific fields, from physics to chemistry, from material sciences to microelectronics and bio-medicine [1,7].

Introducing Au-NPs in polymer, it is possible to change their optical, mechanical, electrical and thermal properties, as reported in literature [1,8]. Depending on the NPs concentration, a transparent polymer can be modified in a very absorbent material, an insulator in a conductive medium, an elastic material in a very strong one [12]. The employment of biocompatible nanoparticles at low concentration in water, physiological solutions and blood determines a different wetting ability, liquid density and viscosity, electrical and thermal conductivity and a different color. For example, the different concentration of Au-NPs in water changes the color solution, the optical absorbance at specific bands in the visible region depends on the NPs size and produces a change in the solution electrical conductivity [8]. The production of ionized gas using pulsed and high intensity lasers irradiating of solids produces plasmas, which expand at high velocity in vacuum. If the irradiated target contains NPs, it is possible to modify the plasma properties. For example, the use of Au-NPs increases the electron density of the plasma and its temperature. Moreover, the electric field generated at the target surface and responsible of the ion acceleration in plasma can be increased, as reported in literature [13]. The high-energy absorption due to NPs enhances the local temperature of the light illumined medium containing metallic nanoparticles. Moreover, metallic NPs in biological tissues can be efficiently employed for photo thermal therapy induced by lamps or lasers operating at specific wavelengths [14].

In this paper, it will be described a physical method to generate nanoparticles, mainly based on gold, using a high intensity pulsed laser. Successively, three applications will be considered for employment of the gold nanoparticles in solids, liquids and gases.

## 2. EXPERIMENTAL SETUP

Metallic NPs, based on Au, Ag, Cu and Ti, were prepared using the "top-down" method by laser ablation in water [15,16]. A Nd:YAG laser operating at 1064 nm wavelength, with 3 ns pulse duration, 200 mJ pulse energy, 1 $mm^2$ focused spot and 10 Hz pulse repetition rate was employed. A metallic target having a surface of 1 $cm^2$ and 1 mm thickness was placed on a bottom of a glass tube filled with 10-30 ml of distilled water. The laser light was focused onto the metallic target with a 500 mm focal length convergent lens to obtain 1 mm of the spot diameter. An exposition time of the order of 10-30 min with repetitive laser shots was used. The ablation yield depends on the irradiated material, generally concentration of solution of the order of 0.1-10 mg/ml is prepared. A scheme of the experimental setup is shown in **Figure 1a** [2].

**Figure 1b** reports on typical curves of ablation yield for different targets (Au, Ag, Cu, Ti) as a function of the laser fluence (energy pulse per surface unit, $J/cm^2$) [17]. One can see that for the same value of fluence, the ablation yield is higher for Au and lower for Ti. The increment of the ablation yield means that the high concentration of NPs in solution can be obtained for relatively low laser fluence and irradiation times. The ablation yield has been measured using the weight loss with a micro-scale of a little target irradiated for long

time (30 min) at the 10 Hz repetition rate. The NP structure was obtained by irradiation the solid target in water, placed in about 5 mm depth with respect to the free water surface. After the laser irradiation, in order to avoid effect of the NP coalescence, 1-5 ml surfactant (sodium citrate) was added to the solution.

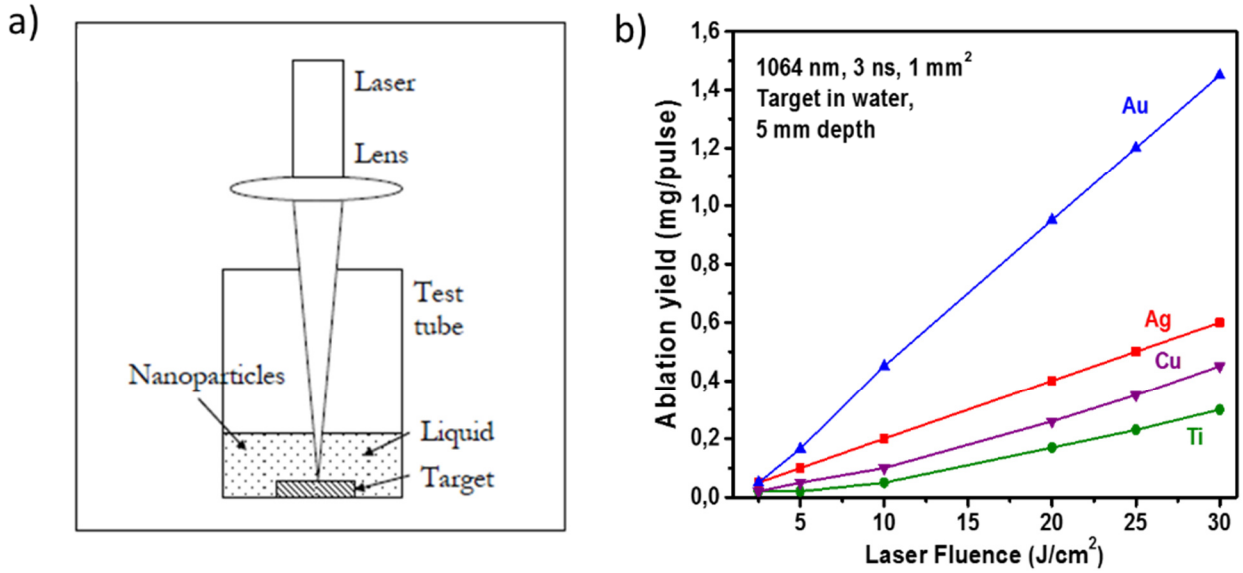


**Figure 1** a) Scheme of the experimental set-up used for the laser generation of nanoparticles in water and b) measurements of ablation yield vs. laser fluence for different metallic targets

The NPs production was investigated using the SEM and TEM microscopy. The EDX analysis were performed using detection of the characteristic X-rays emitted from the nanoparticles in order to verify the purity of the produced nanoparticles and their composition. Their size distribution was plotted in order to obtain information on the average size and on its indetermination by TEM image acquisition, considering a large number of nanoparticles. Using an image containing about 100 NPs or more, the single diameters were considered, employing an appropriate imaging software, as reported in [3].

Liquid solutions containing NPs were characterized using the near-UV-VIS-near-IR wavelengths produced by different lasers and lamps in order to measure the solution absorbance. The wetting ability of the solution was also measured by the contact angle of 1 ml liquid drop placed on different polished substrates. The contact angle was measured using an appropriate optical microscope. Polymers with NPs were obtained by embedding the NPs into the melted polymers. The optical properties of such polymers were measured using the transmission and absorption coefficients in thin films. The electrical conductivity of the polymers with the embedded NPs were measured using a Keithley modules for I-V measurements in DC [18]. Measurements of plasma generation by Nd:YAG laser, operating at 1064 nm in single pulse (3 ns), were generated in high-vacuum conditions. The ion velocity generated in such gas, as well as the properties of NPs employed in laser irradiated target were measured by time-of-flight (TOF) technique, employing ion collectors attached to a fast storage oscilloscope, as reported in literature [19].

## 3. RESULTS

**Figure 2** shows a SEM (a) image of metallic NPs of Au deposited on a carbon substrate on the stab. The average dimension of such spherical NPs is about 10 nm. Their composition was measured using the EDX analysis incited by the 20 keV electron beam. A typical EDX investigation reporting on the Au-NPs purity is presented in **Figure 2b**; TEM microscopy gives an average diameter of 10 nm (c) [17].

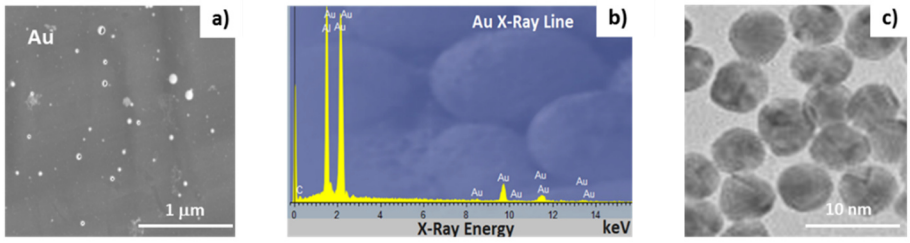


**Figure 2** a) SEM images of Au-NPs on carbon surface, b) typical EDX analysis and c) TEM image.

### 3.1. Applications to liquids

The liquid containing NPs can be analyzed by optical spectroscopy to determine its absorbance in the UV-Vis-IR wavelength regions, to obtain information about the characteristics (shape and size) of the embedded NPs. **Figure 3a** reports on an example of Au-NPs generated in water and analyzed in absorbance vs. wavelength [1]. The optical density of the liquid contained in a cuvette shows an absorption peak at specific wavelength ranges, increasing with the size of the nanoparticles. For nanoparticles of about 20 nm in diameter the SPR peak is localized at about 525 nm, while for NPs with 100 nm in diameter the peaks shifts to about 580 nm. **Figure 3b** reports on the different coloration of the solution, which turns from rose to red and then violet with increasing of the Au-NPs concentration.

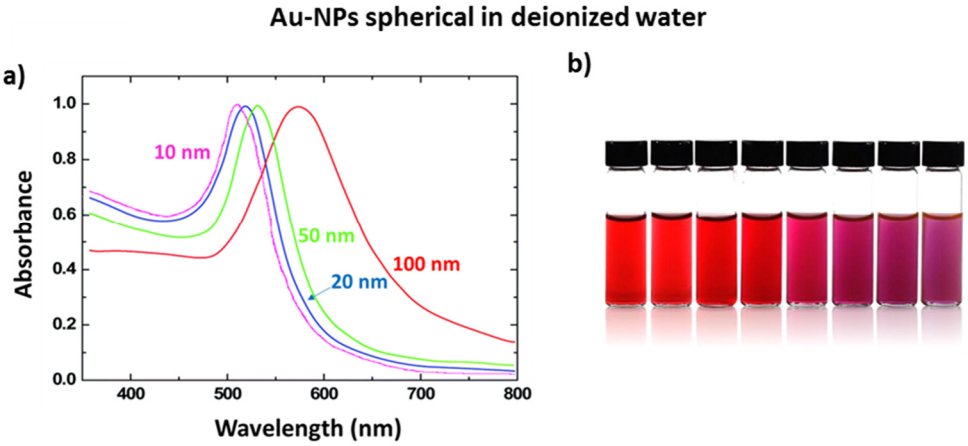


**Figure 3** a) Measurements of absorbance in water containing Au-NPs vs. wavelength and diameter of the NPs, and b) different colorization of the solutions with increasing the NPs concentration [20]

**Figure 4a-f** reports on the typical examples of the contact angle measurements of water without and with Au-NPs deposited as a drop on different polished substrates (polyethylene-PE (a, b), Ti (c, d) and Si (e, f) [8]. The solution had an Au-NPs concentration of 0.3 mg/ml. The contact angle $\theta$ was measured by the resulting angle between the forces applied to the solid-gas interface ($\gamma_{SG}$), solid-liquid interface ($\gamma_{SL}$) and liquid-gas interface ($\gamma_{LG}$), as reported in the equation given in the scheme of **Figure 4g** [8]. One can see that the wetting ability of the solution increases using the gold NPs, as it is demonstrated by the lower contact angle in the presence of NPs. The contact angle in fact decreases from 94° to 85° in PE, from 91° to 76° in Ti and from 67° to 42° in Si. It means that the Au-NPs induce a decreasing of the cohesion forces of the liquid solution molecules and enhancing the adhesion forces with the solid surface. This result was obtained also for other substrates [8], such as Cu, Ag, Al, polymethyl methacrylate (PMMA), $SiO_2$ and glass, demonstrating that the increased wetting ability of the solution containing Au-NPs represents a general behavior. This result is important for applications in different fields, such as in bio-medicine, where to improve the wetting ability of biomaterials with liquids and biological tissues Au-NPs can be injected in the liquid or deposited on the surface of the biomaterials.

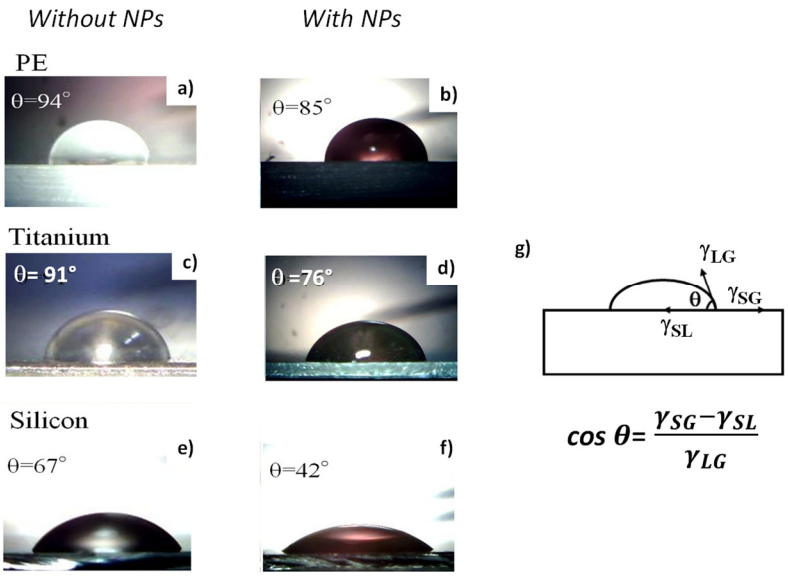


**Figure 4** Examples of contact angle measurements of water (a, c, e) and water containing Au-NPs (right) deposited as a drop on different substrates of b) PE, d) TI and f) Si. In g) a scheme is depicted a relation between contact angle and surface tension is depicted

The employment of metallic NPs both in the liquid and on the solid surfaces increases their hydrophilic trend, as it is reported in literature [8] This behavior can improve the cell growth on the implanted prosthesis stimulating the tissue integration and other physiological processes that prolong the prosthesis life, as indicated in the **Figure 5**.

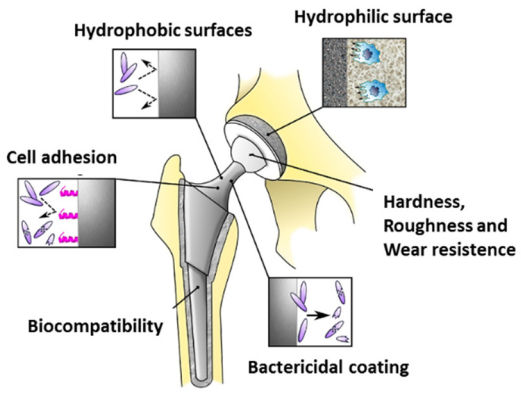


**Figure 5** Scheme of the prosthesis implantation in biological environment with the use of NPs at its surface [21]

### 3.2. Applications to solids

The introduction of NPs in polymers changes their physical and chemical properties. In particular, the optical properties can be modified drastically also by employing low NPs concentrations. **Figure 6a** [17] shows the measured absorbance vs. wavelength for polyethylene pure and containing uniformly embedded graphene nanoparticles at different concentration up to 12 ml solution, and containing also Au-NPs at a concentration of 1 % in weight. One can see that the absorbance in the visible range increases significantly, for example at 500 nm from 50 % in pure PE increases up to 98 % in PE with graphene oxide water dispersion NPs at 0.4 wt%

concentration. In presence of Au-NPs with about 10 nm in diameter, the absorbance shows an evident SPR resonant absorption peak centered at about 510 nm. **Figure 6b** shows another example of PE absorption coefficient vs. wavelength [22]. The polymer is of high density ultra-high-molecular-weight-poly-ethylene) (UHMWPE) in which carbon nanotubes (CNT) are embedded during the melting phase at different concentrations from zero up to 1 % in weight.

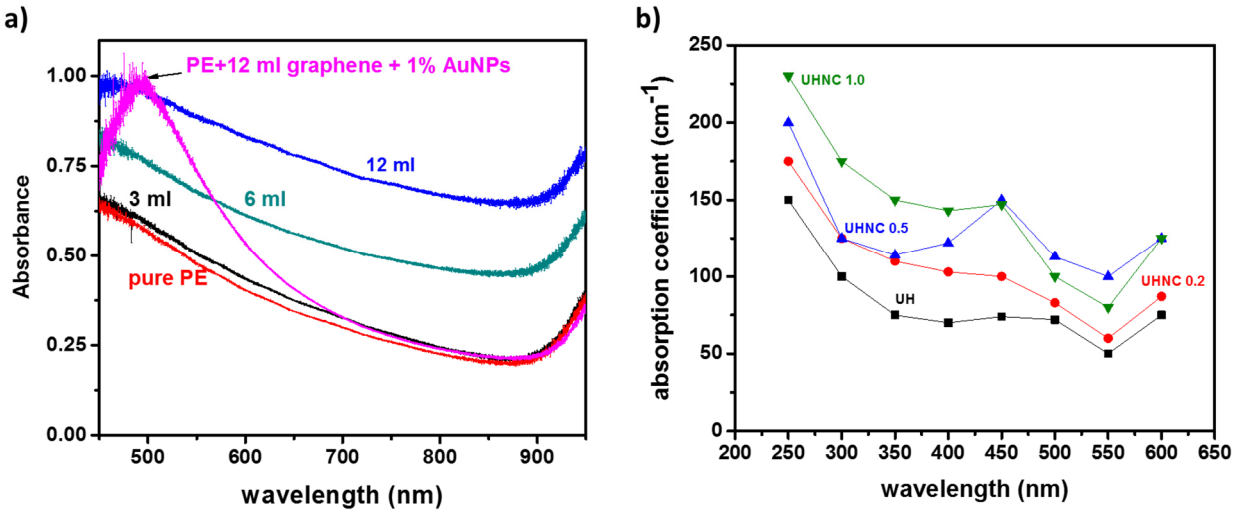


**Figure 6** a) Absorbance vs wavelength for polyethylene containing graphene and Au-NPs, and b) absorption coefficient in UHMWPE vs. wavelength containing the CNT nanoparticles

A special application due to such polymer modification can be found in the field of laser welding of polymeric materials. Two polymers, one as pure and transparent to the laser wavelength and the other rich in C-NPs content, black and strongly absorbent, can be welded at their interface using the technique of known as Laser Transmission Welding (LTD). The laser pulse is transmitted by the first polymer foil and absorbed to the surface of the under-placed second polymer. The laser energy released at the interface of the two pressed foils produces local heating and polymer melting inducing a resistant welding of the two polymeric foils, as was already reported in [22]. **Figure 7a** reports on a scheme of the used experimental set-up for the LTD technique in polymers, and **Figure 7b** a photo of the produced polymeric welding.

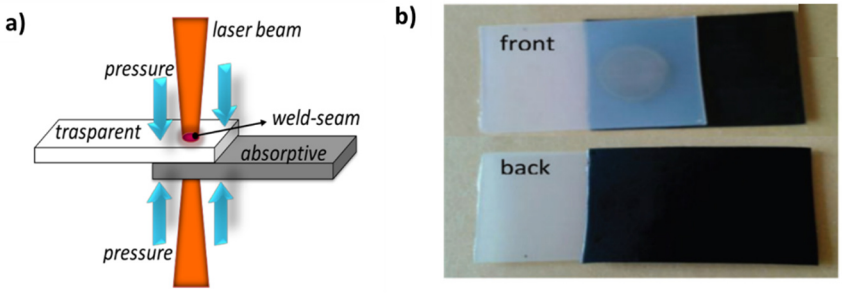


**Figure 7** a) Scheme of the LTD laser welding technique, and b) photo of the welded polymers

### 3.3. Applications to gases

Employment of minimum quantities of PE, of the order of 0.1 % in weight, changes the color of the polymer from white and transparent to black strongly absorbent material. The use of metallic nanoparticles can be extend also to gas phases in order to modify, significantly, their properties. Many applications concern the

modifications of the laser-generating plasma properties. A plasma represents an ionized gas at high temperature and density, which, in absence of charge equilibrium, shows high electric field responsible to high ion acceleration along preferential directions. Nano- and sub-nano laser pulses at high intensity (>$10^{10}$ W/cm$^2$) irradiating a solid material (target) placed in vacuum, generate a non-equilibrium plasma which characteristics of temperature, density, photon, electron and ion emission, etc., can be measured with different on line techniques (TOF, optical spectroscopy, Langmuir probes, ion collectors, semiconductor detectors, mass quadrupole spectrometry, plastic detectors, etc.). A typical scheme of the experimental set-up used to generate plasma is shown in **Figure 8a**.

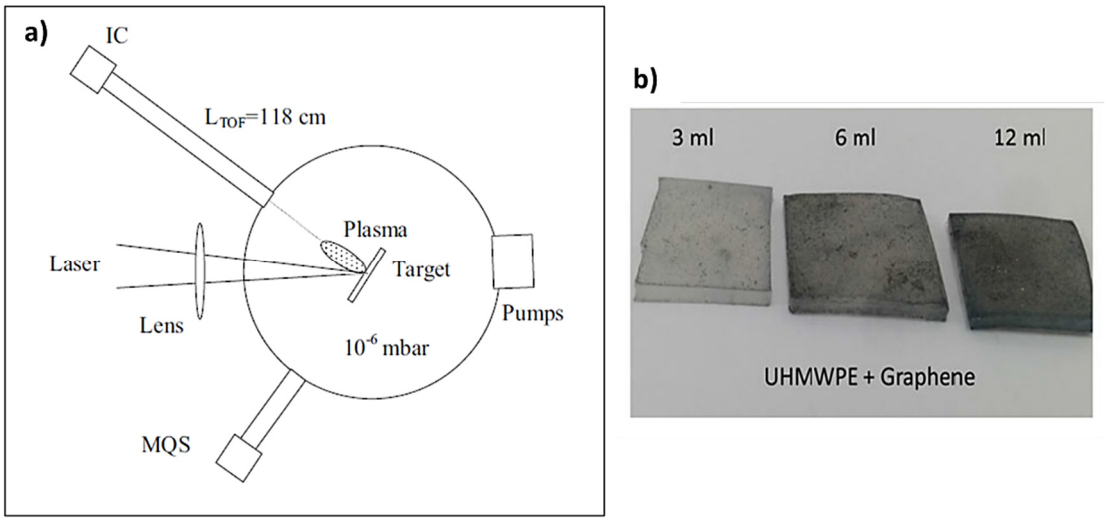


**Figure 8** a) Scheme of the set-up for plasma produced by laser, and b) photo of PE with different C-NPs content

A long tube is employed to detect the emitted ions with an ion-collector (IC) used in TOF approach, i.e., by knowing the detector-target distance and measuring the time of arrival of the ions with a fast storage oscilloscope an energy of ions can be found. The irradiated targets are placed in the centrum of the vacuum chamber and consists of polymers without and with embedded NPs [17]. **Figure 8b** shows the photo of some samples, in which different concentrations of graphene nanoparticles are embedded. The presence of NPs modifies the plasma temperature and electron density, depending strongly on the atomic number and concentration of the used NPs species. For example, the use of Au-NPs enhances the effective atomic number of the target and permits to generate a plasma with a greater electron density and a great charge not-uniformity in the plasma [23]. Typical results can be observed by the TOF spectra acquired during the laser-plasma generation measuring the velocity of the emitted ions. Using a Nd:YAG laser at 3 ns pulse duration and $10^{10}$ W/cm$^2$ intensity operating in single pulse at 1064 nm wavelength, plasmas from polymer targets were generated. **Figure 9** shows an example of the results obtained by embedding graphene NPs and Au-NPs in UHMWPE [17]. Their presence increases the number of emitted particles, as was observed from the higher ion yield (mV), and the higher ion velocity, as was observed from the lower TOF time (μs) necessary to reach the IC detector 118 cm distant form the target. This confirmed high kinetic energy of the emitted ions (protons and carbons) achieving 200 eV/charge state [24].

Using high laser intensity (>$10^{18}$ W/cm$^2$) and brief pulses (tens of femtoseconds), it is possible to accelerate ions in target-normal-sheat-acceleration (TNSA) regime at about 10 MeV per charge state. This allows to use the energetic ions for many applications, from nuclear physics (to produce nuclear reactions) to chemistry (to induce chemical reaction), from microelectronics (to implant ions in substrates) to medicine (to use the ions for radiotherapy), and others [24].

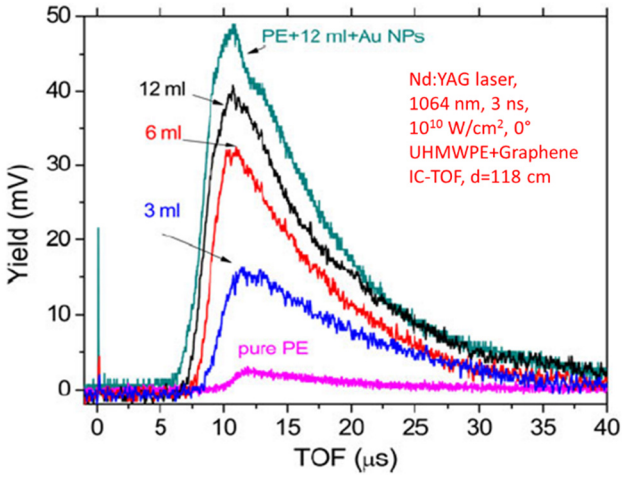


**Figure 9** TOF spectra of the ions emitted form a laser-generated plasma form pure polymer and polymers containing C-NPs and added Au-NPs

## 4. CONCLUSIONS

The production of nanoparticles from the laser ablation in water technique permits to generate metallic and not metallic nanoparticles with narrow size distribution, generally below 100 nm in diameter. The repetitive laser pulse irradiation and the long irradiation time permit to control the solution concentration and the use of surfactants, such as sodium citrate, avoid the nanoparticle coalescence.

These nanoparticles are employed more and more in different scientific fields to modify the properties of liquids, solids and gases. Their composition, shape, size and concentration permit to modify the physical and chemical properties of many materials, such as biological solutions, polymers and plasma gases. The paper presents results about the liquid color and absorbance variation due to SPR effects, the optical properties of polymers in which the NPs are embedded uniformly during the melting phase, and the use of nanoparticles in laser irradiated targets to generate plasma with high temperature, density and energetic particles. Moreover, inhere only few applications of NPs were shown, but, obviously, many other examples can be given, from the preparation of special materials at high mechanical resistance and low density, to the use of special sensors, of chemical and pharmaceutical species and the use of NPs to increase the medical imaging contrast and the enhancement of absorbed dose in radiotherapy.

In this contest, the particular interest is devoted to Au-NPs due to their high atomic number and atomic weight, their easy synthesis and stability, their exhibition of excellent biocompatibility and chemical passivation, their high mass absorption coefficient for X-rays, and high particle stopping powers. Due to the high electron density, Au-NPs significantly enhance the absorption of X-rays in the medium where they are embedded, in dependence of the used concentration. In the same manner, their introduction in biological liquid, soft or hard tissues enhances the electron and ion stopping powers, i.e., the energy released by the incident corpuscular radiation. At microscopic level, Au particles of dimensions below 5-10 nm can be filtered by the kidney and spleen and transferred to all organs. Such nanoparticles may diffuse not only in the extracellular liquids, but can also cross the cell membrane, diffuse in the intracellular liquid arriving in the nucleus and permitting their bonding with the DNA. These effects are of special interest in the case of tumor cells because radiotherapy permits high release of radiation energies sufficient to damage the DNA and the entire cell. Thus, it means to increase the absorbed dose and to destroy more specifically tumor sites containing the gold solution during radiotherapy expositions [14]. Moreover, the SPR effect can be employed to localize heating during photo-thermal therapy induced by lamps or laser light [3].

## ACKNOWLEDGEMENTS

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