1. Introduction

Pulsed laser ablation in liquids (PLAL) is a technique that has gained a lot of attention since 1987 when, for the first time, Patil et al [1] reported the laser ablation of a solid iron target in water. Lately, it has also been discovered that it is possible by means of this technique to produce nanoparticles (NPs). In PLAL, the extraction mechanism is usually interpreted on the basis of different physical and chemical processes. The physical processes are governed by the laser parameters and the chemical processes mainly by the interaction between the particles and the base fluid. To enhance the characteristics of the NPs after the ablation, the colloidal solution is irradiated by the laser again to promote another photo-fragmentation process of the NPs in the fluid [2, 3]. In particular, the strongest fragmentation effect in the second process is obtained when laser fluence is smaller than or about the same as the breakdown threshold of the liquid. Hence, the selection of experimental parameters, such as light wavelength, laser fluence, ablation time, repetition rate, or the base fluid itself can modify the shape and size distribution of particles [4]. For example, the ablation process with laser pulses of few femtoseconds temporal widths allows us to achieve higher purity in the final fluid as well as a lower heat affected zone on the sample than with nanosecond or picosecond pulses [5, 6]. Also, the laser-plume interaction is minimized, which makes the NPs generation process more controllable and the achievement of breakdown threshold in the fluid easier.

Applications of the PLAL technique and the photo-fragmentation additional process include, but are not limited to, the production of NPs of metallic and semiconductor materials [7–11], the morphological modification of nanostructures [12, 13], and the synthesis of nanomaterials with chemically active fluids without needing a physical target [14, 15]. Synthesized like-flower NPs with potential abilities for surface enhanced Raman scattering was also proved by Lu et al [16]. Recently, the selection of the base fluid has been...
shown to be a key parameter in many applications, such as the development of high speed and frequency electronic devices [17, 18] or the synthesis of non-toxic NPs that present infrared emission for biomedical applications [19, 20].

On the other hand, the concept of adding small solid particles into a fluid to increase the thermal properties of the suspension has been practiced since 1873 [21]. However, most of the studies were performed using suspensions of millimeter- or micrometer-sized particles leading to problems, such as poor suspension stability and channel clogging, that limit its practical applicability. To address these drawbacks, Choi proposed in 1995 the use of nanofluids to increase the thermal conductivity of heat transfer fluids [22]. Nanofluids are defined as dilute suspensions with solid NPs.

Thermal oils are widely used in several industrial applications, such as solar thermal power plants. Solar energy is one of the best sources of renewable energy having minimal environmental impact. Nowadays, improvement in the harvesting of solar light is a challenge. One way to increase the efficiency of solar thermal collectors is by fabricating nanofluids using a thermal oil, such as Therminol VP-1 as a base fluid [23, 24].

In this context, Wang et al. [24] experimentally demonstrated that the fabrication of spherical gold NPs with sizes around 121 nm and concentrations of 0.05% (mass percentage) in Therminol VP-1 can enhance its thermal conductivity by up to 6.5%, thus increasing the harvesting of energy in solar plants. This happens at least three days before that the agglomeration of NPs and increment of viscosity appears (it is considered that an increment in nanofluid viscosity is a drawback due to the associated increment in fluid pumping costs). Note that, in the procedure followed by Wang et al., gold NPs are commonly produced separately in the form of colloidal suspensions in a given solution, and subsequently dispersed into Therminol VP-1. Hence, the agglomeration of NPs cannot be disregarded, leading to poor suspension stability and high shear viscosity. In order to mitigate this unwanted effect, alternative procedures based on the production of NPs directly within the fluids have been proposed [25–28]. Unfortunately, most of these (i.e. wet techniques) demonstrate low effectiveness in avoiding agglomeration of NPs and/or show pollution problems due to the surfactants used in the synthesis of the NPs.

In this letter we experimentally demonstrated the fabrication of a thermal oil nanofluid based on femtosecond laser ablation and re-fragmentation of bulk gold inside Therminol VP-1. The morphology, purity, mean size, and size dispersion of our NPs, and the stability and thermal conductivity enhancement of the nanofluid were determined. Owing to the fact that no chemical stabilizer, reducer or dispersant is employed to synthesize the NPs, and thanks to the photo-fragmentation process, we obtained a small particle size and the agglomeration over time was significantly alleviated. This may have a potential impact in using this nanofluid in real applications, for instance in thermal power plants.

2. Experimental setup

In our experiment we produce gold nanoparticles in Therminol VP-1 by PLAL followed by a second photo-fragmentation process. The first stage of the experiment involves a laser ablation process where the ejected fragments of material produced by the ablation are captured in a liquid (in this case we used Therminol VP-1). It was carried out with a Ti:Sapphire laser (Femtopower Compact Pro, Femtolasers), that emits pulses of 30 fs intensity full width at half maximum (FWHM) with a central wavelength of 800 nm, maximum energy per pulses of 0.5 mJ, and 1 kHz repetition rate. Before exit the ultra-short pulses pass through a user-adjustable post-compression stage based on two fused silica Brewster prisms, which allows us to control the dispersion in the beam delivery path. The energy of the pulses is measured with an analogical power-meter (Spectra Physics, Model 407-A) and controlled using a set of calibrated neutral density filters. The cross-section of the pulsed beam is slightly elliptical, with a nominal beam diameter of 15 mm in accordance with the $1/e^2$ criterion, and a beam propagation factor lower than two. To reduce optical aberrations and increase the spatial uniformity, the beam passes through a 2x all-mirror beam expander. In addition, an iris of 6 mm diameter is placed before the focusing optics.

A gold disc of thickness 1 mm and diameter 6.5 mm (99.99% purity) was used as the target. The disc was placed at the bottom of a glass vessel (cuvette) filled with Therminol VP-1. The thickness of the fluid layer above the target was about 7 mm. The cuvette was attached to a 2D motion controlled stage that can be moved at a constant speed during the experiment. The target was irradiated from the air-liquid interface by means of a focused beam with a lens of 75 mm focal length onto the target surface while moving the target perpendicularly to the beam propagation axis at a constant velocity of 4.5 mm s$^{-1}$. The dispersion introduced by the liquid and the lens was compensated with the help of the above mentioned post-compression stage. To adjust the duration of the ablation process, an electronically controlled shutter was utilized. In these conditions, after 15–17 min we obtained a brown coloration in the aqueous solution due to the presence of the gold nanoparticles in the fluid.

In the following experimental stage, we filled a 10 ml glass cuvette with the NP colloidal solution obtained from the first stage of the experiment. Then, the cuvette was irradiated using the light from the Ti:Sapphire laser, previously focused onto its center with the same lens, while the suspension was stirred with a magnet to homogenize the photo-ablation process, which consists of a fragmentation of the biggest particles into smaller particles by means of a second ablation process.

Under free propagation, the fluence of the laser beam at the focal point of the lens is about 1 J cm$^{-2}$. However, due to the refraction effects this value decreases to 0.6 J cm$^{-2}$ approximately. Please also note that the laser fluence inside the cuvette is not constant, but decreases as we move away from the focal position towards the lens.

3. Results and discussion

By using transmission electronic microscopy (TEM), energy dispersive x-ray spectroscopy (EDX), high resolution transmission electronic microscopy (HRTEM) and dynamic light scattering (DLS) we determined the morphology, purity, mean
size, size dispersion, and stability of the fabricated and commercial NPs. This section is divided in two subsections, the production of NPs, where we focus in the properties of the nanofluid just after its fabrication, and an account of nanofluid properties where we study some characteristics of our nanofluid, such as the evolution of the mean size of the particles through time and the nanofluid thermal conductivity.

3.1. Production of nanoparticles

To study the quality of the NPs fabricated with the fs laser we compared their properties with commercial NPs added to Therminol VP-1. In order to obtain highly dispersed NPs, similar to the ones obtained by the PLAL technique, commercial gold NPs were acquired in aqueous suspension from Sigma Aldrich. NPs were stabilized in 0.1 mM of phosphate buffered saline (PBS) solution and the primary particle diameter was 50 nm. To prepare Therminol VP-1/gold nanofluids, first water content was removed from the aqueous nanofluid by evaporation on a hot plate. The solid product obtained was then dispersed in Therminol VP-1 with the help of an ultrasound probe and a concentrated nanofluid was obtained. The sonication time varied from 5 to 10 min depending on the sample volume. Finally, nanofluids were dispersed with pure Therminol VP-1 to achieve the same optical density and solid content in all cases. Optical density has been calculated by measuring the radiation absorption of a laser beam at 635 nm (Model CPS180, ThorLabs) with a photodiode (Model SM05PD1B, Thorlabs) in a rectangular quartz cuvette. To ensure the purity of the gold NPs obtained with the femtosecond laser, the elemental composition of the NPs was determined using an EDX system attached to the TEM (Oxford Instruments INCA Penta FETX3). The EDX detected gold (Au), copper (Cu) and carbon (C) (see figure 2(a)). However, the presence of copper and carbon is due to the grid substrate, which is made of copper and contains a carbon film. In this direction, we also performed HRTEM measurements to see the crystallographic planes of the gold NPs and to corroborate our results. Figure 2(b) shows four typical spherical Au particles with diameters less than 5 nm, embedded in the thermal fluid. The clear lattice fringes indicate the high crystallinity. The inset in figure 2(b) allows us to see the crystallographic planes. As might be expected, the d interplanar spacings represented by (hk0) Miller index obtained from HRTEM micrographs in table 1 are similar to those included in Joint Committee on Powder Diffraction Standards (JCPDS) files for cubic Au crystals (JCPDS: 4-784). As one could extrapolate from these results, the synthesized particles of Au seem to be free from vacancies or defects in the crystal due to the mixture between gold and another element that comes from the fluid.

At this point, we determined the size distributions of the NPs by DLS just few minutes after the fabrication of the nanofluid. This technique provides the size distribution of the particles or agglomerates of particles as they are present in the nanofluid in static conditions. To this end, we used a Zetasizer nano ZS (Malvern Instruments Ltd., UK) with a 173° scattering angle. Particle size was assessed from Brownian motion by means of the Einstein–Stokes equation. Results are shown in figure 3. Nevertheless, we have to take into account that the mean size and size distribution value depicted in figure 3 is a rough value estimation of the original size of fabricated NPs because in the time between the nanofluid fabrication and the measurement, the NPs could start to agglomerate and, in fact, the measured NPs size represents the size of agglomerates. However, for our purposes (particle agglomeration dynamics study) this value can represent a good figure of merit.

Figure 1. TEM micrographs of samples fabricated by (a) PLAL and (b) PLAL followed by the second photo-fragmentation process, and (c) commercial NPs.
From statistical size analysis, the mean size and size dispersion for the commercial NPs were $255 \pm 192$ nm at FWHM. In contrast, the nanofluid produced with the PLAL technique shows a mean size of $122$ nm, while the size dispersion was of $155$ nm. Furthermore, the nanofluid produced by PLAL and the second photo-fragmentation process shows a mean size of $58$ nm and the lower size dispersion (about $31$ nm of FWHM). These results show that the production of gold NPs by PLAL with the second photo-fragmentation process allows a decrease in the size dispersion and the mean size of the NPs inside the thermal oil, avoiding the agglomeration phenomenon in the production process. Consequently, by controlling the time of the second photo-fragmentation process, we are able to control the characteristics of the NPs in the nanofluid.

### 3.2. Nanofluid properties

One of the most important characteristics of nanofluids is that they can remain for prolonged periods of time without significant settling or loss of stability due to Brownian motion. As the particle size decreases, Brownian motion becomes predominant over Stokes sedimentation [29, 30]. Stability in colloid science is used not only in the thermodynamic sense but also in a strictly colloidal sense. Colloidal stability means that the colloidal particles do not settle and do not agglomerate at a significant rate. The classical DLVO (Derjaguin–Landau–Verwey–Overbeek) theory predicts the stability of the nanofluids by knowing the total energy of interaction between two particles [31]. In the range of sizes of nanofluids, the ratio of particle surface to particle volume is so high that all the interactions are controlled by short-range forces, such as Van der Waals attraction. As a consequence of the attractive nature of the forces presented, when primary particles are suspended in a fluid they have a tendency to agglomerate when they come into contact due to their Brownian motion. These agglomerates remain in suspension providing a stable nanofluid unless the agglomerate size becomes big enough to settle.

The stability of Au/Therminol VP-1 nanofluid was determined by the analysis of mean particle size of Au nanoparticles at different times. To do that, the mean size of the NPs inside the fluid was measured 12 times in 96 h. The results are shown in figure 4. The average size of Au particles increases gradually within the first 6 h due to the formation of the clusters. After that time, agglomerate size keeps constant and nanofluids can be considered stable for at least 96 h. From figure 4 one can see that in comparison with the use of commercial NPs, our nanofluid made in two experimental stages reaches its stability with clusters of $523$ nm, while the nanofluid synthesized with commercial NPs does so with clusters of $968$ nm. Thus the nanofluid generated by PLAL with the second photo-fragmentation process alleviates in great measure the issue of unwanted agglomeration.

As mentioned earlier, nanofluids are used as heat transfer fluids because of their improved thermal properties. The

| $d$-spacing/Å (experimental results) | $d$-spacing/Å (JPCDS: 4-784 data) | (hkl) values | Phase assignment |
|-------------------------------------|----------------------------------|--------------|-----------------|
| 2.40                                | 2.35                             | (111)        | cubic           |
| 2.00                                | 2.04                             | (200)        | cubic           |

Figure 2. (a) EDX spectrum of produced nanoparticles (the carbon and copper is derived from the grid used to deposit the Au NPs), (b) HRTEM micrography of produced nanoparticles.

Figure 3. Comparison between distribution of sizes obtained for each fluid.

Table 1. $d$-spacing of the crystalline gold NPs measured from HRTEM micrographs.
addition of solid particles with higher thermal conductivity than the base fluid results in a thermal conductivity enhancement that can be predicted by the Maxwell equation. In this work the thermal conductivity of the nanofluids produced by PLAL (after the first and second experimental stages) and the commercial nanofluid was measured at 80 °C by means of the transient hot wire technique, using a KD2 Pro conductimeter (Decagon Devices Inc.). Six measurements were made for each nanofluid sample so the experimental error could be determined at a 95% confidence level. Results are shown in table 2. It can be seen that thermal conductivity increases when nanoparticles are suspended in the base fluid. The enhancement achieved depends on the size and shape of the particles and clusters of particles in the nanofluid, according to Gao et al (2009) [32]. The best results were obtained for the second experimental stage sample in which particles presented the smallest size. The first experimental stage sample with the largest agglomerates presents the lowest thermal conductivity enhancement.

4. Conclusions

In this letter, we have successfully produced highly pure, size-controlled and well-dispersed gold NPs in Therminol VP-1 by PLAL and a second photo-fragmentation process without using any chemical additives. The analysis of TEM and HRTEM micrographs along with EDX spectra shows that our NPs have a spherical shape, the nanofluids show no pollution and the crystallographic planes suggest that there are no defects because of impurities. We also observed that thanks to the photo-fragmentation process, in general we obtained NPs of a mean size smaller than 58 nm. This small size is difficult to obtain using other methods because NPs tend to agglomerate very fast in Therminol VP-1. Moreover a study of the stability over time reveals that the NPs produced by ablation and the following fragmentation process with a laser are at least 54% smaller than in the other cases. Finally, thermal conductivity measurements revealed that nanofluids have higher thermal conductivity than the base fluid making them suitable for use as heat-transfer fluids. The nanofluid produced by ablation and the following fragmentation process of NPs with femtosecond laser light showed the highest thermal conductivity enhancement. All these results demonstrate a great advantage over other methods to produce NPs in thermal oil that may potentially have a significant impact on the improvement of harvesting efficiency of solar light with nanofluids.

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Table 2. Thermal conductivity enhancement at 80 °C.

| Sample                  | k (W mK⁻¹)          | Δk (%) |
|-------------------------|----------------------|--------|
| Therminol VP-1          | 0.1280 ± 0.0030      | —      |
| Commercial              | 0.1320 ± 0.0018      | 3.13   |
| First stage             | 0.1282 ± 0.0015      | 0.13   |
| Second stage            | 0.1332 ± 0.0014      | 4.06   |

Figure 4. Comparison between agglomeration dynamics over time.

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