Pulsed laser ablation in liquids for the production of gold nanoparticles and carbon quantum dots: from plasmonic to fluorescence and cell labelling

Pulsed laser ablation in liquids for the production of gold nanoparticles and carbon quantum dots: from plasmonic to fluorescence and cell labelling

C Doñate-Buendía[1], M Fernández-Alonso[1], J Lancis[1] and G Mínguez-Vega[1,*]

[1]GROC·UJI, Institute of New Imaging Technologies, Universitat Jaume I, Avda. Sos Baynat s/n, 12071 Castellón, Spain

Corresponding author e-mail: gminguez@uji.es

Abstract. The synthesis of high purity ligand free nanoparticles represents one of the requirements for nanotechnology application in highly relevant fields as nanomedicine and theranostics. Laser synthesis and processing of colloids permits the synthesis of ligand free nanoparticles with reduced impurities from bulk targets and colloidal dispersions. In the present contribution a novel approach for enhanced production of ligand free gold nanoparticles by femtosecond ablation of a bulk target is studied together with a more efficient synthesis of fluorescent carbon quantum dots from a colloidal suspension of carbon microparticles in polyethylene glycol.

1. Introduction

As nanotechnology spreads over more and more applications, the necessity of synthesizing nanoparticles is growing, together with the aim to find specific synthesis routes for application related requirements such as high purity, stability or morphology control. Between the different techniques employed, laser synthesis and processing of colloids (LSPC) represent a group of laser based techniques able to generate nanomaterials from bulk targets, laser ablation in liquids (LAL), and from microparticles dispersions, laser fragmentation in liquids (LFL). These synthesis routes are based on the irradiation with a high power laser of a bulk target immersed in a liquid or a colloidal dispersion of particles to promote the extraction of nanoparticulate materials that get collected in the liquid [1]. The inherent benefits of LAL and LFL are the reduction of byproducts generated in the process as only the base liquid and the target are needed. Besides, it permits the synthesis of ligand free nanoparticles and alloys [2] that are highly demanded in nanomedicine [3], catalysis [4], or additive manufacturing [5].

In that sense, the development of systems with enhanced production efficiency represents a goal to make these techniques become a standard synthesis route in many applications. The achievable production has been already proved to be high enough for industrial applications, up to 4 g/h [6]. However, there are still fundamental limitations whose overcome could open up new routes for enhanced efficiency. While femtosecond pulses are a standard tool for material removal in air with higher ablation rates that longer pulses, in LAL ps has been proved to be the optimum pulse duration for higher production due to nonlinear effects losses in the liquid media [7]. What is more, the effect of the liquid presence and generated nanoparticles can shield the beam also reducing the efficiency of LFL.

In the present contribution, a simultaneous spatial and temporal focusing (SSTF) optical setup is used to study the reduction of nonlinear effects in the liquid and the viability of femtosecond pulses also for high nanoparticle production in LAL [8]. Besides, the limitation of the liquid layer in LFL is addressed by a liquid flowing system [9] and the effect over the synthesis of carbon quantum dots is studied [10].

2. Results and discussion

2.1. Simultaneous spatial and temporal focusing for femtosecond laser ablation in liquids

The proposed nonlinear effect reduction is based on the employment of a SSTF setup for LAL. The working principle is based on the change of the pulse duration with the propagation of the beam. This way, the intensity is reduced out of focus and also the nonlinear interactions [11,12]. To achieve it, the broad spectrum of a 30 fs pulse is spatially separated by a diffraction grating, figure 1 (a). Then, an image system based on two off axis mirror form the image of the diffraction grating plane, hence recombining all the spectral components in the image plane. Exactly in that plane the original pulse duration is recovered, in any intermediate plane, the spatial separation of the spectral component generates a broadening of the pulse duration up to 800 fs, figure 1 (b). The focal spot size, figure 1 (c), is controlled by the ratio between the focal length of the two elements that form the image system, f_2/f_1.

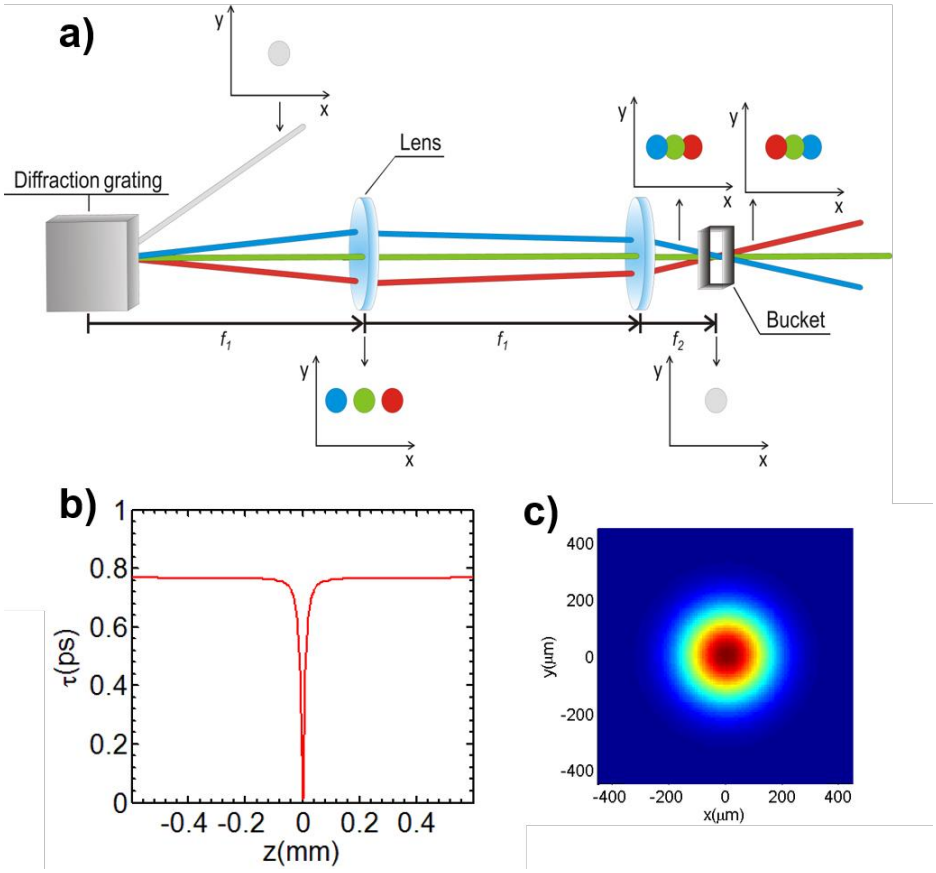

Figure 1. a) Scheme of the SSTF optical setup for nonlinear effects reduction. b) Pulse duration as a function of the propagation distance, where 0 indicates the image plane. c) Simulation of the beam size at the image plane of the SSTF system.

The proposed methodology is proved to increase nanoparticle production a factor 10 compared to an analogous optical system (IOS), and a factor 2 compared to the conventional LAL optical system (COS), figure 2. The IOS system is analogous to the SSTF just replacing the diffraction grating by a mirror, in the COS the laser is focalized on the target by a 75 mm lens. It is interesting to notice that, while in COS

the focal spot is smaller than SSTF, and so the fluence higher, the production is increased employing SSTF [8].

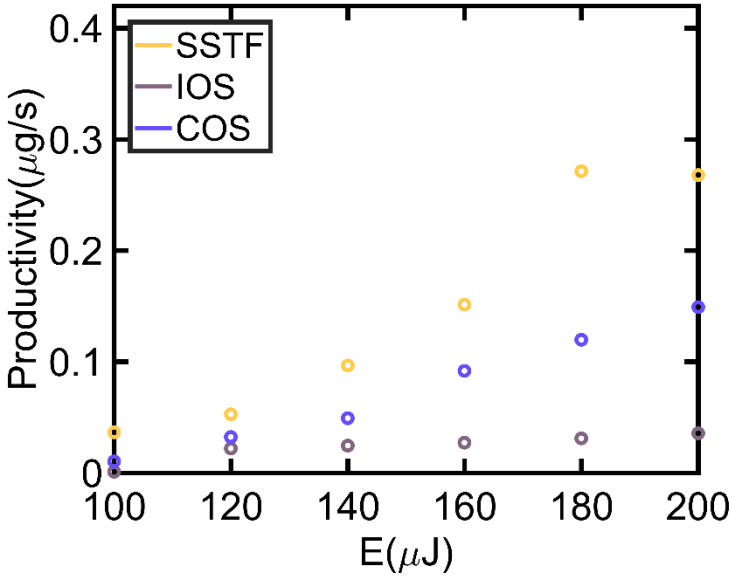

Figure 2. Gold nanoparticle productivity measurements for the different optical setups compared.

2.2. Flow jet reactor for fluorescent carbon quantum dots synthesis.

Carbon quantum dots (CQDs) are a very interesting nanomaterial due to their fluorescence and high biocompatibility. In that sense, LSPC is a very interesting technique for the synthesis of CQDs as the high purity of the samples would permit their direct use in nanomedicine application. There has been reported different approaches to synthesize them, from irradiating graphitic targets [13] in liquid to fragmentation of carbon based microparticles [14]. In the latter case, the liquid and the high absorption of the microparticles can reduce the control over the laser parameters employed. To solve this, we employ a flow jet methodology [9] for increasing the efficiency of CQDs synthesis in polyethylene glycol.

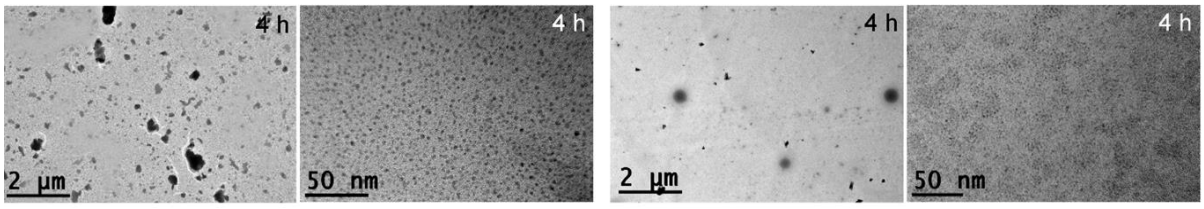

Figure 3. TEM images for two different magnifications of the standard, left, and flow jet setup, right, generated CQDs.

The results obtained, figure 3, together with thermogravimetric analysis, prove that the efficiency of CQDs generation is enhanced a 15% factor when the flow jet methodology is employed in comparison with the standard system. The generated CQDs exhibit a fluorescence response with a quantum yield of 4.5%, then, they are tested as fluorescent labels for cell imaging [10]. The internalization inside cells is easily achieved by direct mixing of a drop of the colloid and the cell culture. Complete internalization is achieved in less than 10 minutes and confocal images of the CQDs distributed all over the cell structure are taken, figure 4.

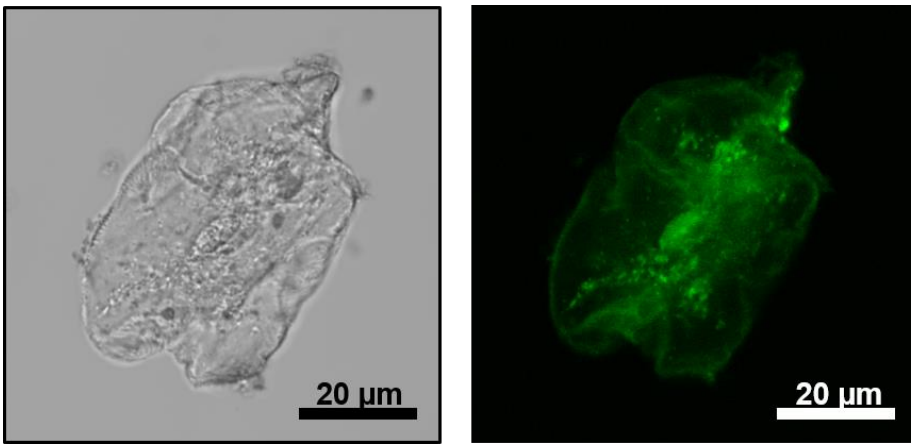

Figure 4. Transmission, left, and fluorescence, right, images of a cell with internalized laser synthesized CQDs.

3. Conclusions

In this contribution an implementation of femtosecond PLAL by employing simultaneous spatial and temporal focusing configuration is explored, finding a significant increase in gold nanoparticle production due to the reduction of nonlinear energy losses in the liquid media previous to the irradiation of the gold bulk target. On the other hand, a continuous liquid flow configuration is proposed for the generation of fluorescent carbon quantum dots (CQDs) from a colloidal carbon microparticles suspension irradiated by a nanosecond laser. The proposed methodology is proved to enhance carbon microparticles size reduction up to a 15 % with an 84 % of the initial microparticles being converted into CQDs of 3 nm average size. The synthesized CQDs exhibit a broad fluorescence response and fast internalization in cancerous and healthy epithelial cells. Therefore, their application as fluorescent labels is studied and demonstrated, finding a straightforward methodology for cell labeling and visualization.

References

[1] Zhang D, Gökce B and Barcikowski S 2017 Laser Synthesis and Processing of Colloids: Fundamentals and Applications *Chem. Rev.* **117** 3990–4103

[2] Torres-Mendieta R, Havelka O, Urbánek M, Cvek M, Wacławek S, Padil V V T, Jašíková D, Kotek M and Černík M 2019 Laser-assisted synthesis of Fe-Cu oxide nanocrystals *Appl. Surf. Sci.* **469** 1007–15

[3] Correard F, Maximova K, Estève M A, Villard C, Roy M, Al-Kattan A, Sentis M, Gingras M, Kabashin A V. and Braguer D 2014 Gold nanoparticles prepared by laser ablation in aqueous biocompatible solutions: Assessment of safety and biological identity for nanomedicine applications *Int. J. Nanomedicine* **9** 5415–30

[4] Reichenberger S, Marzun G, Muhler M and Barcikowski S 2019 Perspective of Surfactant-Free Colloidal Nanoparticles in Heterogeneous Catalysis *ChemCatChem* **11** 4489–518

[5] Doñate-Buendía C, Frömel F, Wilms M B, Streubel R, Tenkamp J, Hupfeld T, Nachev M, Gökce E, Weisheit A, Barcikowski S, Walther F, Schleifenbaum J H and Gökce B 2018 Oxide dispersion-strengthened alloys generated by laser metal deposition of laser-generated nanoparticle-metal powder composites *Mater. Des.* **154** 360–9

[6] Streubel R, Barcikowski S and Gökce B 2016 Continuous multigram nanoparticle synthesis by high-power, high-repetition-rate ultrafast laser ablation in liquids *Opt. Lett.* **41** 1486

[7] Ancona A, Döring S, Jauregui C, Röser F, Limpert J, Nolte S and Tünnermann A 2009 Femtosecond and picosecond laser drilling of metals at high repetition rates and average powers *Opt. Lett.* **34** 3304

[8] Doñate-Buendía C, Fernández-Alonso M, Lancis J and Mínguez-Vega G 2019 Overcoming

the barrier of nanoparticle production by femtosecond laser ablation in liquids using simultaneous spatial and temporal focusing *Photonics Res.* **7** 1249–57

[9] Wagener P and Barcikowski S 2010 Laser fragmentation of organic microparticles into colloidal nanoparticles in a free liquid jet *Appl. Phys. A* **101** 435–9

[10] Doñate-Buendia C, Torres-Mendieta R, Pyatenko A, Falomir E, Fernández-Alonso M and Mínguez-Vega G 2018 Fabrication by Laser Irradiation in a Continuous Flow Jet of Carbon Quantum Dots for Fluorescence Imaging *ACS Omega* **3** 2735–42

[11] Oron D, Tal E and Silberberg Y 2005 Scanningless depth-resolved microscopy. *Opt. Express* **13** 1468–76

[12] Zhu G, van Howe J, Durst M, Zipfel W and Xu C 2005 Simultaneous spatial and temporal focusing of femtosecond pulses. *Opt. Express* **13** 2153–9

[13] Yogesh G K, Shuaib E P, Roopmani P, Gumpu M B, Krishnan U M and Sastikumar D 2020 Synthesis, characterization and bioimaging application of laser-ablated graphene-oxide nanoparticles (nGOs) *Diam. Relat. Mater.* **104**

[14] Li X, Wang H, Shimizu Y, Pyatenko A, Kawaguchi K and Koshizaki N 2011 Preparation of carbon quantum dots with tunable photoluminescence by rapid laser passivation in ordinary organic solvents *Chem. Commun.* **47** 932–4