Green Synthesis of Sub-10 nm Gold Nanoparticles by two-step Laser Irradiation

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Abstract: Size control of laser synthesized gold nanoparticles in different solvents is reported. Our two-step green-synthesis approach employs only the fundamental harmonic of a Nd:YAG laser at kHz repetition rates for sub-10 nm nanoparticles production. **OCIS codes:** (140.3390) Laser materials processing; (160.4230) Nanomaterials.

Introduction

Nanoparticles (NPs) have gained attention in the past years due to their unique chemical and physical properties related to electric field enhancement and electronic confinement near the particle surface [1,2]. There are many ways for the synthesis of nanoparticles and most of them rely on chemical reduction routes giving rise to surface contamination and toxic substances that may hinder several applications. In this respect, special attention has been given to the green-synthesis of nanomaterials [3], and laser ablation plays a major role in this field [4]. Laser ablation is considered an effective alternative for it uses neither chemicals as reactants nor stabilizers as control agents for the production of NPs. The present study shows a way of controlling NPs´ size and distribution through a two-step irradiation process for the production of sub-10 nm NPs. This two-step consists of a first irradiation of the target, for colloid production, followed by irradiation of the colloid aiming at size reduction. It is important to point out that only the fundamental harmonic of a Nd:YAG laser (200ns, 1kHz) is used in the process leading to high NPs production yield in different solvents.

Experimental Details

NPs were prepared by laser ablation of an Au metal plate (>99.99%) placed on the bottom of a glass vial filled with the desired solvent. A Nd:YAG laser was used (Quantronix, Model 117) emitting 200ns pulses @ 1064nm with maximum energy of 3 mJ/pulse at 1kHz. The laser was focused on the target 1mm below the liquid surface with a spot size of 40 μm, leading to a fluence of 75 J/cm^2. The target was randomly moved for 2 minutes in the focusing plane for homogeneous surface illumination during laser ablation. The target was weighted before and after laser ablation for measuring the Au mass present in the colloid and to estimate Au NPs concentration. For the second step, freshly prepared colloids were put in a standard 10mm optical path cuvette and irradiated by the same laser with times varying from 20s to 600s. Care was taken in order to focus the light beam slightly below liquid level, and the liquid was stirred so to achieve self-focusing of the beam.

The absorption spectra were measured by an Ocean Optics USB2000+ spectrometer, 200-1050nm, and 1nm resolution. Dynamic Light Scattering (DLS) was measured with a Microtrac model Nanotrac Ultra NPA-252. Transmission electron microscopy (TEM) for the micrographs of NPs was performed with a JEOL JEM 2010-200 KV transmission microscope.

Results

In Fig. 1(a) we present DLS results for Au NPs produced in isopropyl alcohol (IPA). The purple curve represents the sample after the first step, and the pink curve relates to the colloid obtained in the second step, after 10000 shots. Mean diameter (d) and dispersion (w) of the solution obtained after the first step are d = 20.4nm, and w = 12.5nm. After the second step, the most prominent diameter for fragmented NPs is d = 6.0 nm, with w = 1.7nm. The TEM micrograph of the fragmented nanoparticles is shown in Fig. 1(b). Similar size reduction results can also be achieved in other solvents such as water, tetrahydrofuran and propylene glycol. In the second step, we use the laser to further irradiate the solution produced in the first step. This process leads to size reduction of NPs. Figure 2 shows the evolution of Au NPs´ mean size and size distribution as a function of the number of laser shots. The production rate in IPA at 1 KHz was measured to be 1mg/min, whereas for water it is around 0.1mg/min.

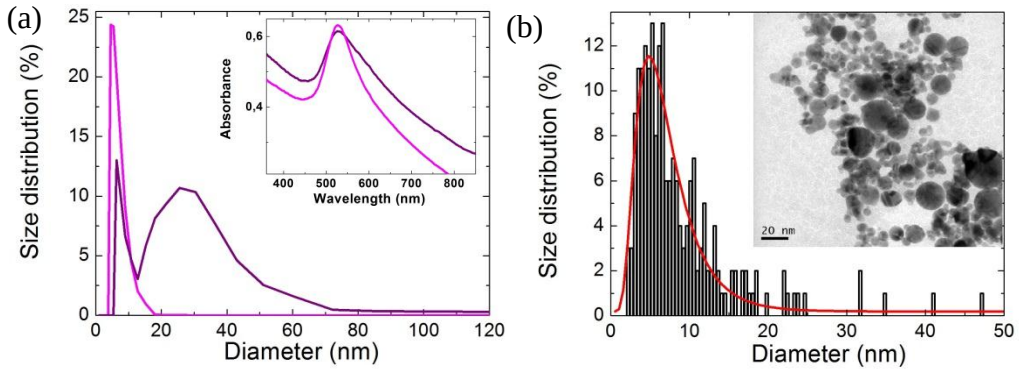

Fig. 1: (a) DLS number distributions corresponding to Au NPs produced by first step laser ablation in isopropyl alcohol after 2 minutes at 1 kHz, (purple curve), and in the second step after 10000 shots (pink curve). Inset: absorption spectra of samples before (purple), and after (pink) colloid irradiation. (b) TEM image and histogram of the colloid obtained in the second step after 10000 shots. A log-normal function (red line) was adjusted to the data with d = 6.3 nm, and w = 0.5 nm.

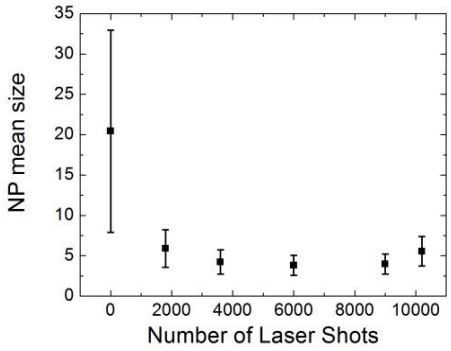

Fig. 2: DLS results of colloids measured after the second step with increasing irradiation times: evolution of size and dispersion (indicated as error bars) as a function of laser shots in isopropyl alcohol.

Discussion and Conclusions

In our proposed two-step ablation technique, the first step leads to NPs with large sizes and broad dispersions (Fig. 1a), which could be related to coalescence of hot nanoclusters in the solution environment, a process discussed by several authors concerning both the use of Ti:Sapphire lasers [5] and Nd:YAG lasers [4]. In order to reduce size and dispersion, we use a second step to further fragment the particles (Fig. 1b and Fig. 2). Note that changes in the absorption spectra in Fig. 1(a) are compatible with size reduction [5]. Coulomb explosion plays a key role in this process, as proposed by several groups [4-6]. What makes our approach unique is that only the fundamental harmonic is necessary which, because of the larger pulses (200ns), leads to beam self-focusing and sequent multiphoton absorption. Together with simplifying the process, our approach also has the advantage of larger NP production rates when compared to the ones obtained by Ti:Sapphire and low repetition rate Nd:YAG lasers.

References

[1] M. A. El-Sayed, “Some Interesting Properties of Metals Confined in Time and Nanometer Space of Different Shapes,” in Acc. Chem. Res., Vol. 34 (American Chemical Society, 2001), pp. 257- 264.

[2] S. Eustis and M. A. El-Sayed, "Why gold nanoparticles are more precious than pretty gold: Noble metal surface plasmon resonance and its enhancement of the radiative and nonradiative properties of nanocrystals of different shapes," in Chem. Soc. Rev., Vol. 35 (Royal Society of Chemistry, 2006), pp. 209-207.

[3] J. A. Dahl et al, “Toward Greener Nanosynthesis” in Chem. Rev Vol. 107 (American Chemical Society, 2007), pp. 2228-2269.

[4] V. Amendola and M. Meneghetti, "Laser ablation synthesis in solution and size manipulation of noble metal nanoparticles," in Phys. Chem. Chem. Phys., Vol. 11 (Royal Society of Chemistry, 2009), pp. 3805-3821.

[5] S. Besner, A. V. Kabashin, M. Meunier, "Two-step femtosecond laser ablation-based method for the synthesis of stable and ultra-pure gold nanoparticles in water," in Appl. Phys. A., Vol. 88 (Springer, 2007), pp. 269-272.

[6] S. Besner, A. V. Kabashin, F. Winnik, M. Meunier, "Ultrafast laser based “green” synthesis of non-toxic NPs in aqueous solutions," in Appl. Phys. A., Vol. 93 (Springer, 2008), pp. 955-959.