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Photo-fragmentation of selenium powder by Excimer laser ablation in liquids

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ABSTRACT

Laser ablation in liquids is especially adapted to produce nanoparticles free of any contamination as suited for biological and medical applications. A KrF Excimer laser delivering an UV light at 248 nm and operating at low fluence ($F \sim 0.5$ J/cm^2) was used to irradiate a micro-sized powder of selenium dispersed into a de-ionized water solution. To avoid any agglomeration of the selenium nanoparticles during the irradiation, surfactants (SDS and CTAB) were added to the solution and their efficiency was compared. The concentration of surfactants had to be chosen around the critical micellar concentration to produce small selenium nanoparticles (< 60 nm). Moreover, SDS shows better mono-disperse size distribution compared to CTAB. Finally, photo-fragmentation is found to be more efficient than bulk thermal ablation to produce very small selenium nanoparticles (less than 10 nm).

1. Introduction

Selenium (Se) is a p-type semi-conductor from the chalcogen family which has different crystallographic structures: trigonal, rhombohedral, monoclinic, cubic, orthorhombic and amorphous [1–3]. This material has an energy bandgap of ~1.79 eV and can therefore exhibit a photovoltaic action by converting sunlight into electricity [4]. As a consequence, it has been identified as an energy-critical element-defined as a chemical element that is required for emerging sustainable energy sources and that might encounter supply disruptions-by the American Physical Society and the Materials Research Society [5,6]. Recent papers show that amorphous selenium has a lot of advantages in numerous applications, such as avalanche solid state imaging devices [7], X-ray detectors [8], and high sensitivity photodetector [9]. The interest of the scientific community for Se-based nanoparticles is now increasing a lot due to its photovoltaic and biological properties. Compared to bulk, Se nanoparticles show size and shape effects on its physical properties due to the increasing surface to volume ratio at small sizes and quantum confinement. On the biological point of view, although it is toxic if adsorbed in large amounts, Se is essential for life as a trace element [10]. Moreover, Se nanoparticles are anti-bacterial [11–13] and have shown strong anti-cancer effect both in vitro and in vivo [14]. Nowadays, the conventional synthesis roads allowing the generation of Se nanoparticles are chemical-based methods [15,16]. However, there exist also biological ways to produce Se nanoparticles using bacteria respiration to reduce selenate and selenite into elemental Se [17–19]. Nevertheless, other methods are more and more explored such as Pulsed Laser Ablation in Liquids (PLAL) [20–22]. The advantages of PLAL in comparison with conventional chemical-based methods are the non-contamination of the nanoparticles by chemical agents, the low cost equipment due to the absence of vacuum chamber and the easy collection of the nanoparticles after the synthesis, into a colloidal solution, which provide a stable storage of the nanoparticles. The synthesis of Se nanoparticles by PLAL has already been reported using a Nd:YAG laser at 1064 nm [13–23], 532 nm [13] and 355 nm [13], a copper vapor laser at 511 nm and 578 nm [24], and a KrF Excimer laser at 248 nm [25]. In this last experiment [25], the nanoparticles were produced in de-ionized water by direct ablation of a bulk pellet of selenium. In this work, we irradiated a micro-sized powder of selenium dispersed in de-ionized water using the same laser as described in Ref. [25], a KrF Excimer laser operating at 248 nm. The goals of this paper are 1) to demonstrate the higher efficiency of photo-fragmentation versus the bulk thermal ablation in terms of size reduction, 2) to study and compare the effect of surfactants (SDS – sodium dodecyl sulfate, CTAB – cetyltrimethylammonium bromide) on the size distribution of selenium nanoparticles produced by photo-fragmentation.

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2. Experimental details

Trigonal Se powder of high purity ($\geq$ 99.999%, Alfa-Aesar) was used as target material and dispersed by ultrasonic homogenization in a cell filled with 0.4 cm^3 of de-ionized water. The solution was mixed with a magnetic stirrer all along the process. The solution was irradiated using a nanosecond laser (ATLEX SP300i, KrF Excimer laser, pulse duration ~6 ns) at 248 nm wavelength during 15 min, 30 min and 45 min at 100 Hz repetition rate (Fig. 1). The laser is integrated into an Optec Promaster workstation especially devoted for micro-fabrication and was used here into a non-conventional way for photo-fragmentation at relatively low fluences F ($F \leq 0.5$ J/cm^2). To compare with other experiments, a higher energy density ($F \geq 5$ J/cm^2) is generally used for nanoparticles synthesis [26–32]. A correct focalization of the UV beam is very important for an efficient generation yield of nanoparticles whereas a collimated beam is preferred with a NIR beam [33]. Here, the total energy is modulated by a UV attenuator and focused by a UV lens, directly on the powder at the bottom of the cuvette, to reduce the spot size to a 250×250 μm^2 square reaching then a fluence value around $F \approx 0.5$ J/cm^2. The solutions were then centrifuged at 6000 rpm for 25 min to separate micron size particles from nanoparticles ($D < 150$ nm) [34,35]. UV–vis–NIR spectrophotometer (CARY 5G, Varian) was used to measure the absorption spectra of the colloidal solutions. The size of the colloids was measured by Dynamic Light Scattering, DLS (Nano-ZS Zetasizer, Malvern) and by Transmission Electron Microscopy (TEM) using a Philips CM200 microscope working at an acceleration voltage of 120 kV. For TEM analysis, a droplet (0.1 cm^3) of each solution was deposited on a commercial copper grid coated with an ultra-thin full carbon film in order to investigate the morphology of the nanoparticles. Finally, the crystal structure of the nanoparticles was investigated by Raman spectroscopy (Senterra micro-Raman, Bruker) operating at 785 nm and 1 mW.

3. Results and discussion

3.1. PLAL in pure de-ionized water

Optical absorption measurements were performed on the as-prepared solutions since the bumps in the absorption spectra provide useful information on the size of the particles [15]. Fig. 2 shows the absorbance of Se colloidal solutions obtained after irradiation of a micro-sized Se powder for 30 min and 45 min in de-ionized water, with F=0.5 J/cm^2. In Fig. 2a, a comparison is done between the irradiation of a bulk pellet and the micro-sized powder; both irradiated exactly in the same conditions: 30 min of irradiation, 100 Hz of repetition rate, 0.4 cm^3 of de-ionized water and same fluence F=0.5 J/cm^2. It is clear from Fig. 2a that the photo-fragmentation process is more efficient to produce smaller nanoparticles compared to bulk thermal ablation. To explain this observation, let us describe the physics behind the formation of

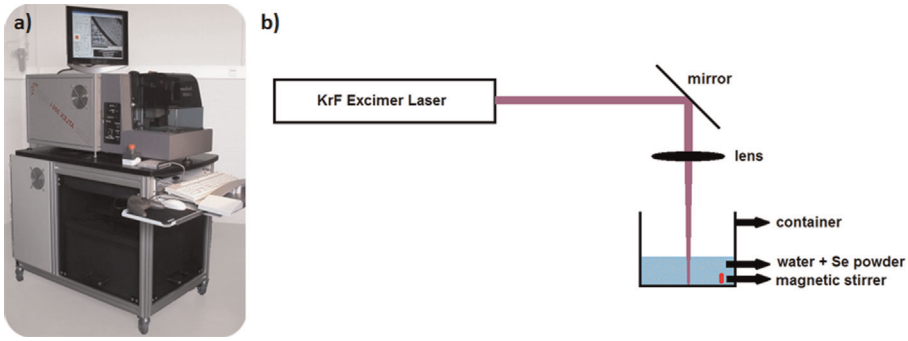

Fig. 1. (a) Photo of the Optec Promaster workstation containing the KrF Excimer laser. (b) Sketch of the experimental setup.

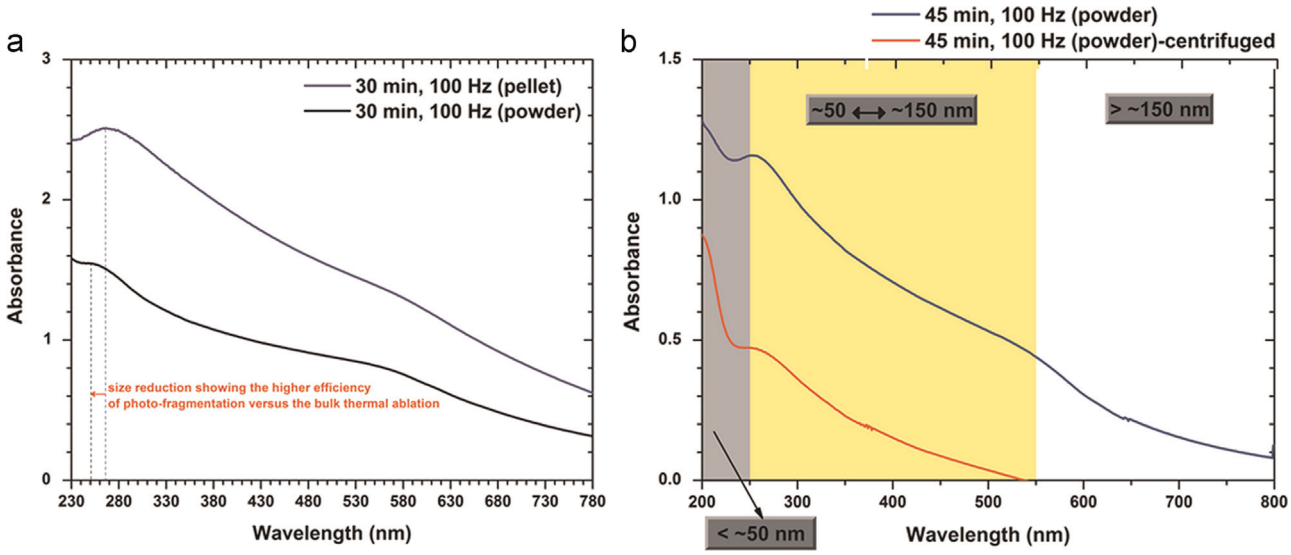

Fig. 2. Absorbance spectra of different colloidal solutions of selenium nanoparticles obtained in de-ionized water after (a) 30 min of irradiation and (b) 45 min of irradiation. (a) Comparison of the absorption of two selenium colloidal solutions, one obtained after 30 min of irradiation of a bulk pellet at 100 Hz and the other one obtained exactly in the same conditions by irradiating a micro-sized powder. (b) The absorbance of two selenium colloidal solutions obtained both after 45 min of irradiation at 100 Hz but one is non-centrifuged while the other is centrifuged at 6000 rpm for 25 min. Let us note that de-ionized water is theoretically transparent at the irradiation wavelength, 248 nm.