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Full Length Article

Size control of nanoparticles by multiple-pulse laser ablation

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ABSTRACT

Bare nanoparticles synthesized by laser ablation in water have found their application in catalysis, spectroscopy and biomedical research fields. In this perspective, how to efficiently produce stable nanoparticles with controllable size is an important topic and has attracted a lot of interests. Here, we introduce a multiple-pulse laser as the ablation source. By changing the number of sub-pulses, the average size of nanoparticles can be tuned in a broad range from ~120 nm to ~4 nm. The demonstration in this article may offer a new approach to fabricate ultrafine nanostructures and also help the scientific study of the mechanism in laser ablation.

1. Introduction

Synthesis by laser ablation in water has been well-known as a green technique in the preparation of a library of nanoparticles (NPs) with the scale spanning from several nanometers to sub-micrometers. Based on a same experiment setup, a variety of nanomaterials can be fabricated, including metals, alloys semiconductors, oxides, organic compounds, etc. [1–5]. The low cost of system, the good purity and uncontaminated surface of the products provide a good access to their broad applications [6–9].

Given the easy execution by laser ablation, how to improve the controllability of NPs would be the next challenge. Many efforts have been made to govern the NPs versatility, and varying laser parameters is a most common method among others [10–12]. For instance, NPs with larger average size and size distribution are usually obtained by increasing pulse energy [13,14]; tuning wavelength to the absorption of already formed NPs is favorable to a decreased average size and a broadened distribution [15,16]; the pulse duration has been recognized as another important influencing factor on NPs' size and shape [17]; and the geometrically configuration of laser and target materials is also proved to have positive effect on the size-control of NPs [18,19]. However, the vast majority of previous works prefer laser sources with relative low repetition rate, like no more than 1 kHz (i.e. the pulse interval >0.1 ms) [2,9,11]. On one hand, low repetition can avoid the cross interference between successive pulses, and simplify the job of analysis afterwards. On the other hand, due to the limitation of pulse energy, the productivity would be diminished for higher repetition [20,21]. Since the threshold for material removal is typically in the range of 1–10^3 J/cm^2, for lasers with repetition of the scale of MHz, the required laser power has to be much more than 30–3000 W for an effective ablation, which is hardly realized for most lasers. Although in some researches the threshold was satisfied by high-power lasers, only foams or clusters were obtained because of the relative low pulse fluence [22,23]. The experimental evidence for MHz-laser ablation in producing well-dispersed nanoparticles and their impact on size control are still missing.

In this study, we introduce a multiple-pulse picosecond fiber laser as ablation source. The influence of pulses with 20 MHz repetition rate is investigated, and strong size dependence is observed when the sub-pulse number is altered. This work provides a new perspective to manipulate the NPs by ablation process.

2. Material and methods

Colloid gold NPs were synthesized by placing a gold cylinder target (99.99%) on the bottom of a 20 ml vessel and immersing it with 18 MΩ deionized water. The level of water over the target was about 4 mm. The laser beam was focused perpendicular to the surface of the target through the liquid surface by a 160 mm focal length plano-convex lens. The laser energy above the liquid could be tuned from 0 to 6 μJ, for a fluence up to about 0.8 J/cm^2. A

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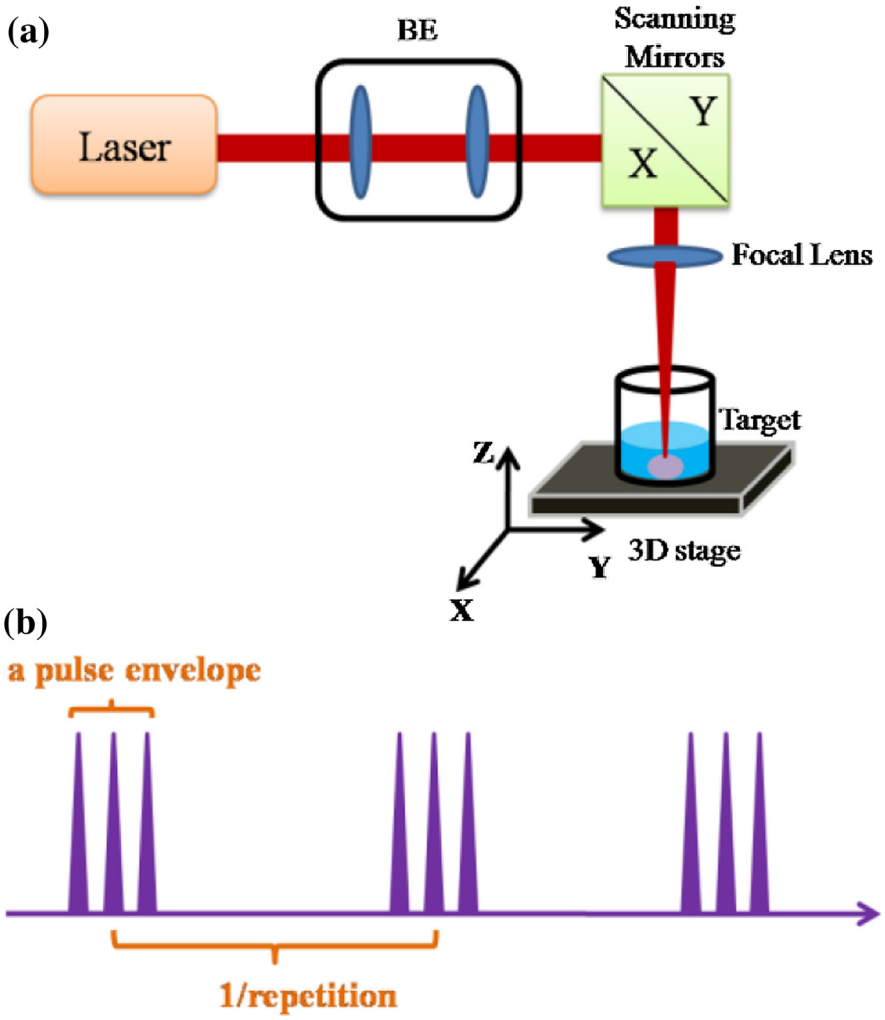

Fig. 1. (a) Scheme of the experimental setup. BE: beam expander. (b) Sketch for a multi-pulse laser with 3 sub-pulses in an envelope.

pair of scanning mirrors was used at a line speed of 100 mm/s with 0.2 ms/step. The vessel was held by a 3D stage, so its lateral and axial position could be adjusted. The experiment setup is sketched in Fig. 1(a).

The laser ablation source worked at the wavelength of 1064 nm with pulse duration of 20 ps and fundamental rate of 20 MHz. To maintain sufficient pulse energy, the laser was modulated by an acoustic optical modulator (AOM) to suppress a portion of pulses. The left pulses for each period were regarded as a pulse envelope, and the number of pulse in it could be altered [24]. The modulating repetition was 100 kHz, which determined the time interval of adjacent pulse envelope to be 10 μs. Fig. 1(b) presents a sketch for the resultant multiple-pulse laser sequence. The interval between "sub-pulses" (i.e. pulses in an envelope) was 50 ns and the output energy of all the pulses were the same.

Prior to synthesis, the gold target was washed with deionized water and pre-irradiated for a few minutes to remove possible oxidation film on it. The working distance of lens was determined by spectrometer where brightest spark was obtained. The 3D stage was then fixed and all the experiments below were practiced under the same condition, so that the influence of the focus could be ruled out. The ablation time for each sample was 10 min unless otherwise stated. All the colloids were afterwards transferred to a 5 ml vessel with lid.

The extinction spectra of gold colloid were recorded by a UV–vis spectrometer (Lambda 1050, PerkinElimer), and the morphology of single NP was characterized by TEM measurement performed at JEOL JEM-1200EX system operating at 300 kV. The calculation of size distribution based on TEM images were analyzed by Nanomeasure software.

3. Results

Fig. 2(a) presents a TEM image of gold NP produced by the laser with sub-pulse number N = 1 and pulse energy of 2 μJ. From the spacing between adjacent lattices in Fig. 2(b), we can confirm that the generated NPs were gold crystal. Under the same settings, we also practice time-dependent laser ablation. Fig. 2(c) displays the comparison between NP colloids ablated for 1 h and 16 h. In the inset panel of Fig. 2(c), the color contrast between the two is obvious. It was understood as more material was ablated into the water after longer-time fabrication, which was verified by the mass loss for the target bulk after ablations. It has been reported the ratio of the extinction at the SPR peak (A_{SPR}) to the extinction at 450 nm (A_{450}) in dependence of the logarithm of the particle diameter in the range from 5 nm to 80 nm (corresponding to SPR peak from ~520 nm to ~550 nm) [25]. Thus for a clearer comparison in Fig. 2(c), we plot both SPR spectra by normalizing them to 450 nm. It can be seen that after extending the ablation time from 1 h to 16 h, although the SPR peak is slightly blue shifted, the ratio A_{450}/A_{SPR} is decreased, which is attributed to an increase of the mean size of the NPs. This result is in conflict with previous research, in which