Optics & Laser Technology 49 (2013) 156–160

Contents lists available at SciVerse ScienceDirect

Optics & Laser Technology

journal homepage: www.elsevier.com/locate/optlastec

Fragmentation of the gold nanoparticles using femtosecond Ti:Sapphire laser and their structural evolution

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ARTICLE INFO

Article history:
Received 20 July 2012
Received in revised form
12 December 2012
Accepted 1 January 2013
Available online 29 January 2013

Keywords:
Metal nanoparticles
Laser ablation
Surface plasmon resonance

ABSTRACT

This paper reports the production of gold nanoparticles (NPs) with controlled morphology in an aqueous solution of sodium dodecyl sulfate (SDS) by Ti:Sapphire laser. When nanostructures were exposed to an additional laser irradiation/exposure at a particular wavelength corresponding to resonant excitation of surface plasmons or to an interband transition, a considerable size reduction of NPs from 78 nm to 15 nm has been achieved. This can simply be defined as size refining of NPs by a two-step laser ablation. The relationship between supercontinuum (SC) emission and absorption spectrum of gold NPs has been explored. Additionally the transformation of gold NPs into fractal-like structures has been examined. At longer exposure periods, it is observed that there is a tendency of assembling of NPs into one-dimensional (1d) nanostructures.

1. Introduction

Due to their unique size-dependent optical, physical, and chemical properties, metal nanoparticles (NPs) have become increasingly popular in a variety of applications including biosensing, imaging, NP-enhanced Raman scattering, catalysis and data storage [1]. Plasmonic properties of silver and gold NPs in visible region show a sharp and distinct optical response, which makes them potentially useful in optoelectronics [2] and sensor applications [3,4]. Chemical methods such as sol-gel, controlled precipitation and solvothermal are well established methods for synthesis of various NPs. In addition to chemical methods Henglein et al. [5] used laser ablation of metal target in liquid medium as a novel method to synthesize nanomaterials with improved purity [6].

The pulsed laser ablation process is quite simple, completely adaptable with different solvents and can lead to production of high purity materials despite being more expensive than other synthesis routes [7]. Use of lasers has been accepted as a versatile tool for the synthesis of nanomaterials due to their extraordinary properties; can be efficiently transmitted through all solid, gas and liquid media and its energy can easily be concentrated into a very small area using optical focusing elements [8].

When a solid target is irradiated by a femtosecond laser, radiation energy is absorbed by the material, followed by the ejection of atoms/small atomic clusters [9]. NPs produced usually have a wide size distribution with a size range of 10–100 nm due to fast coalescence and agglomeration of ablated species [10]. Control of the particle size is an important requirement since exciting physical and chemical properties which NPs exhibit are size-dependent. One of the main problems is change of the primary NP size due to fast agglomeration just after the particle formation [11] as once the particles are formed; it is a rather difficult task to alter their size [12]. It is still a challenge to obtain a suitable method for synthesis route for metal NPs with narrow size distribution and stability over a long period of time [13]. A technique called "laser-assisted size-control" has been applied to different materials using nanosecond and femtosecond lasers at various wavelengths to produce fine and monodispersed NPs [12,14,15]. Following pumping radiation, primary NPs evaporate or fragment which leads to finer particle size [1,16].

In order to explain the subsequent reduction of the size of nanoparticles, two main mechanisms have been recommended; photothermal evaporation model and Coulomb explosion model [17]. For example, Koda et al. [18] observed a change in the shape of gold nanoparticles where they suggest the photothermal evaporation which causes the fragmentation of nanoparticles via melting and evaporation as the main mechanism.

On the other hand, Coulomb explosion model assumes the ejection of electrons to generate multiply ionized NPs that undergo spontaneous fission due to charge repulsion [19]. Kamat et al. [20] concluded from a picosecond photoabsorption spectroscopy study that size reduction is a result of fragmentation caused by the Coulomb explosion of the photoionized metal nanoparticles. Mafune et al. [21] have indicated that when the gold nanoparticles are

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http://dx.doi.org/10.1016/j.optlastec.2013.01.003

irradiated with high intensity laser pulses, many electrons which leave the gold nanoparticles can be observed in the solution. From the charge state of the particles, they estimated that such highly charged particles can be fragmented into the smaller ones by the Coulomb repulsive forces.

Further studies to explain fragmentation mechanisms, several studies have also been reported in order to determine the femtosecond laser absorption mechanism that causes the fragmentation. Besner et al. [10] mentioned three different absorption mechanisms such as; direct absorption of the laser radiation, absorption of energy of the white continuum and interband resonant multiphoton absorption where a particular attention has been drawn to a white light emission; supercontinuum (SC) spectral width which covers absorption band energy of the gold nanoparticles [10].

Videla et al. [22] have concentrated on the effect of SC radiation on the fragmentation of gold NPs in deionised water; giving an analysis of the main optical mechanisms responsible for fragmentation of gold nanoparticles by a femtosecond laser irradiation where they have used two different sources of SC radiation. The first one is the direct SC radiation produced by an external sapphire crystal and the second one is the SC radiation produced via nonlinear interaction of IR femtosecond pulses with nanoparticles. They observed that SC radiation produced via nonlinear interaction has a larger bandwidth extending to blue than the one produced with crystal. They concluded that under similar conditions SC generation in water seems to have an important role over fragmentation of gold NP samples.

In a previously published study, we have shown that, during the production of NPs from a metal target in liquid media, large NP size distribution was obtained due to interaction of NPs with the femtosecond laser pulses [16]. It was found that direct absorption would be the dominant mechanism during the second step when the NP colloidal solution was re-irradiated with a wavelength which is in the absorption band range of nanoparticles.

In addition to size reduction effects, laser irradiation may lead to rearrangement and assembling of NPs into further nanostructures including wire or web like structures [23,24]. Tsuji et al. [23] have observed a formation of the silver nano-size wire structures that have a width between 10 and 100 nm and at lengths more than 1 μm in addition to fragmented particles in irradiated colloidal solutions. Mafune et al. [24] have also shown that using "laser-assisted size reduction" method nano sized networks of gold are produced by a proper choice of laser fluence and the sodium dodecyl sulfate (SDS) concentration. They claimed that size of the gold nanonetworks increases with the number of the laser shots [24]. Generation of network structure of gold directly from the laser ablation of gold plate immersed in water has also been reported by Chen et al. [25]

This paper reports results on the production and size reduction of gold NPs in a liquid environment. Plasmonic evolution of the gold nanoparticles produced in aqueous solution of SDS using the fundamental wavelength of femtosecond Ti:Sapphire laser for different processing times has also been evaluated. The whole process is carried out in liquid which would prevent any possible nanoparticle loss into atmosphere, leading to a virtually constant productivity.

2. Experimental

The production and size reduction of gold NPs have been carried out in two steps using a pulsed Ti.Sapphire laser beam (800 nm) (Quadronix IntenC laser), which operated at 1 kHz repetition rate with a pulse width of <130 fs at a 2.5 mJ/pulse maximum laser beam output. The first step involves focusing 6 mm diameter laser beam with a 600 μJ energy/pulse onto a gold target using a plano-convex lens with a focal distance of 100 mm. Production of gold NPs was carried out in 50 ml of distilled water and sodium dodecyl sulfate (SDS) (1.10^{-3} M) solution for 30 min. In the second step, only 10 ml of the solution containing gold NPs was re-irradiated at different time periods of 10, 50, 90 and 130 min. The measured pulse energies 870 μJ of the Ti:Sapphire laser beam were focused to the middle of the solution using a 50.2 mm lens. A magnetic stirrer was used to ensure a homogeneous particle distribution during both steps. UV-visible extinction spectra of the colloidal solutions were recorded using Varian Cary – 50 UV-Visible spectrophotometer. A Scanning electron

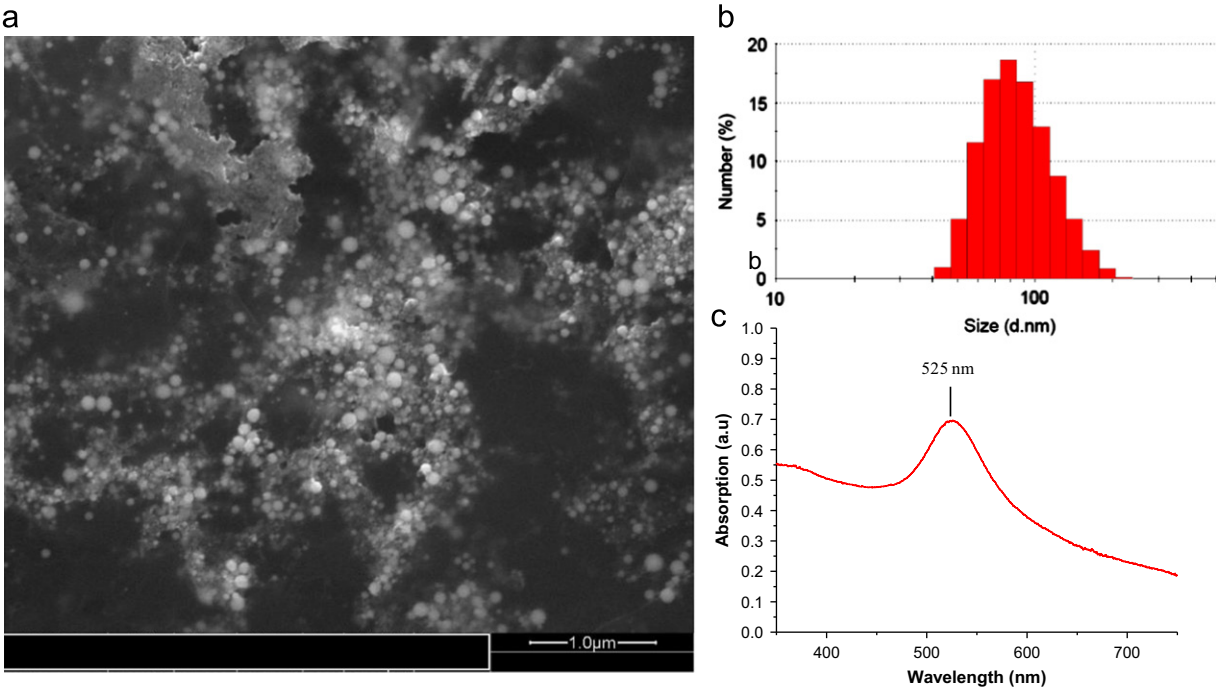

Fig. 1. Agglomerated gold nanoparticles produced using ultrashort Ti:sapphire laser beam in aqueous solution of SDS (a) SEM image (b) Size distributions of the NPs, and (c) absorption spectrum.