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On-line characterization of gold nanoparticles generated by laser ablation in liquids

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Abstract

Size of nanoparticles is an important parameter for their applications. To develop the system for the on-line nanoparticle characterization during their production by a laser, the laser ablation chamber that allows measurement of the surface plasmon resonance spectra during nanoparticle generation process has been designed and fabricated. The mean diameter of nanoparticles was determined using their absorption spectra acquired in the real-time during the ablation experiments. The results were compared with the TEM images analysis and observed differences in size are discussed. The technique was applied to investigate the effect of additional laser irradiation on size distribution in gold colloids prepared by laser ablation in water and in aqueous glucose solution.

Keywords: laser ablation; gold nanoparticles; on-line nanoparticles characterization.

1. Introduction

The laser ablation technique is one of the contaminant-free physical methods developed last two decades [1-8]. It is important to note that laser ablation in liquids provides much better opportunities to manipulate the size and other properties of nanoparticles. In particular, ablation in liquids enables to control the size and size distribution of nanoparticles by the addition of various chemically active compounds into liquid solutions.

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The compounds bind to the surface of newly synthesized nanoparticles and, thus, prevent them from coalescencing and reduce the final nanoparticle size [9]. For example, a reduction of the nanoparticle size was achieved by the use of aqueous solutions of oligosaccharides (β-cyclodextrin) [10, 11] and biopolymers (polyethylene glycol, PVP) [12, 13]. The long chains of organic molecules prevented the particles from coming close to each other. Nevertheless, the problem of the fabrication of mono-dispersed nanoparticles without reaction byproducts has not been completely solved and new approaches need to be developed.

In this study we report results on the synthesis and characterization of Au nanoparticles (NPs) produced by laser ablation of a gold plate immersed in distilled water and aqueous glucose solutions. The motivation of such research lies in the practical great potential applications of noble metal nanoparticles in biotechnology, chemical catalysis, novel types of electronic and optical devices. For such applications, the particles should be stable, with well-defined small size and with narrow size distributions. Gold nanoparticles with dimensions less than 30 nm are particularly suited for these applications because of their chemical stability and a presence of a resonant surface plasmon excitation in the visible spectral region (around 520 nm). In particular, these nanoparticles can be used as efficient and selective optical markers to diagnose different biological objects.

For the on-line nanoparticle characterization during their production, a special laser ablation chamber has been developed. The chamber allows measurement of the surface plasmon resonance spectra during nanoparticle generation process. The mean diameter of nanoparticles was determined using their absorption spectra acquired in the real-time during the ablation experiments. The results were compared with the TEM image analysis and observed differences in size are discussed. The technique was applied to investigate the effect of additional laser irradiation on the size distribution of the gold particles prepared by laser ablation in water and in aqueous glucose solution.

2. Experimental

The main component of the experimental set-up (Fig. 1a) was a laser ablation chamber (Fig. 1b) where generation of nanoparticle took place. The experiments were carried out by using of radiation of a Nd:YAG laser (LOTIS TII, LS2134D), operating in a double-pulse mode at 1064 nm (maximum pulse energy 80 mJ, repetition rate 10 Hz, pulse duration 8 ns). The delay between pulses could be changed from 0 to 100 μs.
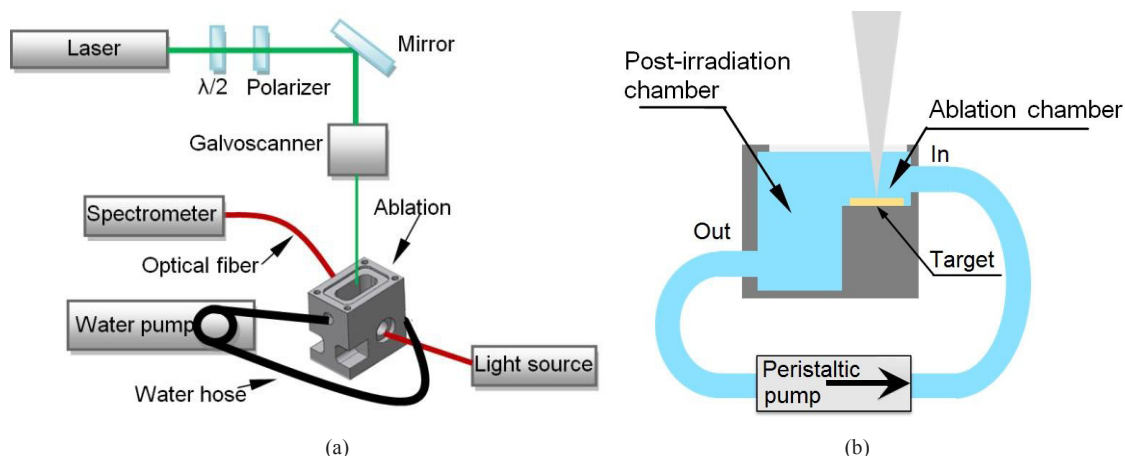

Fig. 1. (a) Experimental setup for on-line SPR detection; (b) Nanoparticle ablation chamber.

The ablation chamber was closed with optical windows. A fiber spectrometer was connected to the system for the on-line measurements of the absorption spectra during the ablation process. This kind of setup enabled us to detect changes in the plasmon resonance spectrum in every few milliseconds. Optical absorption spectra of nanoparticles were studied depending on the experimental conditions (laser irradiation parameters, such as pulse energy and interpulse delay, as well as a type of solution). The comparative analysis of UV/Vis spectra of the solution obtained at different experimental conditions was applied to find the optimal conditions for nanoparticles formation. Along with the absorption spectroscopy, transmission electron microscopy (TEM) was used for studying the size and shape distributions of the resulting nanoparticles.

3. Results and Discussion

Optical absorption spectra of gold colloidal solutions produced by the repetitive laser ablation at different delays between the pulses in distilled water and in 0.28 M aqueous glucose solution are presented in Fig. 2a and Fig. 3a, respectively. Optical absorption spectra of gold colloids exhibited the characteristic peaks of the surface plasmon resonance (SPR) on the tail of the broad band extending toward the UV-wavelength range and originating from the interband transitions in gold nanoparticles. The plasmon peak position was around 525–535 nm indicating formation of particles with dimensions of 5–30 nm in the solution. The gold nanoparticles formed in the solution were also analyzed by TEM, which are discussed below. The height of extinction at 450 nm which is known to be proportional to the concentration of the Au nanoparticles [14] was found to be dependent upon the interpulse delay, but in a different way for nanoparticles prepared in water and in glucose solution. For nanoparticles in water the extinction in the double-pulse mode was approximately twice higher compared to the single pulse mode (0 µs interpulse delay) but it is lowered at delays longer than 60 µs (Fig. 2b). There is some optimal time delay between pulses within 30–50 µs for obtaining the higher concentration of Au nanoparticles. The extinction at 450 nm of the Au nanoparticles prepared in the glucose solution also exhibited (Fig. 3b) an increase in the double-pulse ablation mode in comparison to the single pulse one, but this increase is practically independent on the interpulse delay in the time interval investigated (20–100 µs).
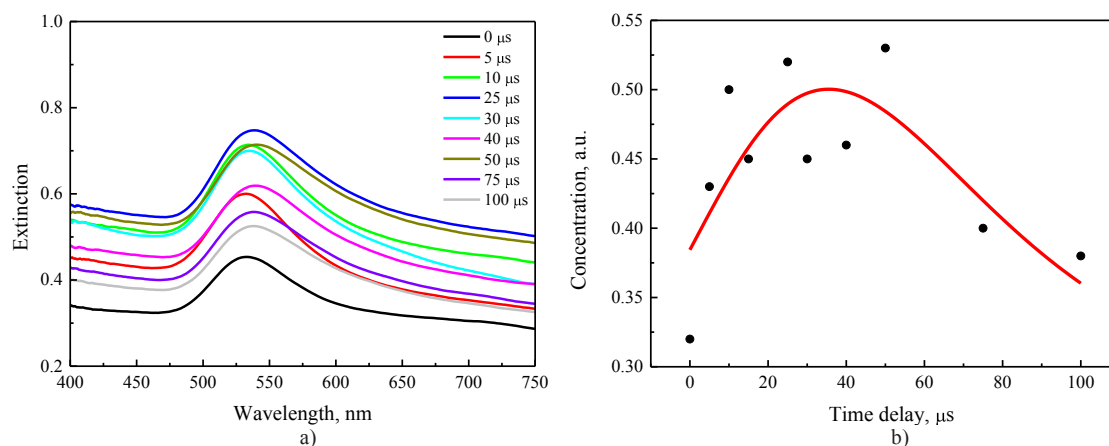

Fig. 2. Optical absorption spectra (a) of gold colloidal solutions produced by the repetitive laser ablation at different delays between the pulses in distilled water (the double-pulse regime) and final concentration of gold PNs NPs in the colloids, depending on the interpulse delay (b). Laser process parameters: pulse energy 65 mJ, repetition rate 10 Hz, irradiation time 90 s.

According to the accepted nanoparticle formation mechanism [15], the laser-ablated plume containing of gold atoms and small clusters is formed over the target during the ablation process. The ablated atoms and clusters tend to aggregate rapidly into small embryonic nanoparticles. These embryonic nanoparticles continue to grow by assembling the clusters and attachment of free atoms to the nanoparticles until all atoms in the vicinity of embryonic nanoparticles are consumed. Therefore the density of ablated species (atoms) in the gas phase plays an important role in the nanoparticles growth. Formation mechanism and stabilization of the gold nanoparticles in glucose solution has not been understood yet. Indeed, surfactants play an important role in controlling both size and the stability of nanoparticles. The growth of the particles practically ceases when the surfaces are covered with surfactant molecules. In the double-pulse ablation mode, the density of the ablated species can be changed by varying the interpulse delay. When two successive laser pulses are used for ablation the first pulse forms a gaseous cavity (bubble) from the ablation products. Having been formed after the laser pulse, the gaseous bubble continuously expands, reaches a maximum size for several hundreds of microseconds (depending on the laser pulse energy and properties of the surrounding liquid), and then collapses [16, 17]. The second laser pulse interacts more efficiently with a target surface in a relatively rarefied medium of the bubble. As a result, the amount of the ablated material and its condensation products dispersed in the liquid and available to form nanoparticles increases.
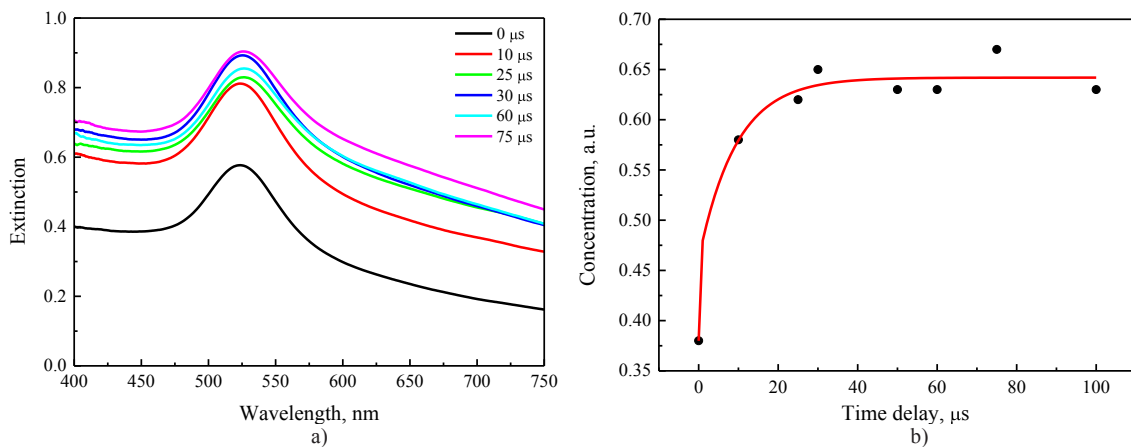

Fig. 3. Optical absorption spectra (a) of colloidal gold produced by the repetitive laser ablation at different delays between the pulses in 0.28 M aqueous glucose solution (the double-pulse regime) and final concentration of gold nanoparticles, depending on the interpulse delay (b). Laser process parameters: pulse energy 65 mJ, repetition rate 10 Hz, irradiation time 90 s.

The observed different behavior of the extinction at 450 nm vs. the interpulse delay for gold colloids in water and glucose may be connected with a different evolution of gaseous bubbles in these two solutions. The more rapid decay of a bubble in pure water can limit the ablation rate due to less efficient interaction of the second laser pulse with the target surface.

The further experiments on laser-induced modification of colloidal gold nanoparticles were carried out using the second harmonic of nanosecond Nd:YAG laser (LOTIS TII, LS2134, wavelength 532 nm). It was found that irradiation of the AuNP colloidal solution with the high-energy laser pulses using the wavelength, which is in the vicinity of the SPR of nanoparticles, induces changes in absorption spectra registered on-line with our setup. Results presented in Fig. 4, Fig. 5 and the data of Table 1 show the influence of the laser radiation on the colloidal solution of gold nanoparticles. The size of nanoparticles can be evaluated by the equation proposed by Khlebtsov et al. [18]:

$$d = \begin{cases} 3 + 7.5 \times 10^{-5} X^4, \ X < 23 \\ \left[\sqrt{X - 17} - 1 \right] / 0.06, \ X \geq 23 \end{cases}, \qquad X = \lambda_{spr} - 500$$

(1)

where all quantities are expressed in nanometers. This equation should be considered as an empirical generalization of a large volume of experimental data, which effectively account for deviations of the particle shape from sphericity.
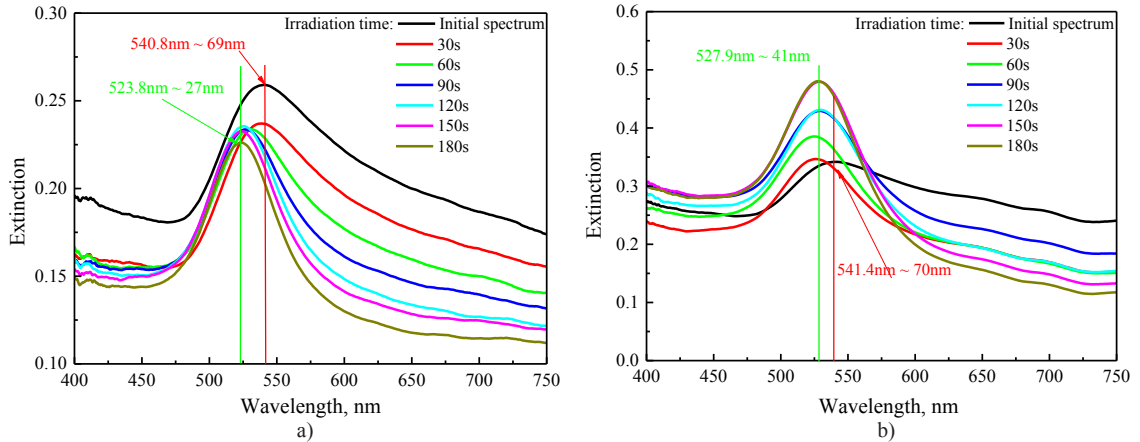

Fig. 4. Temporal variation of the absorption spectra of colloidal gold nanoparticles in water during irradiation with the nanosecond 532 nm laser for the pulse energies of: a) 16 mJ, b) 80 mJ.
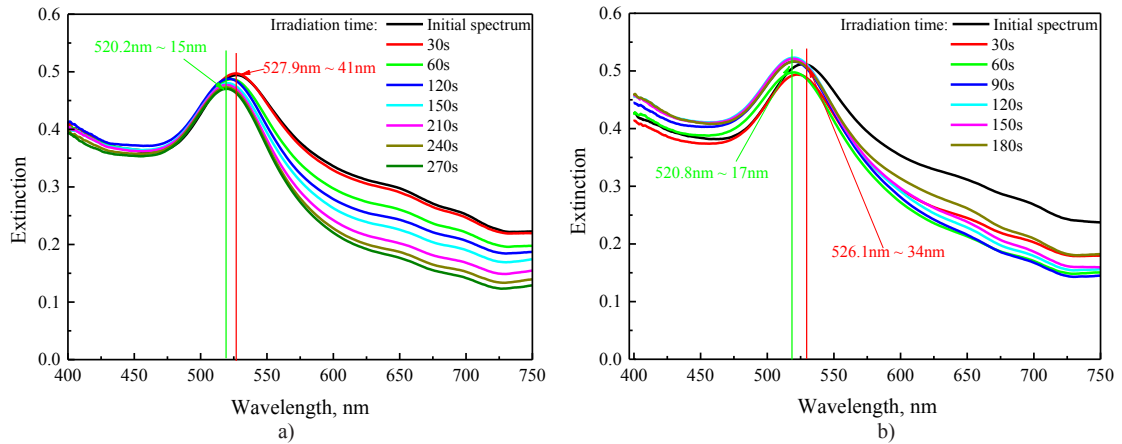

Fig. 5. Temporal variation of the absorption spectra of colloidal gold nanoparticles in glucose during irradiation with the nanosecond 532 nm laser irradiation for the pulse energies of: a) 35 mJ, b) 80 mJ.

The initial spectra in the presented figures show a strong interaction between nanoparticles in the aggregates. The absorption in the near IR region is the characteristic optical absorption due to collective plasmon oscillation of gold nanoparticles in agglomerates, in which nanoparticles aggregate without metallic contact between them [19]. During the laser treatment, large nanoparticles and agglomerates efficiently

absorb radiation and decompose into separate ones, with possible fragmentation into NPs with the smaller dimensions [20, 21]. This is confirmed by the blue shift of the SPR maximum in the absorption spectra. On the other hand, narrowing of the red tail of the plasmon resonance band can be attributed to the depletion of the particle aggregates. Additionally, after the laser irradiation with the higher pulse energy, an increase of the plasmon peak appeared in the extinction spectrum, which corresponds to the increased nanoparticle concentration in the solution. Under laser irradiation with the higher pulse energy, the higher energy is transferred to nanoparticles. Therefore, the probability to heat initial particles with subsequent melting and evaporation is increased.

Table 1. Temporal dynamics of SPR of the colloidal gold nanoparticles by irradiation with the nanosecond 532 nm laser. Optical characteristics and mean diameter of the colloidal gold nanoparticles depending on laser irradiation time.

	Nanoparticles in distilled water						Nanoparticles in aqueous glucose solution					
	Pulse energy 16 mJ			Pulse energy 80 mJ			Pulse energy 35 mJ			Pulse energy 80 mJ		
	SPR position	SPR value	Mean diameter	SPR position	SPR value	Mean diameter	SPR position	SPR value	Mean diameter	SPR position	SPR value	Mean diameter
Initial spectrum	540.8	0.26	64.6	541.4	0.34	65.7	527.9	0.49	38.4	526.1	0.51	33.6
After irradiation:												
30 s	538.4	0.24	60.4	526.1	0.35	33.6	526.7	0.50	35.2	522.6	0.49	22.6
60 s	530.2	0.23	43.9	524.9	0.39	30.2	523.2	0.49	24.8	520.4	0.50	16.0
90 s	526.7	0.23	35.2	529.1	0.43	41.3	522.5	0.49	22.2	519.7	0.52	14.3
120 s	525.5	0.24	31.9	530.2	0.43	43.9	521.4	0.49	18.7	520.2	0.52	15.5
150 s	524.4	0.23	28.7	528.5	0.48	39.9	520.8	0.48	17	519.6	0.52	14.1
180 s	523.8	0.23	26.8	527.9	0.48	38.4	520.1	0.48	15.2	520.8	0.52	17.0

The decrease of the peak height by irradiation with the lower laser fluence (16 mJ, Fig. 4a) can be interpreted that the parent loosely aggregated nanoparticles are melted resulting in formation of well-separated near-spherical particles with narrowing their size distribution.

As can be seen from the Fig. 4 and Fig. 5, the laser irradiation of gold nanoparticles in water has more impact on the optical properties of the nanoparticles. This can be explained by the fact that the initial nanoparticles in glucose solution are more stable and have the narrower size distribution because of the stabilization effect of the glucose solution.

The spectra findings were confirmed by TEM data. The size and size distribution of the nanoparticles were found to be changed after the laser irradiation. Typical TEM images for the initial Au nanoparticles and after the subsequent irradiation with the 532 nm laser beam are presented in Fig. 6. TEM images show that the initial nanoparticles were loosely agglomerated, some presented as chains of small clusters. Laser irradiation by the 532 nm laser beam resulted in formation of well-separated near-spherical particles with an average diameter of 30 nm and the narrower size distribution.
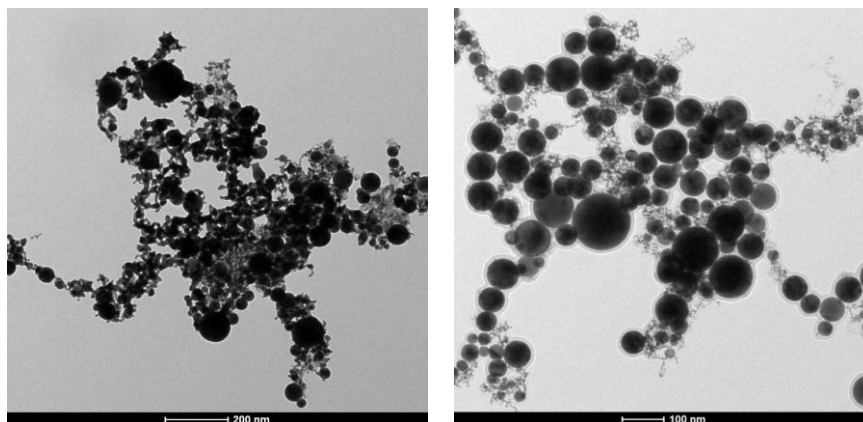
Fig. 6. TEM images of the Au nanoparticles prepared by laser ablation in water (left) and after the 180 s subsequent irradiation with the 80 mJ 532 nm laser beam (right). Mean diameter of the particles after irradiation was 27.5 nm.

4. Summary

The system for the real-time nanoparticle characterization was developed and tested in generation of gold nanoparticles using the nanosecond 1064 nm laser irradiation. The gold nanoparticles were generated in distilled water and in aqueous glucose solution using single and double pulse ablation. There was found some optimal time delay between pulses within 30–50 µs for obtaining the higher concentration of Au nanoparticles in water. It was shown that nanoparticles and their aggregates can be fragmented when the laser radiation of a wavelength, which is close to the SPR wavelength of nanoparticles, is applied to the colloidal solution. It was shown, that additional laser irradiation has more impact on the nanoparticle size distribution in water than in the glucose solution. The initial nanoparticles in glucose solution are more stable and have the narrower size distribution because of a stabilization effect of the glucose solution.

Acknowledgements

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