Femtosecond laser ablation of gold in aqueous biocompatible solutions to produce colloidal gold nanoparticles

Andrei V. Kabashin*, Michel Meunier
Laser Processing Laboratory, Department of Engineering Physics, Ecole Polytechnique de Montreal, Case Postale 6079, Succ. Centre-ville, Montreal, Quebec, Canada, H3C 3A7

John H.T. Luong
Biotechnology Research Institute, National Research Council Canada, Montreal, Quebec, Canada, H4P 2R2

ABSTRACT

Possibilities of the control of the size and size distribution of the colloidal gold particles produced by the 110-fs laser ablation from a gold plate in aqueous environment are studied. Compared to pure deionized water, significant reduction of the mean size and size dispersion of the produced particles was observed when the ablation was performed in aqueous solutions of cyclodextrins (CDs), while the efficiency of the size reduction depended on the concentration and type of the CD (α-CD, β-CD or γ-CD). In particular, ablation at 10 mM of β-CD led to a production of 2-2.4 nm particles with narrow size distribution of less than 1-1.5 FWHM, which were very stable under aerobic conditions without any protective agent present. In the UV-vis spectrum, the gold nanoparticles exhibited an absorption band at 520 nm due to the generation of plasmon resonances. The fabricated particles are of importance for biosensing applications.

Keywords: femtosecond laser ablation, gold nanoparticles, aqueous, cyclodextrins

1. INTRODUCTION

Having nanoscale size, gold colloidal particles possess several features that make them very attractive for intensive research in nanotechnology. In particular, 3-5 nm nanoparticles show a drastic decrease of the melting point[1,2] and display a highly selective catalytic activity for CO oxidation at -70 ºC.[3] In addition, 1-500 nm nanoparticles exhibit a strong dependence of transmitted and reflected spectra on the nanoparticle size and a mean distance between them due to the generation of Mie resonances[4] and to quantum size effects (below 3 nm).[5] It is now actively discussed that gold nanoparticles can serve as efficient markers for selective biological interactions after an appropriate surface modification and linking with biological objects. In this case, the remarkable optical properties of gold colloids could give important sensing parameters to measure a biological interaction.

The gold colloids are generally fabricated by a chemical method, in which a diluted metal salt is reduced in aqueous solution with a reducing reagent.[6] This method enables to fabricate gold nanoparticles in the 10-20 nm diameter range with narrow size dispersion. However, the method is not free of contamination by-products, which complicate further stabilization and functionalization of the gold surface for biological immobilizations. Alternatively, laser-induced ablation from a solid target is known as an effective method to produce metal and semiconductor nanoparticles in a controllable, contamination-free environment. In particular, this method was successfully used for the deposition in inert gases of Si-based nanostructured films, whose photoluminescence properties were very attractive for Si-based optoelectronics applications[7-10]. On the other hand, ablating metals in a liquid environment, one can effectively produce colloidal metal nanoparticles in the liquid.[11,12] However, the size distribution of the nanoparticles in liquids tends to be broadened since the aggregation process of hot ablated atoms after the ablation process cannot be easily overcome.

*akabach@email.phys.polymtl.ca; phone 1-(514)340-4711 ext.4634 ; fax : 1-(514)340-3218

Therefore, several attempts have been made for the size control, including the ablation in liquid helium[13] and an additional irradiation of produced particles by a laser beam, of which wavelength is in the vicinity of the wavelength of the surface plasmon excitation of metal nanoparticles of interest (for gold nanoparticles λ = 520-530 nm).[14,15] In addition, aqueous solutions of surfactants such as sodium dodecyl sulfate (SDS) were used to control the particle growth, [16-20] which enabled to reduce the mean size of Au and Ag nanoparticles down to 4-8 nm and to minimize the particle size dispersion down to 5 nm. However, the fabrication of monodispersed gold nanoparticles in well-controlled, biologically friendly environment and appropriate termination of the gold surface is still under question.

In this paper, we adapted a femtosecond laser technique to ablate a gold target in aqueous solutions and study the possibilities of using important, biologically compatible materials to control the size and distribution of the produced colloidal particles. The test were performed with the use of neutrally charged cyclodextrins (α-CD, β-CD and γ-CD), torus-like macrocycles built up from glucose pyranose units, which are linked by α-1-4-linkages[21]. The femtosecond laser technique was employed with the anticipation to minimize the average particle size of ablated particles due to the absence of target heating effects.[22]

2. EXPERIMENTAL SETUP

The experiments were carried out with a Ti/Sapphire laser (Hurricane, Spectra Physics Lasers, Mountain View, CA), which provided 110 fs full width at half maximum (FWHM) pulses (wavelength 800 nm, maximum energy 1 mJ/pulse, repetition rate of 1 kHz). The radiation was focused by an objective with the focal distance of 7.5 cm onto a gold target, which was placed on the bottom of a 3-mL glass vessel filled with different aqueous solutions, as shown in Fig. 1. The thickness of the liquid layer above the rod was about 12 mm.

A gold rod (99.99%) from Alfa Aesar (Johnson Matthey Company, Ward Hill, MA) with the diameter of 6 mm and the height of 6 mm was used as a target in the experiments. The ablation experiments were carried out in pure deionized water and in aqueous solutions of α-cyclodextrin, β-CD, and γ-CD, which were obtained from Aldrich and used without further purification. All solutions were prepared from high-purity deionized water. CD solutions were prepared as stock solutions in appropriate buffers immediately prior to their use. The concentration of cyclodextrins was varied in different experiments: 0.01 M, 0.001 M and 0.0001 M.

A Transmission Electron Microscope (model Philips CM30, Philips Corp.) with 0.23 nm point-point resolution was used to take the electron images of the nanoparticles in the solution. A drop of a sample solution was placed on a carbon-coated copper grid. The drop was then dried at room temperature and the procedure was repeated 3 times. Normally, the diameters of 500-1000 particles were measured and the distribution of particle size (diameter) distribution was obtained. UV-Vis spectroscopic measurements were performed using a spectrophotometer (DU-640, Beckman) and room temperature in the range of 300-800 nm with a 1-cm optimal length cuvette.

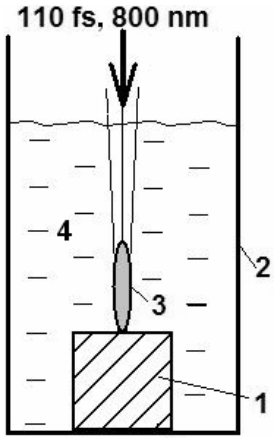

Fig. 1 Experimental setup: 1 – gold target, 2 –glass vessel, 3 – plasma plume, 4 – aqueous solution.

2. EXPERIMENTAL RESULTS

In our experiments, the ablation in liquids was accompanied by the presence of a plasma plume on the gold surface as easily observed by the naked eye. The plume intensity slightly decreased after several seconds of the ablation and then stabilized. The intensity decrease was probably related to certain absorption or scattering of the laser power by gold nanoparticles, which were formed and released to the bulk solution. However, no additional plume along the optical path due to the plasma ignition on separated gold particles was noticed. Besides, no plume was present on the water surface, suggesting that the fluence of the defocused laser beam on the surface was low enough to avoid the ignition of low threshold air optical breakdown.[23]

In pure deionized water, the ablation process led to visible changes of the solution color after several seconds into the ablation. The color was purple-red with some yellow tint. Figure 2 (a) shows a typical TEM micrograph and size distribution of gold nanoparticles obtained in deionized water at 0.8 *mJ*/pulse. Most of the particles had sizes of 40-70 nm, however, a rather broad size distribution ranging from 25 nm to 140 nm was noted. One can also reveal from the TEM micrograph that the periphery of larger particles was surrounded by small particles.

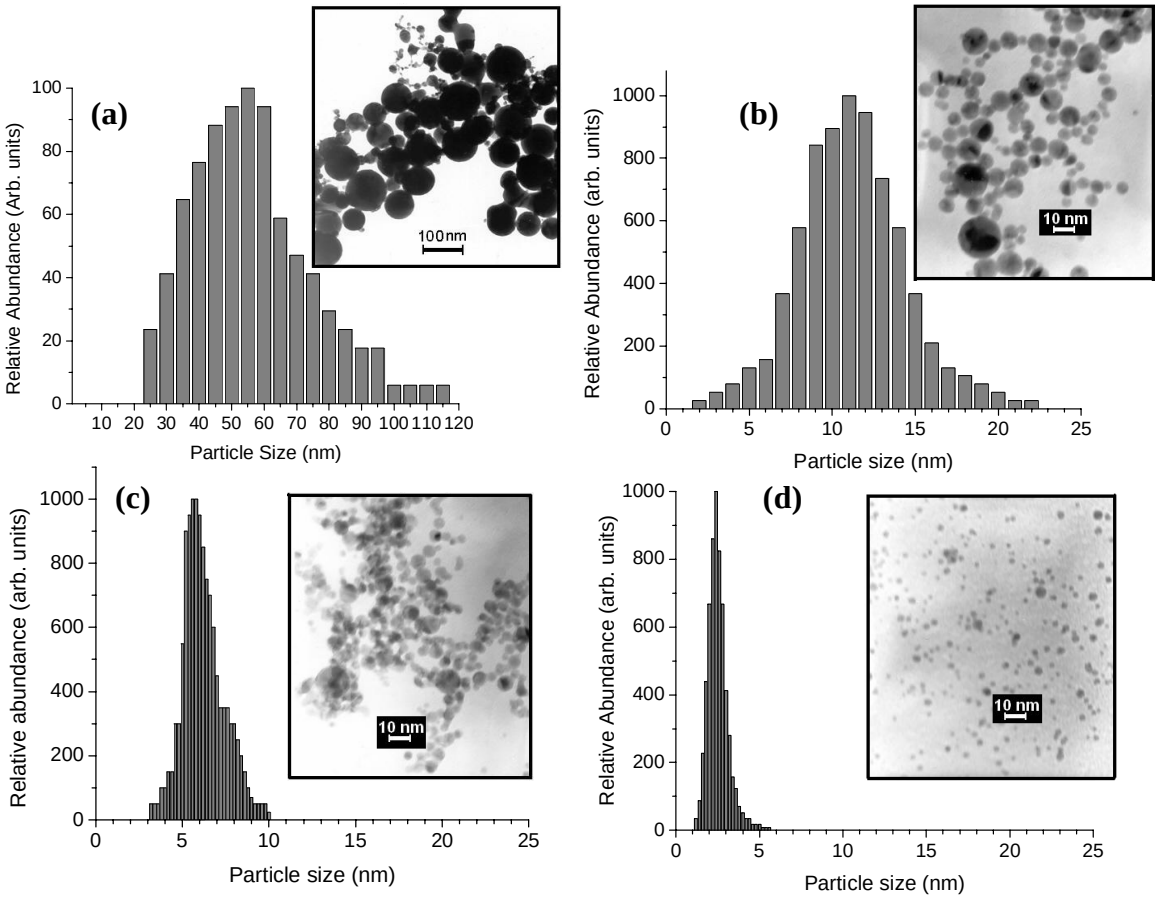

Fig. 2 TEM micrograph images and corresponding size distributions of gold particles prepared by the femtosecond laser ablation in deionized water (a) 0.0001 M β-CD (b), 0.001 M β-CD (c), 0.01 M β-CD (d). The laser energy was 0.8 mJ/pulse

However, the laser ablation in the presence of all three cyclodextrins led to quite different properties of the produced gold nanoparticles. At relatively low concentration of cyclodextrins, the process was accompanied by a deep red coloring of the solution. However, the increase of the CD concentration led to a certain decrease of the red color intensity. This was especially noticeable for 10 mM β-CD or γ-CD, which had only a pink color. An analysis of TEM micrographs clearly revealed that the presence of CDs in the solution led to a drastic decrease of the size of produced particles and their size dispersion, while the increase of the concentration of CDs reinforced the effect. As an example, Fig. 2 (b-d) demonstrates typical TEM micrographs of the produced particles and corresponding size distributions for different concentrations of β-CD. Moreover, the efficiency of size reduction depended on the type of CD. Our experiments showed β-CD provided the smallest particles with the narrowest particle size distribution, followed by γ-CD and α-CD, as one can see from Fig. 3. Ablation in 10 mM β-CD produced particles with the mean size of 2.1-2.3 nm (Figure 3 (a)) with a size dispersion less than 1 nm FWHM (Figure 3 (b)). For comparison, the laser ablation in the presence of 100 mM SDS led to much larger 4.6-8 nm particles with the dispersion of 5 nm FWHM.[16-19] Notice that chemical analysis performed in this study confirmed that not even traces of glucose, a major degradable products of CDs was present in the solution. In view of the very mild condition in laser ablation, it could be reasoned that CD molecules remained intact during the course of experiment.

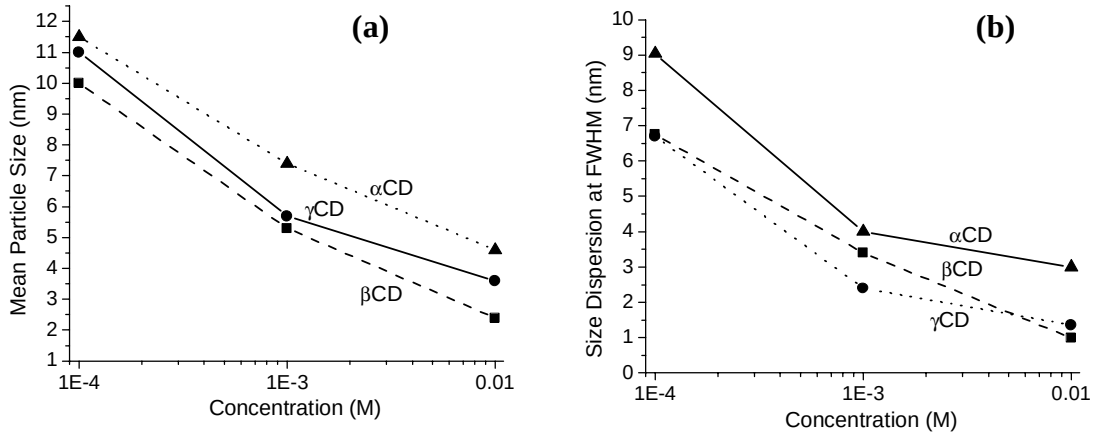

Fig. 3 Effect of the CD concentration on the resulting average particle size (a) and the size dispersion at FWHM (b).

In addition, optical absorption spectra of the samples were recorded. Just after the fabrication, gold colloids produced in deionized water and all cyclodextrins exhibited the characteristic peak of the surface plasmon resonance at 520-530 nm. In pure water, the absorbance measured at 520 nm retained only 7% of its original value after 5 days of aging in ambient conditions. Several precipitates were observed in the storage glass vial and the solution became dark blue, which confirmed that the nanoparticles continued to grow and/or aggregate with time in the solution. This behavior was due largely to the rapid increase in the attractive van der Waals force between nanoparticles as a function of their size. In contrast, gold colloids prepared in the presence of CDs exhibited good stability. In β-CD (0.1 to 10 mM in pure water), the 520 nm-peak height remained constant within this time window. The corresponding value for α-CD and γ-CD was 70% and 60%, respectively. Indeed, nanoclusters β-CD remained well dispersed in 10 mM β-CD for over 45 days with minimal loss of absorption intensity (5-7 %). This was very encouraging since all of the experiments were performed without any precaution taken, such as oxygen-free condition or under protective agents except for CDs.

3. DISCUSSION

It should be noted the mechanisms of the laser-induced ablation from a metal target and of a subsequent nanoparticle formation in aqueous environment are not yet clearly identified. However, some aspects of the phenomenon could be explained in terms of the dynamic formation mechanism suggested by Mafune and co-workers.[19] In brief, a dense cloud of gold atoms (plume) was accumulated in the laser spot of the gold target during the course of ablation. This core was made of a number of small gold atoms that were aggregated accidentally due to the density fluctuation to form embryonic nanoparticles. Even when the ablation process had been terminated, the aggregation continued at a

significantly slower growth rate until all atoms in the vicinity (~40 nm) of the embryonic nanoparticles were depleted.[19] As both ablated atoms and embryonic nanoparticles diffuse through the solution towards each other to form larger clusters, this consecutive nanoparticle growth was slow, random and could not be controlled. It has be proposed[19] that the presence of surfactants like SDS in the solution leads to a decrease of the concentration of free atoms or clusters due to the covering of their surfaces by the surfactant molecules. As a result, the growth of larger clusters decreases or stops.

A mechanism for the formation and/or stabilization of the gold nanoparticles by CDs is not yet clear. However, it was evident that CDs played a critical role in controlling the size as well as the stability of gold nanoparticles. The apolar cavity of the three CDs (internal diameter of 570, 780 and 950 pm, respectively) has been known to form inclusion complexes with various small hydrophobic molecules.[21] With such a dimension, it was very likely that a single gold atom (288 pm in diameter) could be enclosed in the CD cavity. In addition, CD molecules were also expected to bind to ablated atoms by chemisorption through multiple Au-O interactions, a mechanism similar to the binding of gold to resorcinarenes[24] to decrease the abundance of free ablated gold atoms in the plume. Embryonic nanoparticles formed in the plume became limited and had to compete with CD molecules for free ablated gold atoms in the vicinity of this region through diffusion. As CDs could form stable complexes with both free ablated atoms and embryonic nanoparticles, the consecutive particle growth due to the mutual coalescence between such objects was severely limited or terminated, particularly at high CD concentrations. This hypothesis was partly validated by the experimental data to confirm that the nanoparticle size and dispersion decreased with increasing CD concentrations. With the lowest aqueous solubility, β-CD should exhibit the strongest hydrophobic interaction with gold compared to both α- and γ-CD. Because both ablation and attachment of CD molecules to the surface of the developing Au particles took place almost simultaneously, the interplay between the kinetics of the two processes was likely the key factor that governed the average size diameter of the gold nanoparticles.

CONCLUSIONS

Femtosecond laser technique has been used to ablate a gold target in distilled deionized water and aqueous solutions of α-CD, β-CD or γ-CD in order to produce colloidal gold nanoparticles with no disturbing chemical impurities introduced. A drastic nanoparticle size reduction was recorded when the CDs were present in the solution. The gold nanoparticles demonstrated a good stability without an addition of any protective agent. To our knowledge, femtosecond laser and CDs have not been used for size control and stabilization of gold nanoparticles. This promising technique and can be extended for fabrication of other metal nanoparticles including multi-component ones with control of particle size distribution and particle morphology. The CD-modified gold nanospheres can also be used as multisite hosts for binding of hydrophobic guests in the solution.

ACKNOWLEDGEMENTS

The authors thank Dr. E. Sacher and Mr. J-P. Sylvestre of Ecole Polytechniques for several useful discussions and assistance in the laser ablation and TEM experiments. The authors also thank NSERC of Canada for financial assistance.

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