

Biofunctionalization of laser-ablated gold nanoparticles

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ABSTRACT

This paper discusses the influence of gold oxidation on functional properties of gold nanoparticles. Pulsed laser ablation in aqueous media was used for production of partially oxidized gold nanoparticles. This technique ensured a gradual oxidation of gold during laser ablation process. The interaction of gold nanoparticles with silanized glass induced a red-shift of the gold plasmon resonance peak in absorption spectra. An in-depth study of the plasmon-related peak as a function of ablation time gave information about the bonding efficiency of Au nanoparticles to amino-groups. We demonstrated that the gradual oxidation of gold nanoparticles clearly affected their functional properties.

Keywords: laser ablation, gold nanoparticles, plasmon resonance, biofunctionalization

1 INTRODUCTION

At present, there is a growing interest for fabrication of nanomaterials in liquid environment, due to their applications in bioimaging and biosensing. In particular, metal nanoparticles attract a significant attention of scientific community regarding their optical plasmon-related properties [1]. Numerous investigations are devoted to the chemical synthesis of gold and silver colloids. However, chemical methods are often related to the presence of contamination which could limit the biological applications of these nanoparticles [2].

Pulsed laser ablation is well known as a versatile method for production of nanostructured surfaces and nanoparticles [3,4]. The variation of ablation conditions and environment allows to produce nanoparticles of controlled size and chemical composition [5]. Pulsed laser ablation in liquid media (PLAL) has been suggested as an alternative method for synthesis of gold colloids free of contaminants [6]. A large number of publications has been devoted to the study of PLAL of gold colloids but, to the best of our knowledge, none mentions their biofunctional properties.

In this work, we investigated the biofunctional activity of gold nanoparticles (NPs) produced by laser ablation in sodium citrate solution. The efficiency of the linkage between Au nanoparticles and amino-groups is investigated

through plasmon-related peaks in absorption spectra. The influence of the oxidation of gold on the efficiency of bonding of gold to amino-groups was also examined.

2 EXPERIMENTAL

Gold target immersed in a 0.17% sodium citrate solution was ablated with a pulsed nanosecond KrF laser (wavelength 248 nm, pulse width 17 ns, energy 50 mJ/pulse, frequency 20 Hz) during various periods of time (10sec, 30 sec, 60 sec, 120 sec and 240 sec). The laser radiation was focused with a 7.5 cm lens on a gold target placed at the bottom of a 3 ml glass vessel. The thickness of liquid layer above the target was approximately 1 cm. The liquid was constantly mixed during ablation with a magnetic stirrer in order to avoid the “bubbling effect” created by laser-target-liquid interaction [7]. During the ablation process, nanoparticles are synthesized by ablation and oxidized by simultaneous irradiation of colloidal suspension. It was recently shown that PLAL in sodium citrate solution prevents the formation of nanoparticle agglomerations characteristic of PLAL in water [8]. This observation determined the choice of the solution used in this work. During the ablation process, clear orange colloidal solutions were obtained.

A silanized glass covered with amino-groups was then immersed in colloidal solution in order to collect the gold nanoparticles. To stabilize the nanoparticle-amino-group bonding, the glass was maintained in solution for 24 hours.

Nanoparticles were characterized by transmission electron microscopy (TEM), X-Ray Photoelectron Spectroscopy (XPS) and absorption spectroscopy. For TEM measurements, a drop of colloidal solution was dried at room temperature on a carbon-coated copper grid. XPS measurements were performed on a drop of solution which was dried on a Si substrate. The absorption spectra of colloidal solutions in disposable UV-cuvettes and spectra of nanoparticles deposited on silanized glass were measured using a Varian UV-Vis spectrometer in the 450 - 700 nm spectral region.

3 RESULTS AND DISCUSSION

Figure 1 shows a typical TEM image of gold nanoparticles synthesized by laser ablation in a 0.17% sodium citrate solution during 240 sec. Nanoparticles have

a round shape and are isolated. The absence of agglomerations makes these nanoparticles appropriate for potential biological applications. The average size of gold nanoparticles measured directly from TEM images was found to be equal to (8 ± 2) nm.

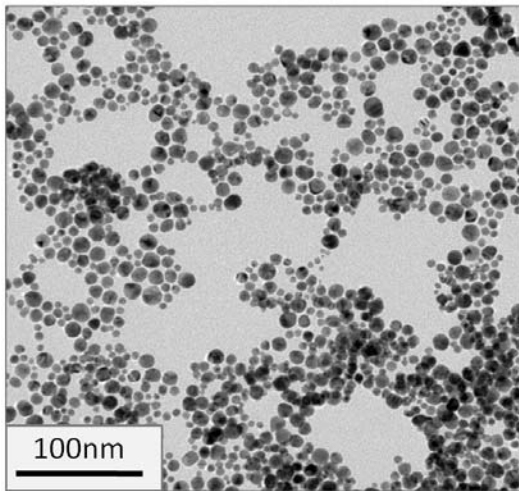


Figure 1: TEM image of gold nanoparticles synthesized by laser ablation during 4 min (248nm, 17ns, 50mJ/pulse, 20Hz).

Figure 2-a shows the absorption spectra of gold nanoparticles in solution for various ablation times from 10 to 240 sec. In case of colloidal gold solutions, a typical plasmon-related peak is observed with maximum at 528 nm for 10-sec sample. The peak position shifts to higher energy with increasing ablation time. According to our previous observations of laser-irradiated gold nanoparticles, this shift can be associated with the gradual gold oxidation rather than with the size modification of nanoparticles [9]. It was recently observed that irradiation time variation from 10 to 300 sec (20Hz, 50 mJ/pulse, pulse width 17 ns) results in 5% to 28% of oxidized gold in the sample. In our case, XPS measurements of laser-ablated gold nanoparticles for 10-sec and 240-sec samples (not shown here) revealed that the oxidation degree of colloids was equal to 5% and 21%, respectively. This result corroborated the hypothesis about the blue-shift of the absorption peak due to the gold oxidation. Also, we observed an additional peak at 640 nm in the absorption spectrum of the 10-sec sample. According to our previous studies [9], this peak was most probably due to the presence of nanoparticle agglomerations in colloidal solution. Such spectral modifications due to nanoparticle agglomerations were found to be easily formed for the samples prepared at short ablation times. At high ablation times, additional peaks disappeared (Figure 2-a).

Figure 2-b shows the absorption spectra of gold nanoparticles fixed on silanized glass, for ablation time variations from 10 sec to 240 sec. The peak maximum for 10-sec sample was observed at 536 nm and underwent a blue-shift with increasing ablation time. The absorption peaks are slightly broadened with respect to the initial

spectra of colloidal solutions which can be explained by agglomeration of gold nanoparticles on silanized glass surface.

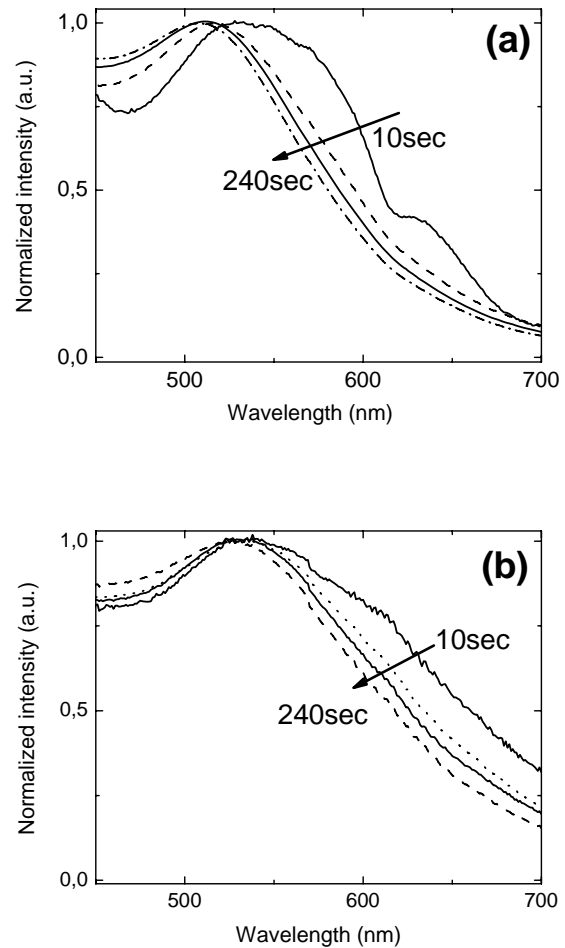


Figure 2: Absorption spectra of (a) colloidal gold solutions and (b) gold nanoparticles on silanized glass for various ablation times (from 10 sec to 240 sec).

We also observed a red-shift of the absorption spectra of gold nanoparticles due to the binding of gold nanoparticles to amino-groups [10]. Figure 3 demonstrates the absorption spectra of gold nanoparticles “in solution” and “on glass” for the sample synthesized during 60 sec. In this Figure, the baseline is extracted from the absorption spectra.

The plasmon-related peak position for colloidal gold in solutions and on glass is plotted in Figure 4 as a function of ablation time. We observed a peak position displacement from 528 nm to 506 nm for gold nanoparticles in solution and from 536 nm to 525 nm for gold on glass, for ablation times increasing from 10 sec to 240 sec, respectively. A constant red-shift of 10-15 nm due to the binding of gold to amino-groups was observed for all investigated ablation times.

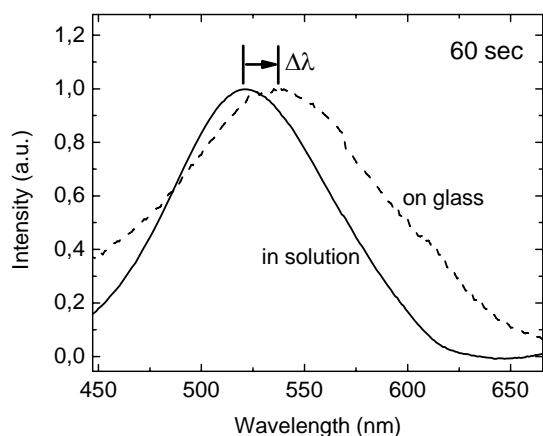


Figure 3: The absorption spectra of gold nanoparticles in solution and on silanized glass, for gold colloids prepared by laser ablation during 60 sec at 20 Hz.

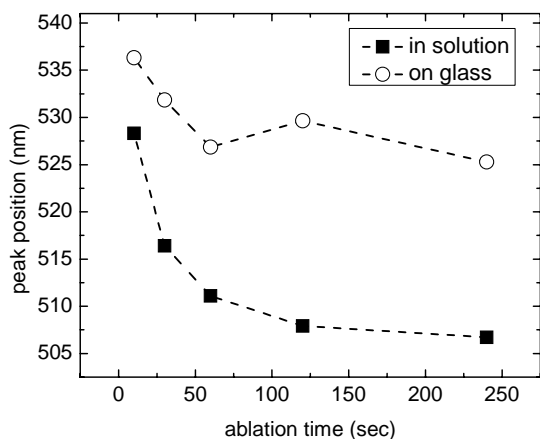


Figure 4: The plasmon-related peak position in the absorption spectra of gold colloids in solution and on glass as a function of ablation time.

We have also studied the relative intensity of the absorption spectra of gold nanoparticles “in solution” and “on glass”. Figure 5 shows the intensity ratio of plasmon-related peak of gold colloids “on glass” vs “in solution”. We associated the evolution of this ratio as a function of ablation time to the bonding efficiency between Au nanoparticles and amino-groups. It is important to note that the absolute value of this ratio does not indicate the relative concentration of Au nanoparticles in solution and on glass. The intensity of the absorption spectra could be influenced by the bonding of Au NPs to amino-groups. The only information that we could extract from this experiment was

the dependence of the “capturing efficiency” as a function of ablation time and oxidation degree of gold NPs.

The intensity ratio reached its maximum at low ablation times (10 sec and 30 sec). Thus, we concluded that maximum possible quantity of nanoparticles was trapped by amino-groups of silanized glass. At 60 sec, a drastic decrease in “capturing efficiency” occurred and the ratio was equal to about 20% for ablation times of more than 120 sec. This behaviour can be explained by the reduced binding capacity of Au nanoparticles due to the oxidation of gold surface during laser ablation/irradiation process.

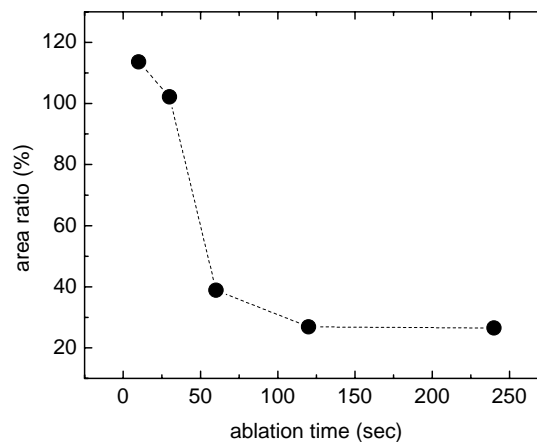


Figure 5: Relative intensity of the absorption spectra of Au nanoparticles “on glass” vs “in solution” as a function of ablation time.

4 CONCLUSION

We have synthesized Au nanoparticles using pulsed laser ablation in aqueous media. Sodium citrate solution was used to eliminate the presence of Au nanoparticle agglomerations characteristic of laser ablation in water. The simultaneous ablation/irradiation process induced partial gold oxidation depending on ablation time. Blue-shift of the absorption peak due to the gold oxidation was observed. Optical properties of Au nanoparticles collected on silanized glass covered with functional amino-groups were studied. A 15-nm red-shift of absorption spectra was associated with the binding of Au colloids to amino-groups. A dependence of binding efficiency as a function of ablation time was associated with the gradual gold oxidation due to the laser irradiation of colloids. Our results have clearly shown that the gradual oxidation of gold nanoparticles affects their functional properties.

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