Dynamics of laser excited colloidal Au nanoparticles conjugated with cysteine

Alexandra FALAMAS[1], Nicoleta TOSA[1,*] and Valer TOSA[1]

[1] National Institute for Research and Development of Isotopic and Molecular Technologies, 65-103 Donath, 400293, Cluj-Napoca, Romania

Corresponding author: nicoleta.tosa@itim-cj.ro

Abstract

The aim of this study was to investigate experimentally the ultrafast dynamics of Au colloidal nanoparticles when excited with femtosecond laser pulses. Also, their interaction with zwitterionic type molecules, such as cysteine and cystine is discussed. The time of the ground state population recovery of Au nanoparticles depends on the pump wavelength, with the highest value at the surface plasmon resonance excitation. In the same pump-probe conditions, the excited states life time of S-functionalized Au nanoparticles with zwitterionic molecules increases due to their chemisorption on the gold surface.

1 Introduction

The development of highly-sensitive, cost-effective, nanosensors for the detection of chemical and biological agents is of great interest in many areas, such as biomedical, forensic, biotechnology. Gold nanoparticles have attracted a great deal of interest due to their distinct physical and chemical properties that make them exceptional candidates for building biomedical nanosensors [1]. Colloidal Au nanoparticles can be synthesized rather easy and cheap, under a wide variety of shapes and sizes. The attachment of an analyte to the Au nanoparticles induces modifications of their physico-chemical properties, which can generate a detectable signal [2]. Functionalized nanoparticles with biologically interesting molecules can be used for applications in life sciences, chemical sensing, biomedicine.

Cysteine plays a critical role in various cellular functions, metabolism and even detoxification. It has a strong tendency to adsorb onto the surface of metals and it can be used to stabilize gold nanoparticles under different physiological conditions. Cysteine is widely used for the investigation of proteins and other biomolecules, which can be exploited by the attachment of a peptide to the surface of nanoparticles [3, 4].

In this study, we used a pump-probe method to investigate the picosecond dynamics of laser excited colloidal gold nanoparticles in aqueous solution, as well as their interaction with cysteine and cystine. The Au nanoparticles functionalized with these active sulphur containing molecules can enhance their selectivity for later reactions with other molecules, due to their -NH2, -COOH, SH groups of cysteine or S-S bonds of cystine [5].

2 Experimental section

Gold colloids were prepared by photochemical reduction of tetrachloroauric (III) acid ((HAuCl$_4$, 99.5%) in water (16.8 mM) with sodium citrate and polystyrene sulfonic acid (PSS), in order to limit the size of colloidal gold nanoparticles [6]. The reactants were purchased from Merck and used as received. The solution was firstly prepared by mixing tetrachloroauric (III) acid and sodium citrate with polystyrene sulfonic acid, and then it was irradiated by UV light at 254 nm for 20 minutes. The obtained solution was subjected to repeated centrifugal purification to obtain a concentrated colloidal solution.

The cysteine and cystine were dissolved in water to obtain $5 \cdot 10^{-3}$ M solutions. For each pump-probe experiments 20 µL of cysteine, respectively cystine aqueous solution was added to the Au colloid and the transient absorption spectra were recorded. The final Au colloid--sample ratio was 1:0.9.

The pump-probe set-up (Light Conversion Co. Ltd.) consists of a diode pumped Yb:KGW femtosecond laser delivering 180 fs laser pulses at a repetition frequency of 80 kHz, 75 nJ energy per pulse at 1030 nm wavelength. The laser is used to pump a collinear optical parametric amplifier delivering the wavelengths used here: 456, 480, 539, and 600 nm. The 539 nm pump used for the pump-probe experiments had a power of 20 mW, while at 456 nm the power was 35 mW.

In our pump-probe set-up, the pump pulse used to excite the sample is obtained in the optical parametric amplifier, and the probe pulse is a white light continuum (480-800 nm) produced by focusing 10% of the 1030 nm beam into a sapphire crystal. The transmitted white light is detected using a spectrograph with a 300 l/mm grating combined with an array detector, which gives a spectral window of approximately 310 nm.

The collected data were fit using the global target analysis technique [7], which describes the time-dependent population of the transient states and how they are connected, following a set of differential equations:

$$\frac{dc_1(t)}{dt} = I(t) - \frac{1}{\tau_1}c_1(t)$$
$$\frac{dc_i(t)}{dt} = \frac{1}{\tau_{i-1}}c_{i-1}(t) - \frac{1}{\tau_i}c_i(t), i \neq 1 \quad (1)$$

where c_i is the time-dependent population of state i, $I(t)$ is the excitation pulse, and τ_i is the time characteristic to the population decay from the ith excited compartment.

3 Results and discussion

The bare and the functionalized Au nanoparticles (GNPs) in their appropriate solutions were characterized by UV-Vis spectroscopy. The visible absorption spectra of the GNPs solution (Figure. 1) presents a well defined peak with a maximum at λmax = 539 nm, characteristic for surface plasmon resonance (SPR) absorbance of nanometric Au particles ascribed to an average size bellow 20 nm.

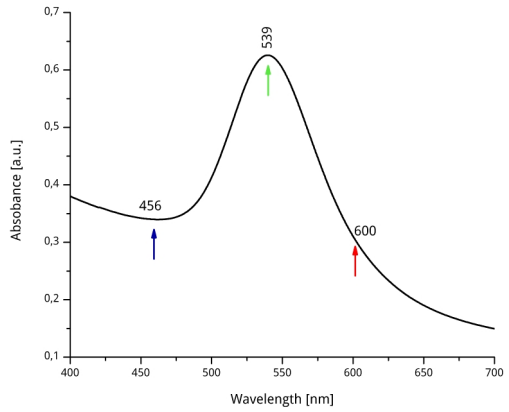

Figure 1 *UV-Vis absorption spectrum of Au nanoparticles. Arrows indicate the pump wavelength used in pump-probe experiment.*

3.1 Pump-probe experiment

The scope of the pump-probe experiment is to measure the sample absorbance differences in the presence and absence of the pump pulse. The pump pulse excites the sample and the probe pulse measures the sample transmittance. Thus, a difference absorbance signal is obtained as a function of both probe wavelength and the delay time between pump and probe pulses.

The picosecond dynamics behaviour of Au nanoparticles was investigated using three different pump wavelengths: 456, 539, and 600 nm. Figure. 2 shows the transient absorption spectra obtained at different time delays between pump and probe beams. The bleaching signal, assigned to the recovery of the ground state of the Au nanoparticles, is observed at 538 nm and recovers in less than 2 ps delay between pump and probe. In the pump-probe experiments the bleaching results from the optical excitation of the free electrons distribution within the nanoparticles. The spectra show two wings at 494 and 590 nm, respectively, assigned to the excited states of the "hot" electrons. The relaxation of the signal takes place through electron-electron scattering, and electron-phonon coupling [8].

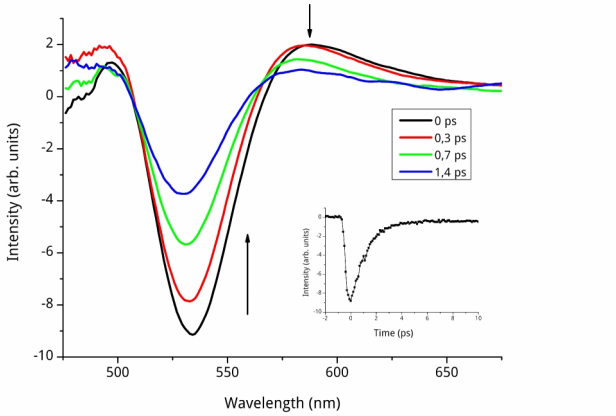

Figure 2 *Transient absorption spectra of Au nanoparticles excited with 456 nm. The inset shows the kinetics at the absorption plasmon band (539 nm).*

When processing the pump-probe data, we used a double exponential for the fitting of the kinetic traces and the same time was obtained for the bleach signal and the rise/ decay of the two wings. Therefore, we took into account only the decay of the signal for which a short time of 1.22 ps was obtained.

The Au colloidal nanoparticles were probed also using the 539 and 600 nm excitation wavelengths. A decay time of 1.30 and 1.19 ps, respectively, were obtained in these cases. This behaviour might be assigned to an increased number of nanoparticles, which absorb at 539 nm and contribute to the excited states population, compared to those absorbing at 600 or 456 nm.

3.2 Functionalization with cysteine derivatives

The Au nanoparticles were functionalized with cysteine and cystine respectively, in order to investigate the pump-probe behaviour of the nanoparticles under progressive surface coverage with S-derivative molecules. After the addition of cysteine to the colloidal solution, a decrease of the absorption maximum is recorded. In the case of cystine, a broadening of the plasmon band is also observed, as well as a weak red-shifted broad band around 800 nm. This indicates the chemisorption of cystine molecules to the Au surface and therefore the aggregation of the nanoparticles.

The functionalized Au nanoparticles were investigated using pump-probe spectroscopy for each addition of the given amount of cysteine/cystine solution. The chemisorption of the S-derivative molecules on the Au nanoparticles induced a rise of the excited states life time

in conjunction with the increase of the surface coverage. This can be assigned to additional oscillations of the free electrons in the functionalized nanoparticles induced by the newly formed S-Au bond.

4 Conclusions

The decay time of the transient absorption signal of the Au nanoparticles is dependent on the pump wavelength, with the highest time value at the surface plasmon resonance excitation. The fit of the decay signal gave a short time of 1.19-1.30 ps, assigned to both the bleaching of the ground state signal and the rise/ decay of excited states of the "hot" electrons. The covering of the Au nanoparticles surface with the S-derivative molecules increases the excited states life time, due to the S- Au bond.

5 Acknowledgement

This work was supported by the grants of the Ministry of National Education, CNCS - UEFISCDI, Romania, project number 169/25.07.2012 (project code the project PN-II-PT-PCCA-2011-3.2-0210) and project number 31/2013 (project code PN-II-ID-PCE-2012-4-0342).

References

[1] R. Bhattacharya, P. Mukherjee, *Biological properties of "naked" metal nanoparticles*, Advanced Drug Delivery Reviews, 60(11):1289-1306 (2008)

[2] P. K. Jain, I. H. El-Sayed, M. A. El-Sayed, *Au nanoparticles target cancer*, Nano Today, 2(1): 18-29 (2007)

[3] F. Wang, X. Liu, C.H. Lu, I. Wilner, *Cysteine-mediated aggregation of Au nanoparticles: The development of a H2O2 sensor and oxidase-based biosensors*, ACS Nano, 7(8):7278-7286 (2013)

[4] P. Tengvall, M. Lestelius, B. Liedberg, I. Lundstrom, *Plasma protein and antisera interactions with L-cysteine and 3-mercaptpropionic acid monolayers on gold surfaces*, Langmuir, 8:1236-1238 (1992)

[5] C. Jing, Y. Fang, *Experimental (SERS) and theorethical (DFT) studies on the adsorption behaviors of L-cysteine on gold/silver nanoparticles*, Chemical Physics, 332:27-32 (2007)

[6] F. Toadere, N. Tosa, *Functioning of the protective UV filters based on gold nanoparticles*, AIP Conference Proceedings, 1425:93-97 (2011)

[7] I. H. M. van Stokkum, D. S. Larsen, R. van Grndelle, *Global and target analysis of time-resolved spectra*, Biochimica et Biophysica Acta, 165:82-104 (2004)

[8] T. S. Ahmadi, S. L. Logunov, M. A. El-Sayed, *Picosecond dynamics of colloidal gold nanoparticles*, J. Phys. Chem, 100:8053-8056 (1996)