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## Dynamics of laser excited colloidal gold nanoparticles functionalized with cysteine derivatives



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### ABSTRACT

The ultrafast dynamics of Au colloidal nanoparticles excited with femtosecond laser pulses is investigated experimentally. The transient absorption signal presents a bleaching of the surface plasmon band and a transient absorption at the wings of the band. The kinetics of the “hot” electrons in Au nanoparticles show a fast component of around 1 ps and a slower one of approximately 300 ps. Additionally, we found that the time of the ground state population recovery of Au nanoparticles depends on the pump wavelength. Furthermore, the interaction of Au nanoparticles with cysteine and cystine is studied at different pump wavelengths. The increase of the ligand concentration produces a variation of the relaxation times, as well as a delay of the time zero kinetics due to the adsorption of the ligands to the Au surface.

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### 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. 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 make them available for applications in life sciences or biomedicine, due to the ultrafast response of metallic nanoparticles to optical stimulation. For example, it is believed that the success of tumor therapy based on gold nanoparticles is

due to the ultrafast dynamics of the electrons and the rapid conversion of the absorbed light to heat, which leads to cell death [3]. The light absorbed by the nanoparticles is transferred to the ligand/antibody and the cells environment through electron–phonon and phonon–phonon interactions. It is therefore essential to properly understand the electron dynamics in nanoparticles.

The electron relaxation dynamics in metallic nanoparticles has been recently highly investigated using transient absorption (TA) spectroscopy based on femtosecond laser pulses [4–6]. By interaction with the electric field of the laser pulse, the electrons are promoted to states above Fermi level and a highly nonthermal electron distribution is created. The first relaxation step is electron thermalization through electron–electron scattering, until a new Fermi distribution with a higher temperature is reached. This is a very fast process of about 500 fs [7,8]. The electron gas further cools down through electron–phonon coupling and phonon–phonon interactions with the surrounding medium. In this way, the excited electrons above Fermi level lose energy, causing the Fermi distribution to narrow down. Therefore, the temperature decreases and

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the system returns to ground state. The electron–phonon relaxation time was found to be size and shape independent for gold and gold–silver alloys nanoparticles [9]. The phonon–phonon decay time was found to be longer when d-band electrons are excited, compared to interband excitation [4]. When the effect of aggregation in gold nanoparticles was investigated, it was found that the electron–phonon relaxation depended on the probe wavelength [10].

In this paper, we report on the ultrafast dynamics of colloidal gold nanoparticles when excited with different pump wavelengths. Both the unmodified colloid and the functionalized one with cysteine derivatives were investigated. 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 [11,12]. We found that the kinetics of the relaxation mechanism of the “hot” electrons in Au nanoparticles show a fast component of around 1 ps and a slower one of approximately 300 ps. Additionally, we observed that the time of the ground state population recovery of Au nanoparticles depends on the pump wavelength. The functionalization of gold nanoparticles induces a delay of the time zero kinetics due to the adsorption of the ligands to the Au surface. Moreover, it was found that the electron–phonon relaxation time varies with increasing the ligand fraction in the sample.

## 2. Materials and methods

Pulses of 170 fs duration are emitted at 1030 nm wavelength by an Yb:KGW laser (Pharos, Light Conversion) at a repetition frequency of 80 kHz and 75  $\mu$ J energy per pulse. The main part of the laser pulse is used for pumping a collinear optical parametric amplifier (Orpheus, Light Conversion) yielding tunable output between 620 and 2600 nm. Additional frequency mixing units can generate second and fourth harmonics of signal and idler beams, extending the total emission range down to 250 nm.

The transient absorption spectrometer (Harpia, Light Conversion) uses the tunable pump pulse to excite the sample and a white light (WL) supercontinuum to probe it. The WL pulse is produced by focusing 10% of the 1030 nm laser beam into a sapphire crystal. The white light supercontinuum extends from 480 to 780 nm. After travelling through an optical delay line, the transmitted WL is detected using a spectrograph with 300 l/mm grating combined with an array detector. For the transient absorption experiments we used four different wavelengths: 370 nm (15 mW), 440 nm (13.5 mW), 535 nm (13.5 mW), and 660 nm (60 mW).

The UV–Vis absorption spectra were recorded on a double beam Jasco V550 UV–Vis spectrophotometer in the 190–900 nm wavelengths range with a 2 nm resolution, using 1 mm length quartz cells. Baseline corrections have been run successively in air, and distilled water.

Measurements in absorption mode were employed using distilled water as a reference.

Gold colloidal nanoparticles were prepared by photochemical reduction of tetrachloroauric (III) acid (HAuCl<sub>4</sub>, 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 [13]. 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 min. The solution was irradiated by UV light because both tetrachloroauric acid and polymer matrix are sensitive to absorption in the UV region. The completion of the process is monitored using the peak at 320 nm, corresponding to the HAuCl<sub>4</sub> absorption [14]. This peak disappears after UV irradiation, proving that the gold salt photodecomposition and neutral gold generation occurred [15]. The obtained solution was subjected to repeated centrifugal purification to obtain a concentrated colloidal solution.

The L-cysteine hydrochloride and cystine were dissolved in water to obtain  $5 \times 10^{-3}$  M solutions. For the TA measurements 15  $\mu$ L of either cysteine, cystine, or distilled water were repeatedly added to 150  $\mu$ L of Au colloid, until the same amount of ligand and gold colloid was obtained.

### 2.1. Data processing

The pre-processing of the TA signal included removal of the pump spectral range (for the 535 nm excited spectra), subtraction of pre-time zero signal from all spectra, and dispersion correction with a polynomial of second order.

For the analysis of the TA results and for obtaining the decay times of the data we performed the fitting of the kinetic traces with a double exponential function

$$y = A_1 \exp(-x/t_1) + A_2 \exp(-x/t_2) + y_0, \quad (1)$$

where  $A_1$  and  $A_2$  are the amplitudes (the number of excited particles),  $t_1$  and  $t_2$  are the decay constants, and  $y_0$  is the offset.

In order to obtain the decay times characteristic to the samples, only the middle part of the bleaching spectral region was considered for the analysis, as the kinetics of the regions closer to the wings are affected by them, especially at long delay times. In the above equation, the zero time for the signal decrease was set as the point in time corresponding to the full width at half maximum of the kinetic trace.

## 3. Results and discussion

The UV–VIS absorption spectra of the samples were measured before each TA experiment. Plotted in Fig. 1 are the spectra of the bare colloidal nanoparticles, functionalized (with cysteine and cystine, respectively) nanoparticles, as well as water diluted colloidal solution. The absorption spectra of the gold solution present a well defined peak with a maximum at 535 nm, characteristic to the surface plasmon absorption band of Au nanoparticles with an average size below 20 nm (see Fig. 2).

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