

TRANSIENT ABSORPTION OF GOLD NANOPARTICLES OF VARIOUS DIAMETERS

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The transient absorption of gold nanoparticles with an average diameter of 13 ± 5 and 48 ± 16 nm upon photoexcitation by nanosecond laser pulses has been studied. It was shown that the maximum of stationary absorption exhibits as a wide structureless band with a maximum at about 520–540 nm. The transient absorption band of gold nanoparticles with a maximum at about 430 nm has a fine structure with a frequency of maxima of 6–8 nm and it does not depend on the size of the nanoparticles. The absorption duration decreases with a decrease in the average size of nanoparticles. The lifetime of transient absorption is equal to 23 ± 2 and 19.5 ± 2 ns for large and small particles, respectively. The nanosecond lifetime of the transient absorption of Au nanoparticles is the result of a prolonged relaxation process in the “interface of Au nanoparticle–solvent molecule” system as a manifestation of hindered heat exchange with the environment.

Keywords: gold nanoparticles, plasmon, size, transient absorption, optical properties.

Introduction

The phenomenon of localized plasmon resonance is the attractive research topic in the last few decades due to the possibilities of its practical application. Plasmon nanoparticles of noble metal increase the efficiency of various optical and optoelectronic phenomena, including Raman scattering and photocatalysis, and also improve the performance of organic light emitting diodes and photovoltaic devices [1–5].

Methods of flash photolysis are used to study the dynamics of electronic excitation in plasmon nanoparticles (NPs) of metals. This method is very sensitive, it allows detecting the single NPs and studying the dynamics of fast processes.

In this method a perturbation of the electron density of metal NPs, leading to the appearance of a plasmon resonance (PR), occurs upon simultaneous photoexcitation by laser pulses and probing beam. The PR lifetime is determined by the electron dephasing process with a typical time constant of 10–100 fs. This process is the first stage in the complex dynamics of electron relaxation in metal NPs [6, 7]. In the time range from 100 fs to 1 ps, the process of electron-electron scattering occurs, which leads to the equalization of the electron temperature inside the metal NPs. Further, in the range of 1–10 ps, electron-phonon scattering occurs, which stabilizes the temperature of the electrons and the surrounding lattice. The electron-phonon relaxation decay time depends on the growth in the electron temperature, which is related to the excitation pulse power and increases linearly with the pump energy [7]. This mechanism can be used for nanoscale heat transfer from metal NPs to biological objects for photothermal therapy, biomedical imaging, etc. [8]. Phonon-phonon scattering (>100 ps) releases heat into the environment and it is the slowest process.

However, there are practically no works devoted to the study of the transient absorption of Au NPs upon nanosecond photoexcitation. The exception is the work of [9], where the transient absorption of Ag NPs of various sizes was studied during photoexcitation by nanosecond laser pulses. The dependence of the intensity and lifetime of transient absorption on the average size of the NPs, their concentration and pump energy was investigated. It has been shown that in a delayed heterophase heat exchange at the boundary of the “particle-medium” interface, the kinetics is “prolonged” up to times of the order of several tens of nanoseconds.

In this work, the transient absorption of gold NPs of various diameters in ethanol solutions was investigated. Gold NPs, due to the position of the plasmon resonance band in the green region, are more attractive for usage in biophysical and biomedical applications, for example in photodynamic and photothermal therapy [10–12], singlet oxygen generation [13, 14], etc.

1. Experiment

Gold NPs were obtained in solution by ablation of a 30 nm thick gold film. 99.999% gold was deposited on the surface of the glass substrate by magnetron sputtering method with Q150RES (Quorum Technologies Ltd.). Ablation was performed by Nd:YAG laser with $\lambda_{\text{gen}}=532$ nm, pulse duration of $\tau=8$ ns according to the method, described in [15]. To change the average diameter of the received NPs, the laser radiation energy was varied from 9.5 to 13.5 mJ. During ablation, the laser beam was focused on a target immersed in ethanol using a collecting lens. The diameter of the laser spot on the target was equal to 0.1 cm. The volume of ethanol in a glass with Au film was equal to 3 mL. The ablation time was equal to 15 minutes.

The absorption spectra of Au NPs in ethanol were measured with Cary-300 spectrophotometer (Agilent). The spectra and kinetics of transient absorption were studied by pulsed photolysis method using the LP-980 spectrometer (Edinburgh Instr.) upon excitation with the second harmonic of Nd:YAG laser (LQ215, SolarLS) with $\lambda_{\text{gen}}=532$ nm and pulse duration of $\tau=7$ ns. To measure the kinetics of transient absorption, the solution was placed in a quartz cell with an optical path length of 10 mm. The kinetics of transient absorption was recorded in the time range up to 4 μs . The plotting of the transient absorption spectra was performed by automatically scanning the kinetics with a step of $\Delta\lambda=2$ nm in the required wavelength range, followed by data slicing using L900-software (Edinburgh Instr.). The processing of individual absorption kinetics was also carried out using this software.

2. Results and discussions

Dynamic light scattering measurements (Zetasizer S90, Malvern) showed that the average diameter of the obtained Au NPs was equal to 13 ± 5 and 48 ± 16 nm (Fig. 1). The concentration of Ag NPs in the resulting solution was equal to $C_{\text{Au}}=6\cdot 10^{-10}$ and $2\cdot 10^{-10}$ mol/L, respectively. For further measurements, solutions of Au NPs with the same concentration were prepared. Images, registered in transmission mode with Mira 3LMU (Tescan) microscope have shown that the prepared NPs are spherical.

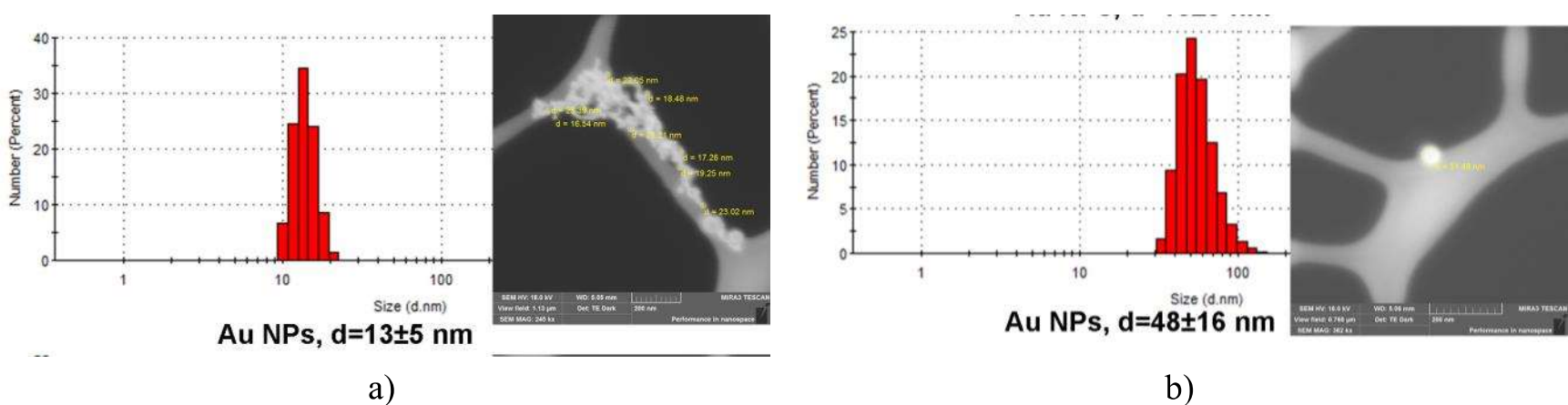


Fig.1. Size distribution and TEM images of Au NPs with various diameter.

The measured stationary absorption spectra of gold NPs in ethanol are shown in Fig. 2. It can be seen that for both types of NPs the spectrum exhibits as a wide structureless band in the region from 450 to 800 nm with a maximum at about 530 nm. Also in the spectrum appears an absorption band at about 350 nm, which refers to the absorption of d-electrons of Au [6]. The spectra of both small and large NPs do not change their shape. However, with an increase in the average diameter of Au NPs, a bathochromic shift of the absorption band maximum from 526 to 540 nm was observed. The broadening of the 48 ± 16 nm absorption band of Au NPs is also noticeable, which is associated with a greater dispersity in size of the prepared NPs.

The observed bathochromic shift of the absorption band of larger Au NPs is the result of the displacement of the boundary electrons relative to the positive ionic lattice during the transmission of the incident light through the metal NPs [16]. This results in a net charge difference at the “NP – environment” interface. In turn, this generates a Coulomb restoring force that tends to bring the system to its equilibrium state and leads to the appearance of the surface plasmon oscillations [17].

It was shown in the Mie theory [18] that when the particle size is much smaller than the wavelength of the incident light ($d\ll\lambda$), then the α polarizability of a metal NP is determined by the Clausius-Mossotti relation [16]:

$$\alpha = 3\varepsilon_0 V \left(\frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \right)^2,$$

where ε is the permittivity of vacuum, ε_m is the dielectric constant of surrounding medium, ε is the dielectric function of the metallic NPs, V is the volume of spherical NP.

Thus, it can be seen that the NP polarizability of NP is directly depends on the size of NPs and on its permittivity. The imaginary part of the permittivity, in turn, determines the absorption of light in a metal NPs [19].

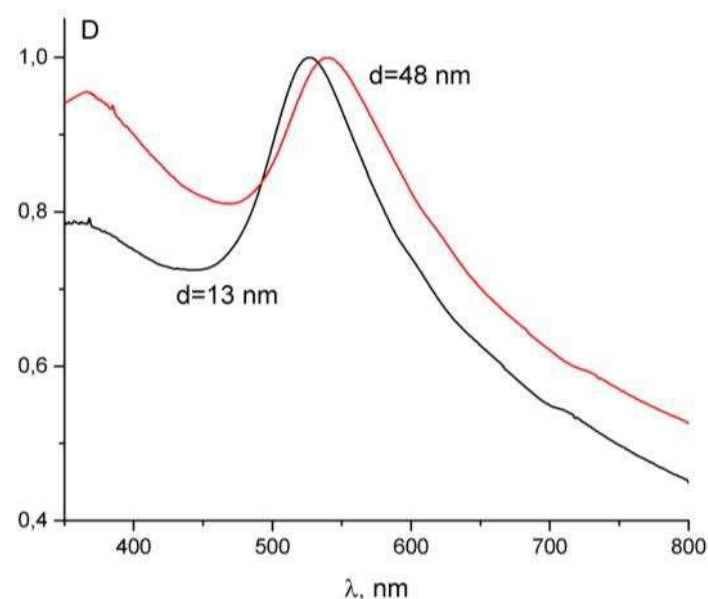


Fig.2. Stationary absorption spectra of Au NPs of various diameters.

The long-wavelength shift of the NP absorption band is associated with the dependence of the contribution of free electrons to the permittivity. The damping of the electromagnetic field, which occurs as a result of the depolarization of the light field on the surface of the particle, leads to a weakening of the Coulomb restoring force on the electron cloud. Therefore, the frequency required to excite surface plasmon oscillations will be decreased [16].

The transient absorption spectra of Au NPs with $d=48\pm 16$ nm are recorded in the region of 370–570 nm (Fig. 3). In this case, the positive part of the spectrum is located in the region of 370–500 nm with a maximum at about 420–450 nm for Au NPs. The spectrum exhibits optical density oscillations both in the positive and negative parts of the absorption curve. The frequency of the maxima is 6–8 nm. The band in the negative part of the spectrum with a maximum at about 520–530 nm coincides with the main absorption band and it is the result of a change in the population of the ground state. The measurements showed that with an increase in the delay of recording time, the structure of the transient absorption spectrum of Au NPs is retained and it practically was not changed.

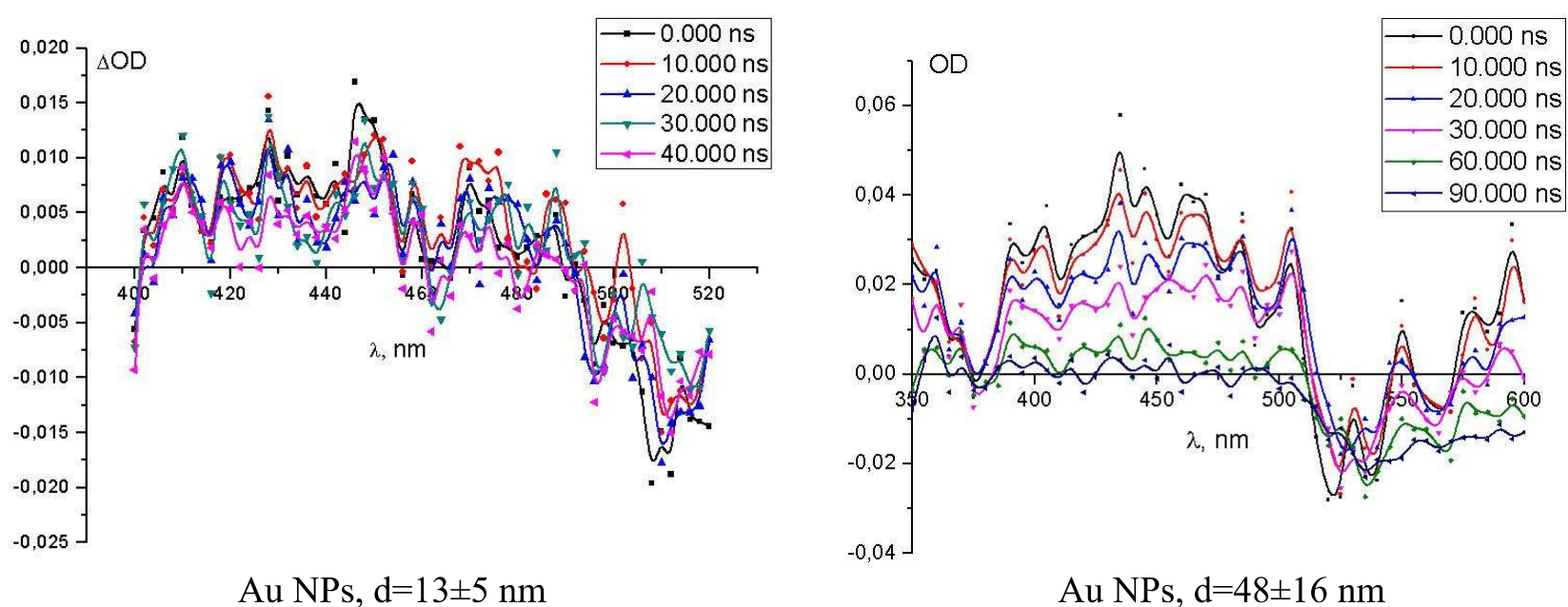


Fig.3. Transient absorption spectra of Au NPs with various diameter at different times of registration, $\lambda_{exc}=532$ nm, $\Delta=2$ nm.

The intensity of the transient absorption of NPs of larger diameter is higher. A decrease in the particle diameter does not change the shape of the transient absorption band, while the fine structure of the spectrum is also retained. At a recording time of more than 60 ns, the absorption signal is almost completely decayed. The transient absorption kinetics of 48 ± 16 nm Au NPs recorded at different wavelengths are shown in Fig. 4.

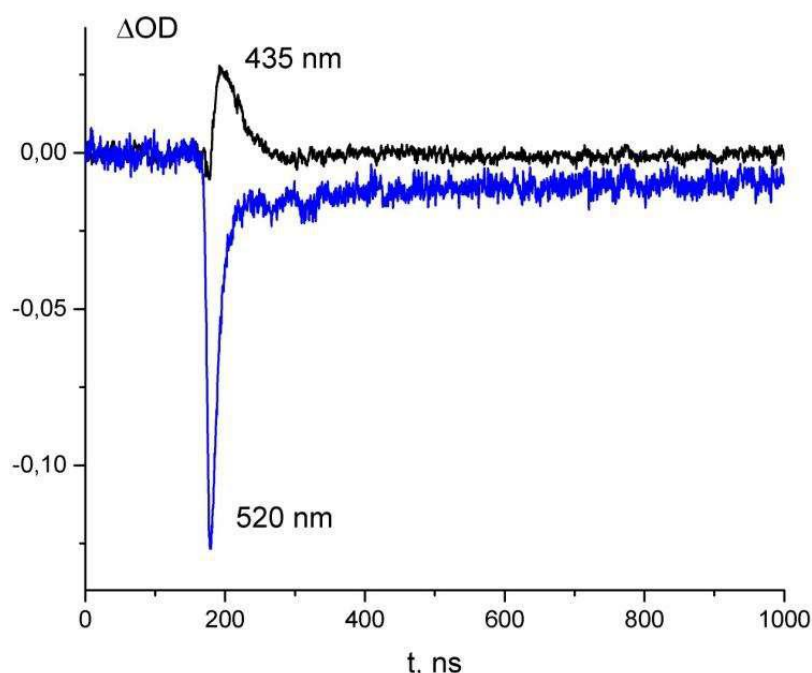


Fig.4. Decay kinetics of the transient absorption of Au NPs ($d=48\pm 16$ nm), $\lambda_{exc}=532$ nm, registered at 435 and 520 nm.

As can be seen from the figure, the absorption kinetics of Au NPs at 435 and 520 nm are different. The kinetics at 435 nm can be described by a monoexponential equation. The estimated decay lifetime was equal to 23 ± 2 ns. The kinetics at 520 nm is better approximated by the bi-exponential decay law. The estimated lifetimes were equal to 21 ± 2 ns and 1.25 ± 0.2 μ s. The duration of transient absorption of Au NPs of smaller diameter was equal to 19.5 ± 2 ns for $\lambda_{reg}=435$ nm. For 520 nm, the duration of absorption was equal to 5.5 ± 2 ns.

Thus, it can be seen that a decrease in the average diameter of Au NPs leads to a decrease in the duration of transient absorption. Nevertheless, the lifetime of transient absorption of Au NPs lies in the nanosecond range, which is uncharacteristic for this process.

It is known that the duration of the transient absorption kinetics is determined by the relaxation time of an ensemble of excited electrons formed under the action of a laser pulse [6]. The relaxation of excited electrons is a complex process that occurs in several stages. It was shown in [9] that nanosecond times are the result of interface phonon energy exchange, which is extended in time up to nanoseconds and more. This does not allow the electrons of a metal NP heated by a laser pulse to quickly cool down rapidly. The surface of a NP conserves the energy of local heating, acting as an adiabatic shell. So, the electrons in a metallic NP remain hot for a very long time due to the relatively low thermal diffusivity of the medium and the hindered energy exchange of the gas of quasiparticles and molecules at the interface.

Conclusion

The transient absorption of gold NPs of various diameters has been studied. For this purpose, the method of pulsed photolysis with photoexcitation by nanosecond laser pulses was used. It has been established that the transient absorption bands for both small and large Au NPs have a maximum at about 430–440 nm and exhibit a fine structure of the spectrum. The decay kinetics of the transient absorption at 435 nm has a monoexponential form. The duration of the absorption decreases with a decrease in the average size of NPs. The nanosecond duration of the transient absorption of Au NPs is the result of a prolonged relaxation process in the “interface of gold NP–solvent molecule” system as a manifestation of hindered heat exchange with the environment.

The results obtained will be useful for the prediction of the dynamics of “hot” electrons in plasmonic NPs of metal. It was shown that under the action of nanosecond pulses, the lifetime of excited electrons in Au NPs is tens and hundreds of nanoseconds. It can be used for heat transfer from metal NPs to biological objects in photothermal therapy, biomedical imaging, activation of photocatalytic reactions and in photovoltaics for additional injection of electrons into a semiconductor layer, etc. [6, 10, 12, 20, 21].

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