Y. SHYNKARENKO,[1] A. DMYTRUK,[1] I. DMITRUK,[1,2] I. BLONSKYI,[1]
P. KORENYUK,[1] C. SÖNNICHSEN,[3] A. KOTKO[4]

[1] Institute of Physics, Nat. Acad. of Sci. of Ukraine
(46, Prosp. Nauky, Kyiv 03028, Ukraine; e-mail: y.shynkarenko@gmail.com)
[2] Faculty of Physics, Taras Shevchenko National University of Kyiv
(2, Academician Glushkov Prosp., Kyiv 03022, Ukraine)
[3] Institute for Physical Chemistry, University of Mainz
(21, Johannes Gutenberg University Mainz Saarstr., Mainz D 55122, Germany)
[4] Frantsevich Institute for Problems of Materials Science
(3, Krzhizhanovsky Str., Kyiv 03680, Ukraine)

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TRANSIENT ABSORPTION OF GOLD NANORODS INDUCED BY FEMTOSECOND LASER IRRADIATION

The action of femtosecond laser irradiation on the optical absorption of gold nanorods has been measured by the pump-probe technique in spectral regions of the longitudinal and transverse modes of surface plasmons. The evolution of the parameters of plasmon absorption bands, namely, peak positions and band widths, after the impact of a pump pulse on a water suspension of nanorods has been revealed by the advanced data processing, accounting for a chirp of the "white continuum" of a probe pulse. The observed kinetics fits the hot electron relaxation theory. In addition, a significant increase of the cross-phase modulation in the spectral range of the surface plasmon absorption band has been found. The irreversible nanorod shape transformation (a change of the aspect ratio) has been observed after long-term irradiation. Pump-probe measurements were performed at the Center for collective use of equipment "Femtosecond Laser Complex" of National Academy of Sciences of Ukraine.

K e y w o r d s: gold nanorods, pump-probe, femtosecond laser irradiation, cross-phase modulation.

1. Introduction

Investigation of optical properties of metal nanoparticles irradiated with femtosecond laser pulses has been actively carried out for last decades and still remains one of the primary directions for nanophysics, nanoelectronics, and nanoplasmonics [1]. Surface plasmons in metal nanoparticles are collective excitations of free electrons and have a lifetime of few femtoseconds, in distinction from nanoseconds, which are typical lifetimes of excitons in semiconductor nanoparticles. Such a short surface plasmon lifetime points a way to drastically improve the temporal performance of optoelectronic devices. At the same time, the dependence of surface plasmon absorption spectra on the shape, material, and dielectric environment of a nanoparticle makes it possible to tune the surface plasmon position throughout the visible spectrum. Moreover, the phenomenon of local field enhancement near the surface of a metal nanoparticle finds a number of striking practical implementations [2, 3].

The process of interaction of a femtosecond laser pulse with a metal nanoparticle is often described in the so-called two-temperature Kaganov's model, which considers the separation of the temperature of a free electron gas from the lattice temperature [4]. Irradiation of a metal nanoparticle with a femtosecond pulse leads to the rapid increase of the electron gas temperature followed by the multistage relaxation: thermalization of the electron gas via the electron-electron (e-e) interaction (10^{-14} s), cooling of the electron gas via the electron-phonon (e-ph)interaction (10^{-12} s), and energy transfer from the ionic lattice to a surrounding media (10^{-10} s).

Quality of a plasmonic material is determined by the ratio of real and imaginary parts of its dielectric permittivity. Excluding alkali metals, which are the best of this ratio, but are highly reactive and thus extremely difficult for applications, gold is number two after silver by this parameter [5, 6]. However, it surpasses silver in many applications due to a high stabil-

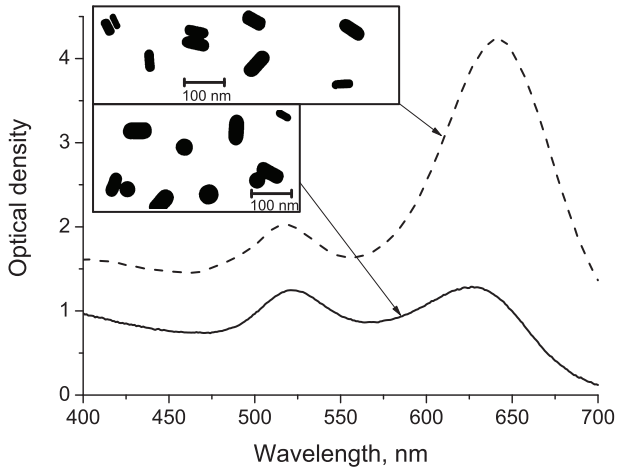

Fig. 1. Optical density spectra of a gold nanorod water suspension. Dashed line is the spectrum of the initial sample (before the femtosecond laser irradiation). Solid line is the spectrum of the sample after the long-term femtosecond laser irradiation. Insets show the corresponding TEM images of gold nanorods. Scale bar at each inset shows 100 nm

ity, biocompatibility, and more convenient location of surface plasmons in the middle of the visible spectral range. It should be noted that the spectral tuning of the plasmon resonance can be achieved by varying the dielectric environment or the shape of nanoparticles. Elongated nanoparticles demonstrate the splitting of a surface plasmon into transverse and longitudinal modes. Nanorods are one of the simplest shapes of optical antennas, and it is of interest to study their response to intence femtosecond pulses. Composites of gold nanoparticles are known for a huge cubic nonlinear susceptibility $\chi^{(3)}$ [7].

The aim of this work was the advanced study of the transient optical absorption of gold nanorods induced by femtosecond laser pulses. Special attention was paid to the account for the temporal and spectral profiles of probe pulses, which allowed us to find the unusual increase of the cross-phase modulation (XPM) intensity.

2. Experimental

The sample, a water suspension of gold nanorods, was prepared at the University of Mainz, Germany. To determine the size and the shape of nanoparticles, transmission electron microscopic (TEM) studies were carried out using a JEM100CX2 microscope operating at 100 kV. A typical TEM photo of the sample is presented in the top inset in Fig. 1. One can see that nanoparticles have the shape of nanorods with the average length of 62 nm and width of 29 nm, which correspond to the aspect ratio about 2.1:1. The optical absorption spectrum of this sample (Fig. 1, upper curve) has two bands with maxima at 516 and 643 nm, which correspond to the transverse and longitudinal surface plasmon modes, respectively.

Time-resolved optical studies were performed at the Center for collective use of equiment "Femtosecond Laser Complex" of NASU, which is described in review [8] in detail.

We used the Coherent laser system consisting of a femtosecond oscillator MIRA-900F and a regenerative amplifier Legend HT with a fundamental laser wavelength at 800 nm. Output energy was 1 mJ at the 1-kHz repetition rate. The pulse duration revealed from the autocorrelation function was 130 fs. The laser output was split into two beams: the pump and probe ones. "White light continuum" was generated by focusing the probe beam into a sapphire plate. A part of the "white light continuum" was used as the reference beam for the absorption calculation. The wavelength of the pump beam was either the fundamental one (800 nm) or its second harmonic (400 nm), while the energy of a pulse was about 10 μJ in any case. The sample in a 1-cm quartz cell was placed in the focus of the probe beam. The pump beam was slightly unfocused to prevent a bubble formation in the sample. The probe beam after the sample and the reference beam were collected in an Imaging Spectrograph SP-2500i (Acton Research) after a set of filters necessary to cut the pump wavelength.

The data of pump-probe measurements were corrected by a home-made software to account for the chirp of a "white light continuum" pulse. Details of the correction method will be reported elsewhere. It should be noted that the use of 800-nm pump pulses leads to the dramatic changes in the probe beam at and around temporal coincidence of the beams, caused by the cross-phase modulation effect [9]. We used a zero-order half-wave plate in the pump beam to make its polarization perpendicular to the probe one and thus to decrease the XPM effect by almost three times. However, the occurrence of XPM effects helps to determine "time-zero" between the pump and probe pulses, and so to set the zero value on the temporal axis for every wavelength measured in case of an 800-nm pump. Otherwise, in case of a 400-nm

pump, when the XPM effect was not observed, the time zero was set as the beginning of any change in transient absorption spectra.

3. Results

We investigated changes in the optical density of the sample for the longitudinal and transverse surface plasmon modes of gold nanorods in a water suspension induced by femtosecond laser irradiation.

Transient optical absorption spectra were measured using different time delays between the pump beam that changed optical properties of the system and the "white light" probe beam. Figure 2 shows the evolution of the both transverse and longitudinal plasmon bands before (marked in the figure as the time delay -2 ps) and after the femtosecond laser pump pulse (0, 0.2, 0.6, 1, 2, 5, 10, 20 ps of time delay).

All spectra were fitted in the Gaussian peak approximation. The evolution of the parameters of the plasmon bands, namely, the peak position and the full width at half maximum (FWHM), was determined and is presented in Figs. 3 and 4. Basically, the results follow the model of hot electron gas [4] and correspond to similar studies on other gold colloids (see, e.g., [10, 11]).

It should be noted that the behavior of FWHM of both peaks is similar and reflects a change of the temperature of the electron gas. But spectral shifts of the transverse and longitudinal peaks are substantially different: the longitudinal peak shifts to longer wavelengths, while the transverse one shifts to shorter ones. These different spectral shifts were not reported up to date to the best of our knowledge. Such spectral shifts of two peaks correspond to a stretching deformation of nanorods, however, their fast kinetics are incompatible with a mechanical deformation. We can suppose that it can be a deformation of the electron gas cloud as a consequence of the spill-out or skin effect.

The most intriguing finding of our work is the unusual temporal behavior of the longitudinal surface plasmon mode band near the "time-zero", presented in Fig. 5. The observed phenomenon can be explained as a significant enhancement of the cross-phase modulation effect in the spectral range of the surface plasmon absorption band. The presumed nature of the phenomenon is an increase of the cubic nonlinear susceptibility of the gold nanorod water suspension caused by a local field enhancement in vicinities of the metal

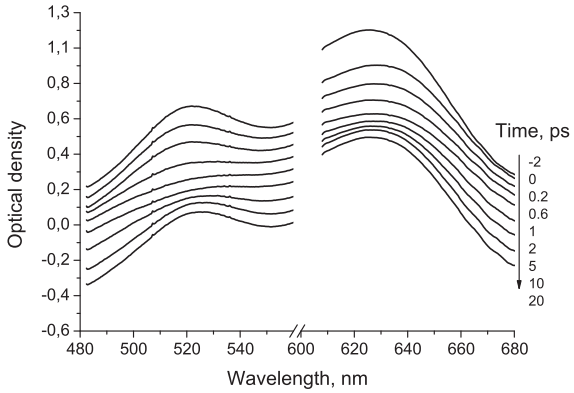

Fig. 2. Evolution of the both longitudinal (peak at 520 nm) and transverse (peak at 630 nm) plasmon absorption bands of gold nanorods after the femtosecond laser irradiation at 400 nm. The spectra are shifted vertically for clarity of presentation. Numbers on the right indicate the time delay in picoseconds between the pump and probe pulses

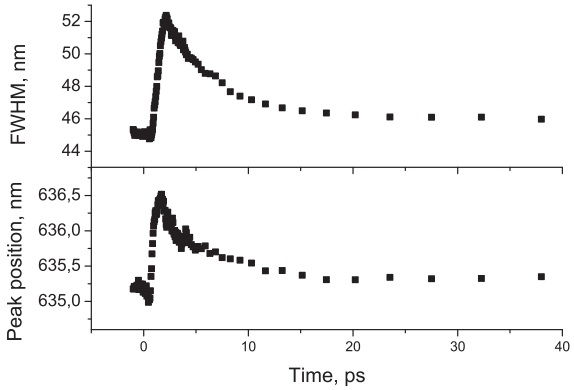

Fig. 3. Evolution of longitudinal plasmon peak parameters. Pump at 400 nm

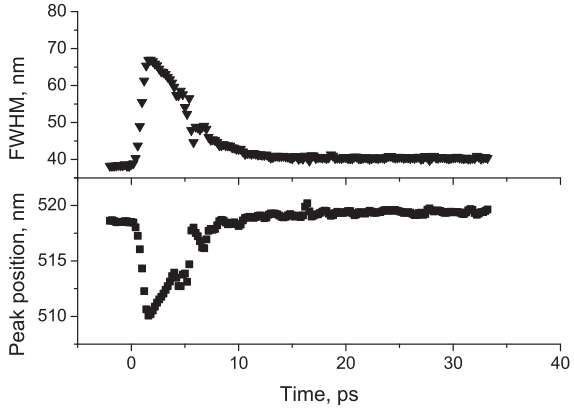

Fig. 4. Evolution of transverse plasmon peak parameters. Pump at 400 nm

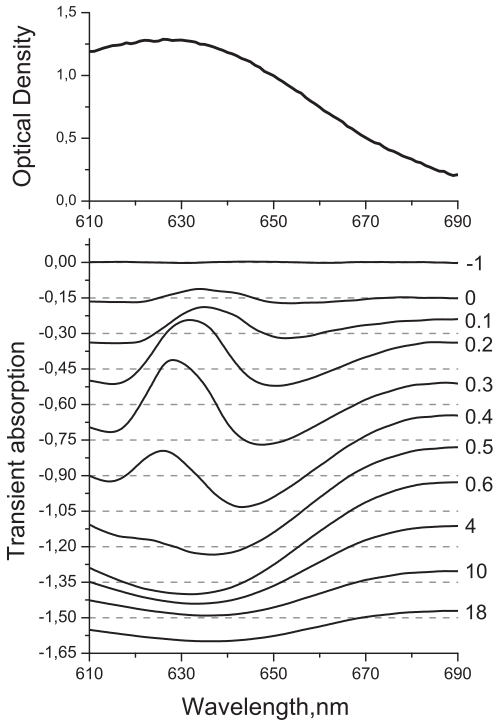

Fig. 5. Upper figure: Absorption spectrum of longitudinal plasmon mode. Lower figure: Transient absorption spectra measured at different time delays after the excitation by femtosecond laser pulses at 800 nm. The spectra are shifted vertically for clarity of presentation. Numbers on the right indicate the time delay in picoseconds between the pump and probe pulses

nanoparticles. The further investigation of the phenomenon is carried out now and its results will be reported elsewhere.

Besides the above-described rapid changes (in a femto- picosecond time domain) of optical properties of the sample, we have also observed irreversible changes after a long-term femtosecond laser irradiation. The essence of the changes is a decrease and a blue shift of the longitudinal surface plasmon band of the absorption spectrum, and a slight red shift of the transverse surface plasmon band. The lower curve in Fig. 1 demonstrates the absorption spectrum of the sample after several hours of the irradiation. The effect can be observed with the naked eye as a color change of the sample. The irreversible change of the optical absorption of the sample arises from the shape transformation of nanoparticles. The TEM image in the lower inset in Fig. 1 shows the nanoparticles after the long-term femtosecond laser irradiation. It could be seen that the aspect ratio of some particles decreased, so the almost spherical particles appeared in the sample. We should mention that the irreversible transformation of the nanorods is slow enough to neglect it during transient absorption measurements in the subnanosecond time domain.

4. Conclusions

The pump-probe investigation of the transient optical absorption reveals the evolution of relaxation processes after the femtosecond laser impact on gold nanorods. The kinetics fits the hot electron relaxation theory (two-temperature Kaganov's model).

The cross-phase modulation effect exerts transient absorption data obtained from the pump-probe measurements and complicates their interpretation. A significant enhancement of the effect has been found at the longitudinal surface plasmon mode band, presumably due to a local field enhancement by surface plasmons in vicinities of the nanorods. The phenomenon requires the further investigation that is being conducted at the moment.

The irreversible nanorod aspect ratio transformation occurs after a long-term femtosecond laser irradiation: particles becomes shorter, almost spherical. The possibility of such sample degradation should be kept in mind during long-term studies, which involve a femtosecond laser irradiation of nanorods.

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Є. Шинкаренко, А. Дмитрук, І. Дмитрук,
І. Блонський, П. Коренюк, К. Зоніхсен, А. Котко

НЕСТАЦІОНАРНЕ ПОГЛИНАННЯ СВІТЛА ЗОЛОТИМИ НАНОЦИЛІНДРАМИ, ЗУМОВЛЕНЕ ДІЄЮ ФЕМТОСЕКУНДНОГО ЛАЗЕРНОГО ВИПРОМІНЮВАННЯ

Р е з ю м е

За допомогою методики “збудження-зондування” було виміряно вплив фемтосекундного лазерного випромінювання на оптичне поглинання золотих наноциліндрів в області поздовжньої та поперечної мод поверхневих плазмонів. Еволюція параметрів плазмонних смуг поглинання водних колоїдів золотих наноциліндрів, а саме, положення піка, ширина смуги після взаємодії з імпульсом збудження були визначені з використанням удосконаленої системи обробки даних, яка включала врахування чірпу “білого континууму” імпульсу зондування. Отримана кінетика добре узгоджується з моделлю остигання розігрітого електронного газу. Крім цього, спостерігалось значне підсилення ефекту крос-фазової модуляції в спектральній області смуг поглинання поверхневих плазмонів. Показані незворотні зміни форми наноциліндрів, які спостерігались в спектрах оптичного поглинання та знімках електронної мікроскопії після тривалого опромінення фемтосекундними лазерними імпульсами.

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