FEMTOSECOND NANOPHOTONICS AND MICROSCOPY

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Contents

Summary

The novel experimental technique – femtospectroscopy, that uses femtosecond laser pulses, as well as ultrashort electron and X-ray pulses, is illustrated by its applying for studies of nanoscale objects, molecular aggregates, carbon nanotubes, living cell.

1. Introduction

Femtosecond nanophotonics — the basic physical phenomena behind the interaction of ultrashort laser pulses with nanoscale objects, nanocomposite materials, supramolecular structures, and molecular aggregates. Femtosecond laser pulses pave a way to achieving high intensities of electromagnetic radiation without irreversible damage to materials, making it possible to observe unique regimes of interaction of the light field with nanostructures and molecular aggregates. Dielectric and electron confinement, as well as resonances due to quantum size effects and collective phenomena in supramolecular and aggregate structures, radically enhance nonlinear-optical interactions of ultrashort pulses. These phenomena offer interesting solutions for a high-sensitivity nonlinear-optical metrology of nanostructured materials, including the analysis of their composition, structure, and morphology, suggesting new attractive strategies for the control, switching, and transformation of ultrashort pulses.

2. Femtosecond Nanophotonics

Time-resolved femtosecond spectroscopy can be used for solving various problems related to research on nanoscale particles. For example, studies of noble metal nanoparticles (Ag and Au) were reviewed by Hartland (2006). The attention of researchers to these systems is due to the fact that plasmon resonance is of great interest for practical applications. Plasmon resonance is suitable for local enhancement of the electromagnetic field strength by several orders of magnitude. Manifestation of plasmon resonance is strongly dependent on the nanoparticle shape and size and on the dielectric environment. A feature of the Ag and Au metals is that plasmon resonance in them can be achieved in the visible spectral region. Electromagnetic field enhancement has found increasing application in optical methods of detection of biological objects, in photocatalysis, microscopy, and in devices for manipulation of visible light.

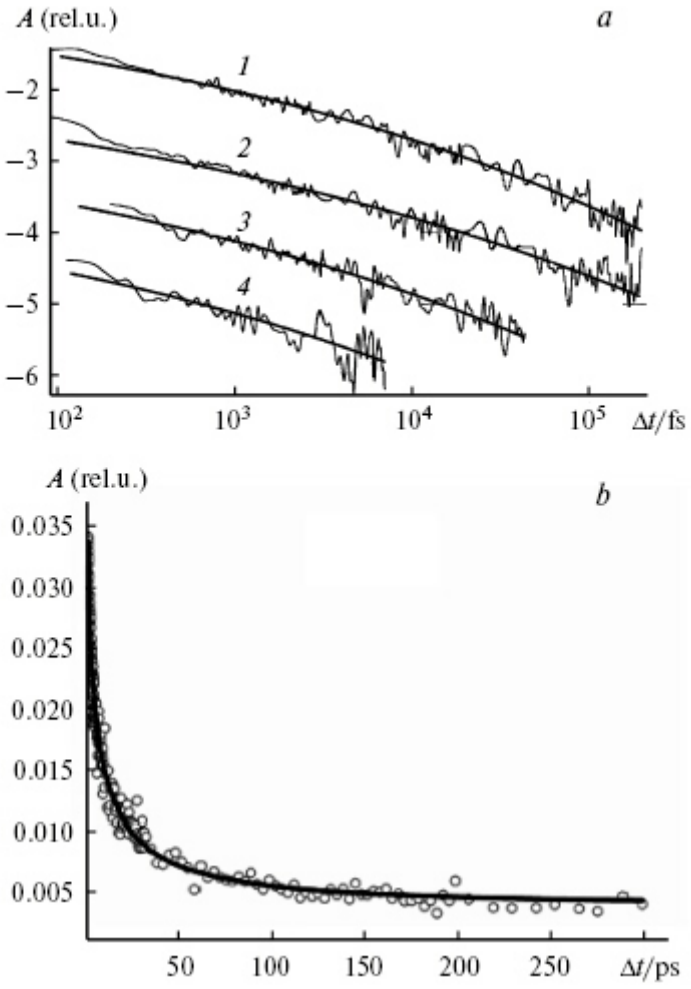

Figure 1. Kinetics of photoinduced charge carriers in iron oxide (*a*) and titania (*b*) nanocrystals; *a* — in $\gamma - Fe_2O_3$ (*1*) and $\alpha - Fe_2O_3$ (*2*) colloidal nanocrystals, in $\alpha - Fe_2O_3$ nanocrystals formed in ferritin protein vesicle (*3*), and in Nafion ion-exchange membrane (*4*). Mathematical expression for the "stretched" exponent used to describe the experimental data has the form

$$\Delta A(t) = A_0 exp[-(t/\tau)^{\beta}].$$

Yet another avenue of research is represented by investigations on interparticle interaction and the interaction between nanoparticles and their environment. In 2005, say, Huang with coathors studied small-amplitude laser-induced oscillations. By analyzing these oscillations one can obtain information on interparticle interactions. Measurements of vibrational beats in individual particles make it possible to determine the dephasing time of the vibrational motion and thus obtain information on the interaction between particles and their environment (see van Dijk *et al.*, 2005).

The trapping and recombination dynamics of photoexcited charge carriers in titania (TiO_2) (Sobennikov *et al.*, 2005) and iron oxide (Fe_2O_3) (Gostev *et al.*, 2004) nanocrystals was studied for different crystal structures and particle size, shape and surface type. It was shown that the relaxation mechanism of the excitation energy of iron oxides is governed by the electronic structure of the Fe^{3+} 3d-shell, being basically different from the relaxation mechanism for titanium oxides. Despite different relaxation mechanisms, in both cases the dynamics is described by a "stretched exponent" (Figure 1) with two parameters, namely, β is a characteristic of the sample, and τ is the characteristic time of relaxation. The parameter β determines the difference between relaxation mechanisms. It was established that the pH value of suspension affects the duration of relaxation processes on TiO_2 surface and does not influence the parameter β.

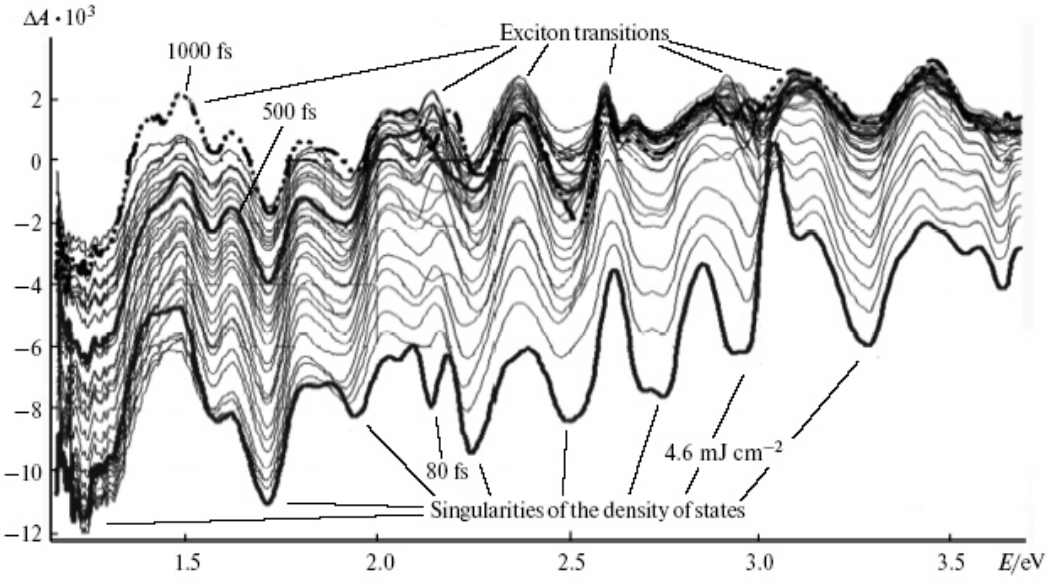

Figure 2. Dynamics of differential photo-initiated bleaching and absorption spectra of single-wall carbon nanotubes on the time scale from 80 to 1000 fs. Along the abscissa axis the energies of the probe pulse photons are shown. Along the ordinate axis the differential optical density is shown. Dashed lines denote the absorption spectra of excitons.

Qualitatively new spectral and dynamic features of the bleaching and absorption spectra of single-wall carbon nanotubes under the action of femtosecond pulses applied at λ = 308, 455, 616, and 700 nm (Figure 2) were discovered (see Nadtochenko *et al*., 2005). A broad bleaching band due to collective electron motions depends only slightly on the wavelength of the excitation pulse. Analysis showed that peaks in the bleaching region correspond to singularities of the density of states and the peaks in the absorption region correspond to exciton transitions. Intra- and inter-band relaxation processes were studied experimentally. Spectral indications were revealed and the hierarchy of relaxation processes of various excitations created in single-wall carbon nanotubes was interpreted. The experimentally established order of characteristic times of relaxation processes is as follows: plasmon scattering (<50 fs); formation of screened electrons and holes (50—500 fs); and formation and loss of excitonic states (10—100 ps).

3. Femtosecond Biophotonics

Studies on femtobiology were devoted to primary processes in retinal-containing proteins (Antipin *et al*., 2004), rearrangement of water-protein medium in the primary photosynthesis processes (Paschenko *et al*., 2004), dynamics of primary photosynthesis processes (Shuvalov and Yakovlev, 2003), and mechanisms of response to microscopic environment of fluorescent probes in biological objects (Smitienko *et al.*, 2008).

We will only consider a study made by Smitienko *et al*., of visual pigment rhodopsin whose molecule is comprised of a protein fragment and a chromophore group (retinal). The system was studied under pulsed irradiation with (i) visible light absorbed by the chromophore fragment of the molecule and (ii) UV light. The novelty of the investigations using UV light consisted in that the rhodopsin photocycle could be switched on by absorption of not only visible, but also UV light (λ = 308 nm) in the chromophore moiety. It was assumed that in the latter case the formation of retinal in the S_1 electronic state is due to intramolecular energy transfer from the tryptophan amino acid residue nearest to the chromophore to retinal. The characteristic times of these processes were determined. Subsequent stages of the photocycle are characterized by the same characteristic times as upon exposure to visible light.

4. Femtosecond Microscopy

High intensity (peak power) of femtosecond light pulses allows multiphonon light absorption and generation of ultrashort electron and X-ray pulses. These features of femtosecond light pulses are employed in femtosecond optical, electron, and X-ray microscopy.

4.1. Femtosecond Optical Microscopy

Femtosecond spectroscopy methods are widely used to improve the selectivity and contrast in optical microscopy. Short pulse durations allow multiphoton absorption to be efficient even at low pulse energies. This makes it possible to eliminate the undesired background and improve the image contrast. The use of IR radiation for multiphonon absorption in biological systems offers additional advantages because it can fall in the

transparency window of biological tissues, have a weak photo action on living systems, and penetrate deeply into their interiors.

Now we will consider two examples of application of two-photon femtosecond microscopy in studies of nanoscale (Zolovatin *et al.,* 2008) and biological objects (Gularyan *et al*., 2006).

Excitation of Ag nanoparticles photocatalytically deposited on the surface of TiO_2 nanoparticles to form a mesoporous (Ag/TiO_2) film with light of a titanium-sapphire laser (λ = 800 nm, pulse duration 100 fs) gave rise to two-photon luminescence observed as bright "hot spots". Their luminescence spectra and the dependence of luminescence intensity on the polarization and wavelength of incident femtosecond light pulse were studied by scanning femtosecond microscopy. It was shown that "hot-spot" luminescence is about 1000 times brighter than the background luminescence. The high brightness of "hot spots" is due to electromagnetic field enhancement owing to plasmon resonance. Possible configurations of Ag nanoparticles, for which maximal field enhancement due to plasmon resonance occurs, were analyzed. Specific features of the Ag/TiO_2 system determine its prospects for applications in photocatalysis, single-molecule spectroscopy, and in visualization of biological objects.

The second example concerns investigations of HeLa living cells. A living cell was dyed with a membrane fluorescent probe 4-dimethylaminochalcone (DMC), which mainly fluoresces from lipid-containing organelles. A fluorescent image of a single cell and subcell organelles was obtained for the first time. Two-photon excitation made it possible to avoid cell photodamage, to improve the contrast of its fluorescent image, and to achieve a high spatial resolution.

The resolution of conventional optical microscopes including a system of lenses is limited to the diffraction limit approximately equal to half the wavelength of incident light. Near-field microscopy uses a highly localized (spot size 10—100 nm) electromagnetic field produced near the tip of the optical probe. The spatial resolution of such microscopes is much higher than the diffraction limit. A fluorescent femtosecond near-field microscopy study (Zubova *et al*., 2005) revealed that protein films contain fluorescing ellipsoidal granules. An investigation of the dependence of fluorescence on various parameters suggested the existence of two forms of yellow fluorescent protein from coral (zFP538). Ultrafast spectroscopic technique characterized by nanometer spatial resolution and femtosecond temporal resolution was proposed and analyzed (Brixner *et al.,*2005).

Note that currently femtosecond microscopy uses nonlinear optical methods. For instance, optical microscopy employs coherent anti-Stokes Raman scattering (CARS) to improve the selectivity, contrast, and sensitivity in femtosecond optical microscopy — methods of coherent control as it shown by Dudovich *et al.*, 2002). Using selective two-photon excitation with sinusoidal phase modulation, endogenous fluorescence was distinguished against the fluorescence of labels in biological samples (Ogivie *et al.*, 2006).

Combining optical microscopy and femtosecond pulses allowed one to construct a femtosecond optical manipulator for moving nanoparticles and biological objects. The device can operate as a "lancet", which cleaves chemical bonds due to multiphonon absorption of femtosecond light pulse (see Zalesskii *et al.*, 2008).

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