Seeing clearly: 2D nanoscopy achieves direct imaging of nanoscale coherence

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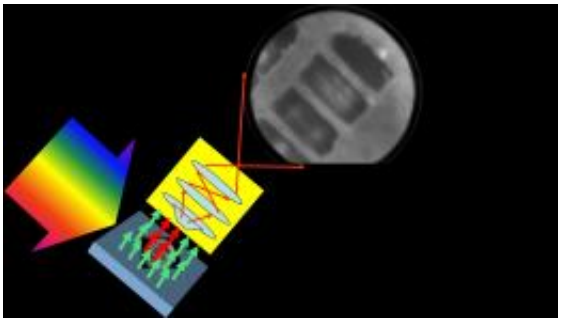

Photoemission electron microscopy (PEEM). Source: Synchrotron Radiation Center

(PhysOrg.com) -- Light has its limitations – in this case not velocity, but rather its diffraction limit, which determines the spatial interaction volume in all implementations of optical spectroscopy and is in general also valid for time-resolved studies. One specific technique that has recently become very successful is *coherent two-dimensional (2D) spectroscopy*. However, because it uses three ingoing waves and one outgoing wave, nanoscale events can be imaged only indirectly by averaging a population of quantum systems in the spectroscopic space.

Recently, however, researchers at Fachbereich Physik and Research Center OPTIMAS, Technische Universität Kaiserslautern; Institut für Physikalische und Theoretische Chemie, Universität Würzburg; and Fakultät für Physik, Universität Bielefeld funded within the German

Science Foundation Priority Program Ultrafast Nanooptics (SPP 1391)have demonstrated a spectroscopic method that goes beyond the optical diffraction limit. In that work they presented a modified 2D spectroscopy scheme to directly image nanoscale coherence. This is achieved by combining four ingoing waves and *photoemission electron microscopy* (PEEM) yielding 50-nanometer spatial resolution in coherent nonlinear spectroscopy.

Although the research, conducted by Martin Aeschlimann, Tobias Brixner, Walter Pfeiffer and other scientists, faced a number of challenges, Brixner notes that despite a number of technical issues, designing and implementing the four ingoing wave system was relatively straightforward. “The key insight,” he points out, “was that sub-diffraction optical resolution in four-wave mixing spectroscopy could be achieved with four ingoing rather than three ingoing and one outgoing optical field, and that nevertheless the obtained information is quite similar.” To the team’s knowledge, this was the first combination of coherent two-dimensional spectroscopy with spatially resolved imaging.

“Experimentally,” he continues, “we were successful relatively quickly after we’d developed the concept because our three groups have been collaborating for several years. Thus the technical requirements, general laboratory infrastructure, sample preparation procedures, data evaluation, femtosecond pulse shaping, and other factors had already been established and were available for our current work.” For the particular issue of generating four ingoing waves, for example, they then had only to calculate the correct pulse-shaper settings to manipulate the excitation laser beam and feed it in the data acquisition program.

Commenting on the process of detecting the final state via photoemission electron microscopy, Aeschlimann adds that the team first had to prove that a photoemission electron microscope (PEEM) is indeed an ideal technique for mapping near-field distributions of

nanostructures illuminated by laser light. “We were able to show that under weak excitation conditions the response of the structure is still in the linear regime.”

The main advantage of PEEM is parallel data acquisition – the whole field of view is mapped simultaneously, so the behavior of different locations on a single surface becomes directly comparable within a single experiment. The researchers extended PEEM to a time-resolved spectroscopy technique that allowed them to investigate ultrafast plasmonic excitations in real time – that is, at femtosecond (fs) time scales.

There were some surprises as well. “Personally,” Pfeiffer admits, “it came as a big surprise that mode hybridization on a randomly structured surface sustains quantum coherences for almost 200 fs – I expected a maximum 10 fs coherence lifetime.” Observing this phenomenon became possible solely because the high spatial resolution achieved in 2D nanoscopy avoids destructive interference of different modes. “We think that such long-lived coherences are much more common than usually believed, since they’re systematically overlooked in spatially averaging spectroscopies.”

Particularly fascinating is the fact that the coherence lifetime directly determines the time window in which coherent control of nanoscale excitations is possible. The involvement of a bright mode – where the collective plasmonic excitation has a large dipole moment and interacts strongly with the transverse radiation field – ensures the effective manipulation of the system. The observation of nanoscale coherence trapping in a dark plasmonic mode that interacts not directly with the transverse fields and thus exhibits long lifetimes opens new design roads for improved coherent control schemes. “We’re looking forward to use 2D nanoscopy to develop, implement and study such control schemes,” says Pfeiffer. “The hybridization of bright and dark modes is a rather

common model in quantum optics and plasmonics[1], but the coupling in complex quantum structures is still not fully understood. Coherent 2D nanoscopy will enable the detailed study of individual nanostructures, such as coupled quantum dots or supramolecular chromophore aggregates."

Going forward, the group plans to make strong use of the pulse-shaping capabilities that allow them to generate arbitrary optical waveforms. "For example," Brixner illustrates, "with polarization shaping we can investigate the vector character – that is, the tensorial nature of optical response functions." They also want to apply the technique to different quantum systems to investigate nanoscale couplings, coherences, and transport phenomena.

"The qualitative model of bright and dark mode hybridization provides us with a guideline to design and optimize nanostructures exhibiting long-lived coherences," adds Pfeiffer. "We'll therefore fabricate and investigate such structures to both verify the qualitative model and develop a deeper understanding of the relevant coupling mechanisms and design considerations." Since the researchers see light localization, or light trapping, in nanostructures as being closely related to the observed phenomenon, their technique could find interesting applications: As an example, light trapping is a critical factor in determining the efficiency of thin film solar cells.

Moreover, Pfeiffer continues, "In the present implementation of the method we use a single color excitation scheme." In other words, the same wavelength is used for all excitation steps – including the final photoemission process. "With a wavelength around 800 nm this means that photoelectrons with very little kinetic energy are emitted and very little selectivity is achieved. Using an ultrashort extreme ultraviolet probe pulse would broaden the applicability of the method considerably."

An important next step in the PEEM technique for this kind of investigations, says Aeschlimann, is the implementation of a normal-incident geometry of the light pulses. “The fixed glancing angle of incidence of the light in a common PEEM setup makes the interpretation of the time-resolved investigation of propagation of plasmon-polariton waves difficult,” he explains. “One problem is caused by the fact that by turning the polarization of the light, not only the in-plane component of the electric field is rotated. Due to the oblique incidence of the laser pulse the rotation of the light polarization also results in an additional field component perpendicular to the surface which influences the measurement by exciting plasmonic modes perpendicular to the surface of the nanostructures. In addition, the difference in the dispersion of the incoming light field and the surface plasmon–polariton, or SPP, wave causes an interference pattern induced by a beating effect.” A normal-incident PEEM setup would allow overcoming both problems, since the phase of the probe pulse would have the same value on every point of the investigated structure.

In looking forward, Brixner recalls that “the project started about eight years ago as a theoretical investigation between Walter Pfeiffer and me in coherent control of electromagnetic fields near nanostructures. We showed that femtosecond pulse shaping can be used to manipulate quite generally the near-fields on a femtosecond time scale below the optical diffraction limit[2]. We then worked with Martin Aeschlimann to realize an experimental implementation[3]. During the last few years we obtained a pretty good understanding about the control of electromagnetic near-fields in a combination of simulation and experiment. However, an interesting situation arises when we apply these concepts to the spectroscopy of quantum systems that are attached to nanostructures: Theory gets much more complicated, but of course the situation is also more interesting. We’re looking forward to investigating such hybrid systems in the future.”

One way of conducting such investigations might be *in silico*. “On the present level of modeling,” says Pfeiffer, “the simulated data reveal just a qualitative picture of the underlying mechanism. A quantitative description of the involved multiphoton photoemission from a complex quantum system involves many not yet completely understood processes.” A quantitative model must, for example, include details about nanostructure geometry, involved transition dipole moments, excited transient electronic states and polarization state of the incident light. “We expect that 2D nanoscopy will stimulate the development of improved models for both the interesting quantum mechanical coupling phenomena on the nanoscale and the processes involved in the multiphoton photoemission.”

Looking further afield, Brixner believes that, although the group’s main interest so far has been fundamental research in physics-related nanoscale phenomena, a wide range of different sample types could potentially be investigated following this first proof-of-principle experiment. “For example,” he concludes, “the issue of energy transport is very relevant in biological and artificial light harvesting. Whether or not the technique can lead to real-world applications is difficult to predict. Let’s see what the future brings us.”

More information: Coherent Two-Dimensional Nanoscopy. Published Online August 11 2011, *Science* 23 September 2011: Vol. 333 no. 6050 pp. 1723-1726, doi: 10.1126/science.1209206

1 *Nature Materials* 9, 707 (2010)
2 *Phys. Rev. Lett.* 95, 093901 (2005)
3 *Nature* 446, 301 (2007); *Proc. Natl. Acad. Sci. USA* 107, 5329 (2010)