

# Coherent spectroscopies on ultrashort time and length scales

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**Abstract.** Three spectroscopic techniques are presented that provide simultaneous spatial and temporal resolution: modified confocal microscopy with heterodyne detection, space-time-resolved spectroscopy using coherent control concepts, and coherent two-dimensional nano-spectroscopy. Latest experimental results are discussed.

## 1 Introduction

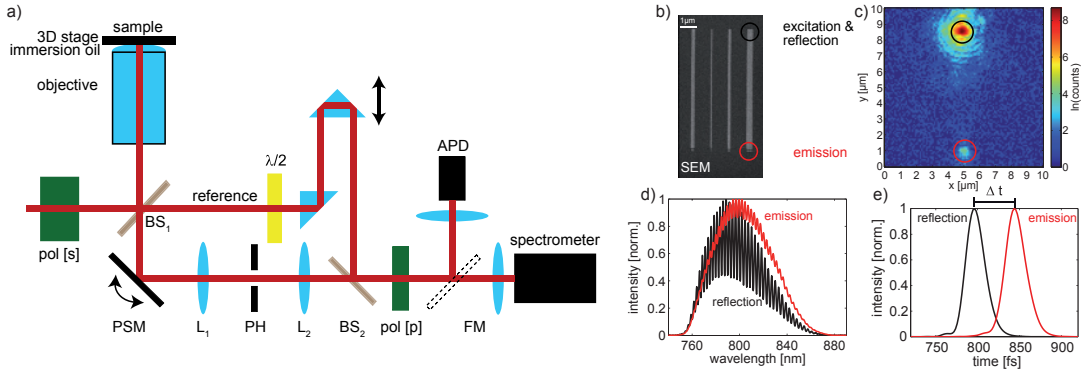
The investigation of ultrafast phenomena in nanoscale systems calls for spectroscopic techniques that combine ultrahigh spatial with ultrahigh temporal resolution. In ultrafast nanooptics [1], several methods were developed to analyze and manipulate the dynamics of individual nanoobjects. The challenges are to realize simultaneously and independently the required spatial and temporal degrees of freedom within one method. Propagation along spatial coordinates may be relevant and the properties of electromagnetic near-fields in the vicinity of the object have to be taken into account. This leads to additional complications but also to new exploitable degrees of freedom like longitudinal field variations below the diffraction limit. Here three coherent spectroscopies that we have recently developed are discussed. They all offer spatial and temporal resolution and are suitable for investigating nanooptical ultrafast phenomena.

## 2 Space-time-resolved microscopy using spectral interferometry

In the first method (Fig. 1a), we use a confocal microscope in which the excitation is raster-scanned over the sample, and the detection can be chosen independently with help of an additional piezo-scanning mirror (PSM) and selection through a pinhole (PH) [2]. Thus we have measured the plasmon group velocity and dispersion in chemically grown Ag nanowires [3]. We also analyzed

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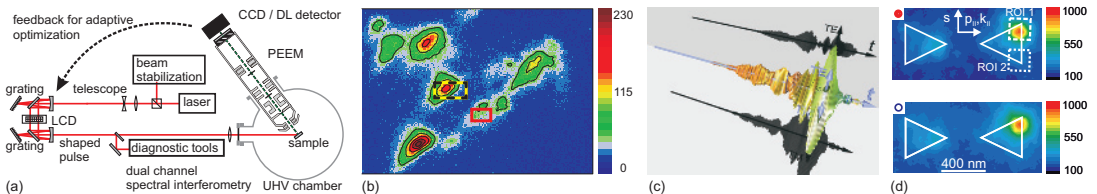
single-crystal Au samples in which artificial nanoantennas were structured by focused ion-beam (FIB) milling (Fig. 1b). Analysis of reflection versus emission (Fig. 1c) with spectral interferometry (Fig. 1d) provides the time-domain data (Fig. 1e). Our method opens the possibility to construct and analyze complex nanoplasmonic “circuits”.



**Fig. 1.** Space-time-resolved plasmon propagation. (a) Modified confocal microscope. (b) We analyze single-crystal Au nanowires with antennas made by FIB milling (1  $\mu\text{m}$  scale bar in upper left corner). (c) Reflection (black upper circle) and emission after propagation (red lower circle) lead to (d) spectral interferograms providing (e) temporal information such as the propagation time  $\Delta t$ .

### 3 Space-time-resolved spectroscopy below the diffraction limit using coherent control

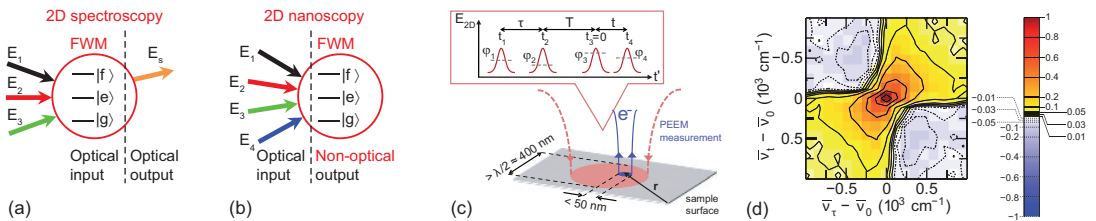
In the second method, we aim at spatially separated excitation and detection with a resolution below the optical diffraction limit. This is achieved with coherent control concepts employing femtosecond (polarization) pulse shaping in connection with photoemission electron microscopy (PEEM) for spatial resolution (Fig. 2a). Using the proper pulse shape enables ultrafast excitation sequences in which the first pulsed interaction (“excitation”) is spatially separated from the second pulsed interaction (“probe”) below the diffraction limit [4]. This concept can be used for selective excitation of photoemission “hot spots” on a corrugated Ag surface (Fig. 2b) [5]. The optimal polarization-shaped pulse with 400 fs duration is quite long (Fig. 2c) and hence points at surprisingly long electronic coherence lifetimes (see Section 4). For spectroscopic applications, the adaptive control approach with a learning loop may be too cumbersome because of separate optimization for each particular target. We show that recently derived analytic control rules can also be employed experimentally and provide the desired nanooptical excitation in a direct fashion (Fig. 2d) [6].



**Fig. 2.** Coherent nanocontrol. (a) Experimental setup. (b) The PEEM image shows maximization of photoemission from the black-yellow dashed versus the red region of interest on a corrugated Ag surface. (c) The duration of the optimal laser pulse (time axis  $\sim 2.1$  ps) indicates long coherence times. (d) Analytic control of near-fields is also possible. In a triangular structure, adaptive maximization of the ROI1/ROI2 PEEM yield ratio (top) provides results similar to those resulting from application of an “analytic rule” for excitation switching (bottom).

## 4 Coherent two-dimensional nanoscopy

In the third method, we generalize coherent two-dimensional (2D) spectroscopy such that it provides additional spatial resolution below the diffraction limit [7]. While in conventional 2D spectroscopy, three input fields create a third-order polarization that is then radiated off as a signal field (Fig. 3a), our scheme for 2D nanometer-resolved spectroscopy (“nanoscopy”) employs four optical input fields and no optical output (Fig. 3b). In that way, the diffraction limit can be avoided. We detect the emitted photoelectrons with PEEM after interaction with a four-pulse sequence as generated with a pulse shaper (Fig. 3c). Then 2D spectra can be obtained with 50 nm spatial resolution (Fig. 3d). With the corrugated Ag surface from Figs. 2b,c it is thus possible to map out the coherence lifetimes via modeling and analysis of the 2D lineshapes [7]. Preliminary results have been recorded for other nanostructured systems such as thin-film solar cells in which local lifetimes, as revealed by coherent 2D nanoscopy, are relevant for the cell’s efficiency.



**Fig. 3.** Coherent 2D nanoscopy [7]. (a) Conventional four-wave mixing (FWM) with three input and one optical output field is analogous to (b) the new scheme with four input and zero optical output fields. (c) A sequence of four femtosecond pulses excites the sample in a spot larger than the diffraction limit, but PEEM provides 50-nm spatial resolution. (d) An exemplary 2D nanospectrum is shown for a corrugated Ag surface.

## 5 Conclusion

The nanoscopic realm is made accessible on an ultrafast timescale by a number of new spectroscopic methods. They all offer information on the coherent evolution of a quantum system via phase-sensitive analysis. This is achieved in a combination of concepts from three different research communities: ultrafast nano-optics, coherent control, and coherent two-dimensional spectroscopy. We expect broad applicability to many different nanoscopic systems in the future.

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