Nonlinear optics and spectroscopy at the nanoscale with a hollow-pyramid aperture SNOM

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Abstract. We report on a novel near-field microscope in which ultrashort laser pulses are coupled into hollow-pyramid cantilever probes. The high throughput, absence of polarization pinning and absence of chirping, which are premium features of such probes, enable obtaining sufficient peak power in the near-field to perform nonlinear optical experiments. We show experimental results on second-harmonic generation from metal nanostructures and two-photon excitation of fluorescent conjugated polymers on the subwavelength scale.

1. Introduction

The interest in the investigation of nanoscale optical fields has been gaining increasing attention over the past decade [1]. A high degree of field enhancement and confinement is expected for small particles, rough metal surfaces, resonant plasmonic structures and resonant optical antennas. The understanding of these phenomena is a fundamental step toward their exploitation in applications such as nanophotonic circuits or surface-enhanced, high-sensitivity spectroscopy of molecules.

Field enhancement and confinement are best observed by exploiting nonlinear optical effects, such as Second Harmonic Generation (SHG) and Two-Photon Photo-Luminescence (TPPL), which are intrinsically sensitive to high fields. Besides its interest for studying metal nanostructures, multiphoton excitation has also been for long a fundamental tool for fluorescence microscopy in polymer- and life-science. High resolution nonlinear optical imaging of nanostructured surfaces is therefore a natural quest in several branches of nanotechnology.

Aperture Scanning Near-field Optical Microscopy (SNOM) allows beating the diffraction limit by scanning the sample with a confined light source, as a subwavelength aperture, approached at a distance much smaller than the wavelength, that is, in its near-field. Standard implementation of aperture-SNOM is based upon tapered optical fibers with a metal coating, leaving at the tip a small hole of the order of 50-100 nm; such probes have the drawback of a low throughput, pulse chirping due to positive dispersion and birefringence disturbing the polarization state of the illumination beam.
Recently, a novel class of SNOM probes has been introduced, based on a silicon or silicon nitride cantilever, similar to the ones used in Atomic Force Microscopy (AFM), with a hollow pyramid tip [2]. The pyramid is metal-coated, usually by aluminum or gold, leaving a hole at its apex, with a diameter ranging from 50 to 200 nm. These cantilevered tips offer several advantages compared to tapered fibers, namely: (i) the larger taper angle produces higher power throughputs; (ii) the lower absorption allows one to couple higher average power before reaching the onset of thermal damage of the metal coating; (iii) all tip-sample distance stabilization methods used in AFM can be employed, thus ensuring longer probe lifetimes as compared to the standard shear-force method used with fiber probes. Moreover, as light travels mainly in air before reaching the aperture, both pulse chirping and depolarization effects can be effectively avoided.

In a previous experiment [3], we performed an in-situ characterization of femtosecond pulses transmitted by hollow-pyramid near-field probes by second-order optical autocorrelation. In our test we demonstrate that transmission through probes with diameter down to 65 nm has negligible effects on pulses with duration as short as 30 fs, thus allowing simultaneous strong localization both in space and time. This experiment also demonstrated that such probes allow obtaining sufficient peak power at their output to perform nonlinear optical experiments in the near-field. Moreover, in another experimental work [4], we studied the polarization properties of light in the near-field by means of a thin dichroic fluorescent polymer layer. We showed that no polarization pinning is found in the proximity of the aperture, irrespectively of its shape being circular or ellipsoidal, at variance with standard far-field characterizations.

In this paper we report on the development of a novel instrument, coupling femtosecond light pulses with a SNOM apparatus based on metal-coated hollow-pyramid tips. This tool enables the observation of the nonlinear optical response of nanostructured surfaces with sub-100-nm spatial resolution. As examples of its capabilities of non-linear optical imaging in the near-field, we present results on SHG from Au projection patterns and TPPL from a blend of conjugated polymers.

2. Experimental setup

A schematic of the experimental setup is shown in Fig. 1. The laser system is a Ti:sapphire oscillator in a home-made standard asymmetric cavity for Kerr-lens mode-locking, stretched by a 1:1 telescope in order to lower the repetition rate down to 26 MHz. For a given average power, as limited by thermal effects in the near-field probe, this allows an increase of the peak power by a factor of ~4 with respect to a standard 100-MHz cavity, and a corresponding enhancement of non-linear optical effects. The laser generates pulses at about 800 nm central wavelength with 10 THz bandwidth and energy up to 20 nJ. The pulses are sent to a pre-compressor consisting of a double pass in a Brewster-cut fused-silica prism pair, then to a Keplerian telescope which enlarges the beam size in order to fill the focusing lens. A spatial filter (50 µm diameter) is inserted in the focus of the telescope to improve the beam spatial quality. The beam is then effectively focused into Al-coated hollow-pyramid tips by means of an aspherical lens, providing throughputs as high as 10⁴ for 100 nm-aperture tips.

![Fig.1: Schematic of the experimental setup.](image)
Two near-field microscopes have been used during this experimental work: a home-made one [5] and a commercial one (AlphaSNOM, Witec GmbH), the latter modified to allow the coupling to an external laser source. Both systems are based on the same scheme: tip-sample distance stabilization is achieved by the optical lever method, therefore the instrument can work in contact, tapping or non-contact mode. The latter mode is preferred for samples, such as gold nanostructures and organic films, that can be damaged by tip friction forces due to lateral scanning of the tip. The sample is mounted on a xyz piezo-actuator for distance stabilization and sample raster scanning. The light transmitted through the aperture is collected by a 0.8 numerical-aperture microscope objective and sent to a photon-counting photomultiplier detector through a pinhole to reject stray light. Adjustable waveplates and polarizers allow for the definition of the polarization state in the illumination and collection paths, while a set of suitable spectral filters is used to select the collected wavelength. For the non-linear SNOM experiments, the average power incident on the probe is typically between 1 and 20 mW. No tip damage was detected even at the highest power level.

3. Experimental results

In the following subsections, we show some results obtained with our setup. SHG is exploited as a direct technique to probe local field enhancements in metal nanostructures, while TPPL imaging is an ideal tool to study organic materials, like polymers, which can be subjected to photodamage under visible light illumination.

3.1. Second-harmonic generation from Au projection patterns

As a first standard sample to test the performances of the apparatus, Au projection patterns from 453 nm latex spheres (Kentax GmbH) have been used. SHG images have been taken, together with topography and transmission optical images, with a 200-nm aperture tip (fig. 2). The topography shows the regular array of Au triangles left by the latex spheres, while the transmission image (not shown) is almost featureless, as expected on the basis of the quite large diameter of the aperture. Nevertheless, very strong and well-resolved SHG from the gold triangles has been detected, and from a line profile of one of the smallest structures we find a very good signal-to-background ratio (around 10) with respect to the glass substrate and a high spatial resolution (around 95 nm with the 10%-90% criterion), consistent with a multiphoton process. The fine structure of the Au triangles, not addressable in our topographic image, most probably determines the conditions for SHG, together with possible resonances of the bow-tie structures present on the sample [6]. There are also some larger spots in the optical image, coming from Au aggregates left on the projection pattern sample, as can be seen in the topographic image.

![Fig. 2: a) topography of the Au projection pattern; b) SHG image; c) line profile from the SHG image.](image-url)
A small lateral shift of the optical image with respect to the topographic image denotes that tip-sample stabilization resulted from a protrusion at one side of the aperture rims. The high resolution of the shown topographic image might indicate the presence of a “tip-on-aperture” structure, which could be the main source of the field-enhancement providing SHG. However, in another experimental measurement (not shown here) the topographic resolution was completely missing; yet, a clear and well-resolved SHG image could still be collected. Further characterizations are needed in order to clarify the role of field-enhancement at the aperture metal rims in providing the localized high field intensity required for SHG.

3.2. Two-photon excited fluorescence from polymer blends

We finally show TPPL from a blend of poly (9,9-dioctylfluorene) (PFO) with poly (methylmethacrylate) (PMMA). PFO is a highly-efficient fluorescent polymer, widely used as active layer for organic LEDs [7]. We performed near-field fluorescence imaging with two-photon excitation from 800 nm fs laser pulses and with single-photon excitation by a 405 nm CW laser source on the same scanning area, and compared the fluorescence response of the sample with subwavelength resolution.

![Fig. 3: Topography (a), single-photon excited fluorescence by 405 nm laser source (b) and TPPL from 800 nm fs laser pulses (c) of a blend of PFO with PMMA.](image)

In fig. 3a the topography of the sample shows a clear phase separation between the polymer and the host matrix. In fig. 3b single-photon fluorescence image shows that the PFO polymer is almost completely concentrated inside the rounded depressions that can be seen in the topography. Fig. 3c is the corresponding TPPE image. Again, it is shown that our apparatus provides enough peak power out of the tip aperture to perform non-linear optical experiments. Surprisingly, many differences can be seen in the distribution of the polymer fluorescence, although the energy involved in the absorption transition is practically the same for the one- and two-photon excitation. This unexpected feature, which has been checked to be free from possible artefacts due to sample or tip degradation, is currently under investigation.

4. Conclusions and future perspectives
In this paper we report on a novel experimental setup combining an aperture SNOM with femtosecond laser pulses. This system enables nonlinear optical imaging in the near field with ≈100 nm spatial resolution and very good reproducibility and signal-to-background ratios. SHG from metal nanostructures and TPPL imaging of polymer blends have been shown as typical applications already available. Further work is in progress to improve the sensitivity and spatial resolution of the apparatus, apply non-linear imaging to new samples and implement femtosecond pump-and-probe spectroscopic techniques in the near-field.

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