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Investigation of heating effects in near-field experiments with luminescent organic semiconductors

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Abstract

We present a study of heating effects in apertured near-field gold-coated probes which makes use of the temperature dependence of the photoluminescence spectra of the polymer semiconductor poly(*p*-phenylene vinylene) (PPV). The small throughput of metal-coated probes used for aperture-scanning near-field optical microscopy (aperture-SNOM) can induce significant probe heating, even when operated with laser powers of only a few mW. According to recent literature the probe apex can reach several hundred degrees celsius, possibly producing local heating of the specimen. Such a possibility needs to be investigated carefully, since it could affect the results of both near-field spectroscopy or lithography, especially where the photosensitive material happens to be sensitive to high temperatures, as for the PPV precursor. Interestingly, the sensitivity of conjugated polymers optical properties to changes in temperature (blue-shift of either photoluminescence or absorption upon heating), can be used as a convenient tool for investigation of the sample heating. Here, we report a comparison between photoluminescence spectra collected in the far-field but with excitation in either the far- or near-field, which demonstrate the absence of any significant difference, and thus indicate a negligible heating of the polymers during SNOM experiments. In addition, we demonstrate that near-field illumination of PPV precursor films with red light (i.e. with a wavelength longer than the absorption edge of PPV precursor), does not result in any lithographic effect, confirming that thermolithography of the PPV precursor is not significant in our lithography experiments.

Keywords: SNOM; Tip-heating; Polyphenylenevinylenes; Photoluminescence; Spectral shifts; Nanolithography

1. Introduction

Scanning near-field optical microscopy (SNOM) has become a well established technique, not only for providing optical images of surfaces with sub-diffraction resolution, but also as a viable tool for the fabrication of well-defined nanostructures (scanning near-field lithography, or SNOL) [1–4].

The generation and/or collection of spatially localized optical fields in scanning near-field microscopes is made possible by the use of special probes consisting of some sort of waveguide featuring a subwavelength aperture, e.g., tapered optical fibers with an opaque metallic coating and a small aperture at the fiber apex (aperture-SNOM), or sharp metallic tips (e.g. atomic force or scanning tunneling microscopy probes) that can enhance the electromagnetic fields due to a combination of plasmon resonances and geometric factors(apertureless-SNOM) [5,6]. Aperture-SNOM was the first to be developed and used and still represents the

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most common implementation of this type of instruments [7,8].

One of the most significant features of aperture probes is the low power throughput of the fibers themselves, that is at best of the order of 10^{-3} to 10^{-4}, but can be as low as 10^{-6}, as a result of the particular shape of the probes, and concomitant absorption of the optical radiation in the metal coating. Probe heating, especially in proximity of the apex, is therefore inevitable, and increased operational temperatures have indeed been reported by a number of authors. In recent years the temperature profile of metal-coated fiber tips has been modeled theoretically and measured experimentally by different groups [9–14]. Temperatures of upto some hundred degrees have been measured along the fiber, close to the aperture, when using an optical input similar to that used in SNOL in terms of launched power (some mW) and spectral range (UV and visible) [10,11].

The question arises as to whether the heating of the tip may lead to local heating of the samples. Although a variety of different mechanisms are possible in theory, recent studies have shown that in practice thermal conduction and direct optical transfer are the two dominant heat-transfer mechanisms between the probe and sample [15–17]. Local heating of the sample is particularly relevant to SNOL of thermosensitive materials, such as the precursor of poly(*p*-phenylene vinylene) (PPV) which can be made insoluble by exposure to high temperatures in addition to exposure to UV light. The presence of thermolithographic effects needs to be carefully understood and controlled to obtain optimum resolution from the SNOL process, since undesired thermal conversion by a hot probe could affect lateral resolution.

In this work we carried out a variety of experiments to investigate the occurrence of sample surface heating effects that may occur in SNOM experiments making use of metal-coated, apertured probes. In particular, we used the inherent sensitivity of the optical properties of conjugated polymers (both absorption and emission) to changes in temperature (thermochromism) [18–23] to detect the local heating of the sample surface. The polymer photoluminescence and absorption spectra are blue-shifted upon heating due to the excitation of progressively higher vibrational, rotational, and librational levels, and the subsequent loss of conjugation along the chains. Thermochromism of conjugated polymers arises from strong electron–phonon coupling due to the “softness” of the sp^2-carbons backbone. Indeed, a molecular conformational rearrangement accompanies formation of excited states (both charged and neutral) in these materials. The depopulation of the vibrational states that follows cooling processes results in a more planar geometrical configuration of the polymer strands, and therefore in a more extended conjugation, whose signature is a red-shift of both emission and absorption.

We have used commercially available chemically etched and gold-coated probes, with far-field optical power throughputs of the order of 10^{-3} to illuminate thin films of the prototypical electroluminescent polymer PPV [19,21,23,24], and aimed at detecting a blue-shift of the photoluminescence (PL) spectra collected in the far-field following near-field illumination, with respect to spectra collected in the far-field with far-field illumination (in the following near-field and far-field spectra respectively, for brevity). Far-field PL spectra were also collected as a function of the temperature to provide a reference that could allow an indirect, optical measurement of the local film temperature.

Finally, to conclusively rule out the potential presence of thermal effects in near-field lithography experiments, we also compared the results achieved with illumination in the UV (325 nm, 0.8 mW) with those obtained with illumination in the red (670 nm, 4 mW).

2. Experimental

We have looked at spin-coated (1300 rpm) thin films of PPV on fused silica substrates. The PPV was prepared by thermal conversion of a film of the PPV water-soluble precursor (Aldrich) at 220 °C overnight, in vacuo (pressure $<10^{-3}$ mbar) [24]. The thickness of the fully converted PPV film was ∼50 nm.

We acquired time-integrated, temperature-dependent far-field PL spectra in a cryostat under a dynamic flow of helium. Excitation and detection was provided by a time-correlated single-photon counting (TCSPC) system described in detail elsewhere [25]. The sample was excited with a pulsed diode laser (PicoQuant LDH 400, emitting at 407 nm) and the luminescence detected with a Peltier-cooled microchannel plate photomultiplier coupled to a monochromator and TCSPC electronics (Lifespec-ps and VTC900 PC card, Edinburgh Instruments). Far-field PL spectra for direct comparison with the near-field ones were also taken with the same excitation energy used in near-field (325 nm) to completely rule out any possible shift due to the use of different excitations. We note however that PL spectra and their relevant features (e.g. peaks) are typically independent of the excitation energy for energies greater than the so-called localization threshold [26]. For such experiment, we used the full He–Cd laser beam diameter (1.1 mm) and collected the PL signal at about 45° to the beam direction.

For the near-field experiments we used a SNOM of our own design and construction [2] which uses a tuning-fork mechanism with shear force feedback for the probe-sample distance regulation. The apertured probe was brought in shear force contact and acted as a near-field excitation source for PL measurements. The PL signal was collected in far-field in transmission mode by means of a long working distance 10× achromatic objective (N.A. = 0.25) and then recorded by a spectrometer [Ocean Optics S2000-UV–vis]. We used gold-coated UV probes purchased from Jasco Inc. [type NPU-50D]. These probes have a flat, circular end of diameter of approximately 1.4 μm, as opposed to a traditional taper. The aperture size is typically in the range 20–80 nm and the far-field throughput is $\sim 10^{-3}$ to 10^{-4}. Such commercial probes have also been used recently for the fabrication of PPV nanostructures [2].

Near-field PL was excited by the 325 nm line of a He–Cd laser (8.2 mW, higher than that used in SNOL experiments, which is typically less than 0.2 mW [2]). To minimize photo-oxidation at the illuminated spot, which may lead to bleaching of the absorption and to a major degradation of the PL efficiency that could also prevent the observation of a blue-shift, we did not keep the probe at a fixed position on the sample, but we scanned the surface at a speed of 0.5 μm s^{-1}. This is comparable with typical SNOL scan speeds.

3. Results

In Fig. 1 we report the far-field PL spectra of PPV as a function of temperature in the range 213–413 K. Two subsequent measurements, on different days, have been taken on the same sample to verify the general reproducibility of the experiment and in particular that heating of the polymer did not lead to further "conversion" of the PPV, which would have resulted in a permanent spectral shift of the PL, owing to the variation of the average conjugation length of the polymer sample. The spectra consist of three main peaks whose room temperature maxima occur at 508 nm (peak 1), 544 nm (peak 2) and 593 nm (peak 3). When the temperature increases, the spectra show a decrease of the PL intensity, and a blue-shift. The decreased intensity is due to the decrease of the PL efficiency, which is most likely connected with a variation of the non-radiative decay rate resulting from higher exciton mobility. We used Gaussian functions to fit the main peaks and extract their evolution as a function of temperature, which is reported in Fig. 2 for peaks 1 and 2. As expected, we observe a distinct blue-shift with increasing temperature, which we estimate to be 0.44 meV/K for peak 1 and 0.50 meV/K for peak 2, in the range 293–373 K.

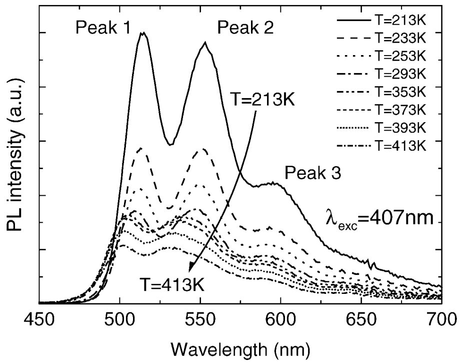

Fig. 1. Photoluminescence spectra of a PPV film as a function of temperature. The fully converted PPV film has been prepared by spin-coating a water soluble precursor on a spectrosil substrate so as to give a 50 nm thickness after thermal conversion at 220 °C, overnight at $<10^{-3}$ mbar residual pressure. The sample temperature was varied in the range 213–413 K in a He-flow cryostat. Excitation was provided by a diode laser emitting at 407 nm.

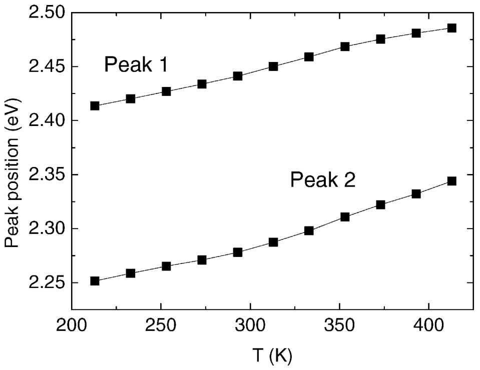

Fig. 2. Temperature variation of the position of peaks 1 and 2 as determined by fitting the peaks with Gaussian functions.

In Fig. 3 we report the near- and far-field spectra of a PPV sample following excitation at 325 nm. Although the near-field spectrum is significantly noisier than the far-field one, owing to the smaller signals achievable with near-field excitation, it is sufficiently well resolved to allow comparison with the far-field spectrum, from which we conclude that there is no significant blue-shift. More precisely, by comparing the far-field temperature calibration with the most blue-shifted data points of the blue-edge of the near-field spectra in Fig. 3 (in the range 490–500 nm), we can conservatively estimate that any local heating of the PPV film, if present, should not be greater than 40 K. Even smaller values of the higher bound for the local heating would result from considering Gaussian best fits of the various peaks (10 K or so), but the near-field spectra are too noisy to allow good-quality fits. Similar results were obtained in experiments on poly(4,4′-diphenylene diphenylvinylene) or PDPV in short [27], which thus corroborate the conclusion that the polymer samples do not suffer from significant heating as a result of the interaction with the SNOM probes.

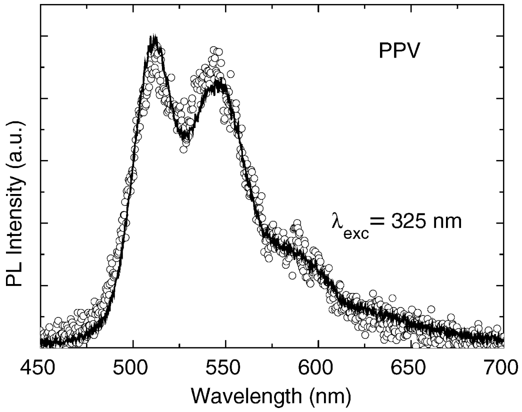

Fig. 3. PL intensity spectra of a PPV film (~50 nm thick) prepared on a spectrosil substrate. The solid line and open symbols show the far- and near-field spectra, respectively, measured at room temperature. Both spectra have been obtained by excitation at 325 nm from a He–Cd laser. For the near-field measurement we launched 8.2 mW of a 325 nm beam (from a He–Cd laser). Into a gold-coated UV fiber probe with a certified aperture of 20 ± 5 nm of about 10^{-3}.

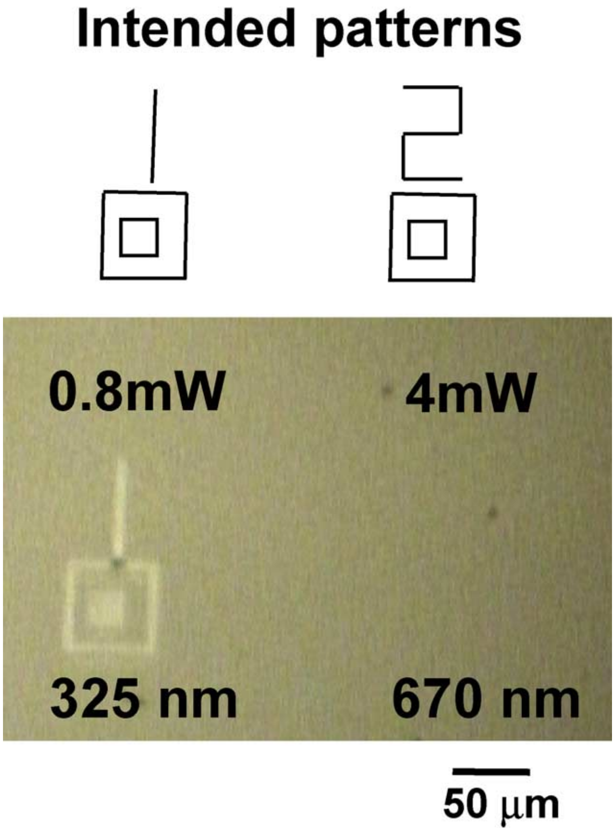

Fig. 4. Optical microphotograph of the structures obtained by near-field lithography of PPV precursor with illumination from either a He–Cd laser emitting at 325 nm (left, 0.8 mW launched into the fiber), or from a diode laser emitting at 670 nm (right, 4 mW launched into the fiber, to account for the lower reflectivity of gold in the visible and in the UV, note that the fiber transmission at 670 nm is larger by a factor of 1.5 than the fiber transmission at 325 nm). Only the 325 nm beam falls within the absorption region of the PPV precursor. For both experiments we used a gold-coated UV fiber probe from Jasco Inc. with a certified aperture of 80 ± 5 nm, and a far-field throughput of about 10^{-3}. The intended patterns are shown at the top of the image.

To conclusively rule out the possible presence of thermolithographic effects in SNOL patterning we carried out two different lithography experiments using the same apparatus, the same sample and probe for both experiments but different wavelengths, above and below the absorption edge of the PPV precursor, namely: 325 nm (below the absorption edge) and 670 nm (above the absorption edge, with virtually no absorption by the PPV precursor), respectively. In spite of a launched laser power five times more intense for the visible light than for the UV, no lithographic features were present on the surface after development, in the case of red illumination. The intended patterns are shown at the top of Fig. 4, whereas the image at the bottom of Fig. 4 is an optical microscope image that shows the final result after development and thermal conversion. We observe a fully converted PPV structure where UV light was used, but a complete absence of any lithographic feature where visible light was used. Such results confirm that heat transfer from the SNOM probe to the specimen does not affect the photolithographic process.

4. Conclusions

We have used the thermochromic properties of the conjugated polymers PPV and PDPV to explore probe-induced sample heating effects in aperture-SNOM experiments. We found no significant blue-shift of the near-field PL spectra in comparison to far-field spectra. This result points to lack of significant sample heating in near-field experiments with the high-throughput probes that we have tested, and that we had previously used for near-field lithography experiments. From investigation of the temperature dependence of the far-field PL of fully converted PPV films we have found that the highest-energy peak (corresponding to the so-called 0–0 transition) shifts by approximately 0.44 meV/K in the range 293–373 K, whereas the peak corresponding to the 0–1 transition shifts of approximately 0.50 meV/K in the same range. From such data we are able to estimate a higher bound of 40 K for the temperature increase of the film surface in our experimental conditions. Such a weak sample heating ensures the feasibility of SNOL on thermally sensitive specimens, such as the PPV precursor itself. In this regard, we also investigated the possibility of patterning the PPV precursor by pure thermolithographic effects, by using 670 nm radiation, which is not absorbed by the PPV precursor, but contributes to heating of the probes in a similar manner to UV radiation. Our results confirm the fully optical process in SNOL experiments on PPV precursor that we had previously reported.

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