

Nanoscale Optical Microscopy of Conjugated Polymer Films

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Abstract

Near-field scanning optical microscopy (NSOM) has been used to probe the photoluminescence, linear dichroism and photoconductivity of free-standing poly(p-phenylene vinylene) (PPV) films with spatial resolution better than 100 nm. We observe a strong correlation between each of these properties and film morphology in both non-oriented and stretch-oriented films. The non-oriented PPV thin films exhibit mesoscale non-uniform photoluminescence correlated to polymer clusters. Upon stretch-orientation, PPV thin films show average polymer chain orientation parallel to the stretch axis as well as distinct areas of perpendicular molecular orientation correlated to film topography.

Keywords: NSOM, photoconductivity, photoluminescence, PPV, conjugated polymers

1. Introduction

Semiconducting conjugated polymers such as poly(p-phenylene vinylene) (PPV) and derivatives are interesting materials due to their opto-electronic properties and application in opto-electronic devices.[1-5] As a result, the photophysics of PPV has been investigated with various optical spectroscopy methods.[6-9] Most of these measurements, however, have been performed with conventional optical methods, and the properties of the sample are spatially averaged. It is known that PPV exhibits a rather complex morphology containing locally ordered areas with characteristic lengths well below the wavelength of visible light.[10-12] In order to reduce spatial averaging we use near-field scanning optical microscopy (NSOM) to probe the photoluminescence, linear dichroism and photoconductivity in PPV films on a mesoscopic scale (of the order of 100 nm).

2. Experimental

The reflection NSOM apparatus used in these experiments has been described in detail elsewhere.[13-15] Resolution below the diffraction-limit is made possible through the use of a standard metal coated, tapered optical fiber tip with apertures of 100 ± 10 nm.[16] The NSOM tip aperture is maintained in the near field of the sample surface (~ 15 nm) using optically-detected shear force feedback.[17] The feedback signal provides a topographical image of the sample simultaneously generated with the optical image. The NSOM image is acquired in illumination mode where the NSOM tip as a local excitation source of the 514 nm or 488 nm line of an argon ion laser. For absorption (or photoluminescence) imaging, the reflected (or

emitted) light is collected with a conventional microscope and routed to a photomultiplier tube (PMT). In photoluminescence NSOM (PL-NSOM) experiments, a holographic notch filter is used to suppress the excitation wavelength. For near-field photoconductivity (NPC) experiments, gold contacts are applied on top of the polymer film by vacuum evaporation using an optical fiber as a mask. The gap created between the electrodes is ~ 20 μm . A bias voltage is applied to the contacts and the photocurrent resulting from near-field excitation is imaged.

3. Results

Figure 1 shows a PL-NSOM image of a non-oriented PPV film. The NSOM image (Fig. 1b) shows a number of dark spots

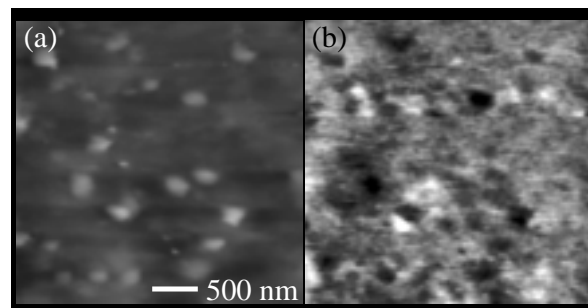


Figure 1. NSOM topography (a) and photoluminescence (b) images of a free standing PPV thin film. Note the one to one correspondence of the 100-200 nm dark spots in the PL image with the topographic features which are ~ 50 nm tall.

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~100–200 nm in diameter which correlate one-to-one with bumps in the topography image (Fig. 1a). The topography features are approximately 50 nm tall. PL spectra of dark spots compared with spectra from the film, are identical except in intensity, indicating that the bumps are polymer clusters. Note also that dark spots exist in the PL image which do not correlate with topography features. This is most likely due to polymer clusters below the surface of the polymer film which are not detected in the topography image.[18]

Figure 2 shows a PL-NSOM image of a stretch-oriented PPV film. Light and dark regions in the PL are observed to run parallel to the stretching direction and are correlated with features in the topography. The topography of the stretch-oriented sample is much different than that of the non-oriented sample. Most of the polymer clusters were annealed by the stretching process leaving fiber-like topography features oriented parallel to the stretching direction. These fibrils are approximately 50–100 nm tall, 100 nm–1 μm wide and have extremely high aspect ratios ($> 15 \mu\text{m}$ long). The emission at the edges of these fibrils is reduced but is relatively uniform over the remainder of the film. Polarized absorption NSOM images[18] reveal regions of well-oriented polymers in between the fibrils, with higher polarization anisotropy (100:1) than the spatially-averaged value of 30:1. This work also indicated that along the edges of some fibrils, the average orientation of the polymer film was perpendicular to the stretching direction. Chain defects and dislocations in the polymer film that accompany the change in average orientation near the edges of the fibrils are the most likely cause of the reduced emission in this region.

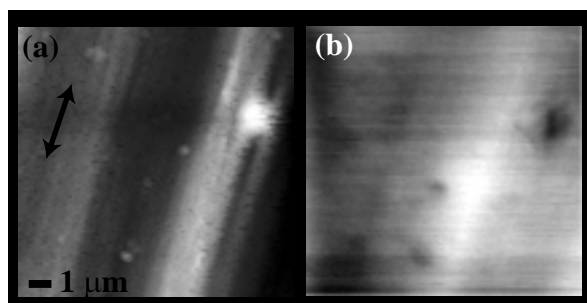


Figure 2. NSOM topography (a) and photoluminescence (b) of a stretch-oriented PPV film. This sample is different than the non-oriented film, with few polymer bumps and fibril features which run parallel to the stretch-direction indicated by the double-headed arrow. The PL image shows a relatively uniform emission except for striations correlated to the fiber-like topographic features.

Figure 3 shows an NPC image of a stretch-oriented film with the electric field applied parallel to the stretching direction. The fibril topography features are visible in the topography and cause striations in the photoconductivity signal. The NPC signal is uniform across the 20 μm gap. The vacuum evaporation technique used to create the Au electrodes leaves a rough edge with small particles of gold ~500 nm, concentrated near the edge of the electrode as seen in the topography, but this roughness appears to have no effect on the NPC signal.

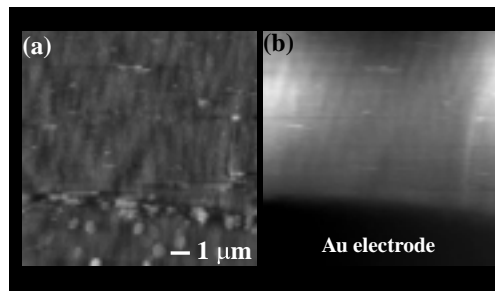


Figure 3. NSOM topography (a) and NPC (b) of a stretch-oriented PPV flat LED device. The Au electrode is seen in the topography as a rough edge and as the dark area in the NPC image.

4. Conclusions

We have shown that NSOM techniques can be successfully applied to PPV films to probe the optical and transport properties on a mesoscopic scale. The photoluminescence, absorption and photoconductivity are all shown to vary on a 100 nm scale as well as a strong dependence on the film morphology.

5. References

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