AIP | Applied Physics Letters

Nanometerscale absorption spectroscopy by nearfield photodetection optical microscopy

R. C. Davis and C. C. Williams

Citation: Applied Physics Letters **69**, 1179 (1996); doi: 10.1063/1.117403
View online: http://dx.doi.org/10.1063/1.117403
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/69/9?ver=pdfcov
Published by the AIP Publishing

Nanometer-scale absorption spectroscopy by near-field photodetection optical microscopy

R. C. Davis and C. C. Williams[a)]
Department of Physics, University of Utah, Salt Lake City, Utah 84112

(Received 19 January 1996; accepted for publication 17 June 1996)

Near-field photodetection optical microscopy (NPOM) is a fundamentally new approach to near-field optical microscopy. This scanning probe technique uses a nanometer-scale photodiode detector which absorbs optical power directly as it is scanned in the near field of an illuminated sample surface. We have applied NPOM to measure the visible absorption spectrum of dye molecules embedded in a single 300 nm polystyrene sphere. The near-field absorption spectrum is obtained by measuring the NPOM probe photocurrent while the wavelength of the illumination pump beam is scanned from 450 to 800 nm. Peaks are identified at 567, 608, and 657 nm in the near-field spectrum of the single-dyed polystyrene sphere. These peak positions are in good agreement with far-field absorption measurements performed on many dyed polystyrene spheres. [S0003-6951(96)01635-X]

Chemical and molecular identification on a nanometer scale has many important applications. Examples include the identification of biological structures such as proteins in heterogeneous environments. The ability to perform such measurements under liquid would aid in the understanding of biomolecular interactions at surfaces. The identification of trace chemical quantities is another related problem important to many areas of science and technology. The capability for generic molecular identification on the nanometer scale is largely unachieved. Optical spectroscopy is a potent method for performing chemical and molecular identification—either directly or through the use of fluorescent labels. However, due to the diffraction limitation, conventional far-field optical techniques do not extend far into the nanometer scale. Near-field optical microscopy offers the possibility of combining the power of optical spectroscopy with nanometer-scale spatial resolution.

Near-field scanning optical microscopy (NSOM) is a technique based on the collection or transmission of light through a subwavelength aperture scanned near a surface.[1–4] Nanometer-scale optical microscopy has also been performed without an aperture using an interferometric technique based on scattering from an atomic force microscope (AFM) tip near the sample.[5,6] In another measurement requiring a conducting surface, a scanning tunneling microscope (STM) tip has been used to perform nanometer-scale absorption microscopy and spectroscopy.[7]

Near-field photodetection optical microscopy[8–15] (NPOM) is a new, fundamentally different, approach to near-field optical microscopy and spectroscopy. It utilizes a photodetector of subwavelength dimensions. The localized photodetector probe is brought into the optical near field of an illuminated surface (conducting or nonconducting) where it can directly absorb optical power. As the photodetector is raster scanned across the surface, the photocurrent signal is recorded to create a two dimensional image of the optical intensity distribution. NPOM photodetectors with subwavelength tip radii, but with total photosensitive areas of many square micrometers, have been used to measure evanescent fields at surfaces.[8,10,13,14] Imaging results with such photodetectors have recently been published.[13,14] However, we contend that NPOM images can be generated with apparent high ''optical'' spatial resolution caused by topographic coupling. This effect has also been seen in NSOM.[1] Using our previous probes,[12] we have also observed high-resolution (20 nm) ''optical'' images that show direct correlation to the topographic structure. However, we have found it impossible to positively identify subwavelength ''optical'' spatial resolution in the presence of topographic variation. Recently, we have demonstrated NPOM imaging with a probe having a true subwavelength optically sensitive area of 100 nm $\times$ 100 nm.[15] In that work, it is shown clearly that the optical NPOM image is not directly correlated with surface topography. The spectroscopic work here also provides certain verification that the NPOM optical signal is not simply mapping topography.

Our photodetection probe is good choice for the near-field absorption spectroscopy performed here because of its high conversion efficiency relative to fiber probes. The setup for the NPOM probe is also simpler than NSOM in photon counting mode. Additionally, the direct absorption of power from evanescent fields in the optical near field is a physically different measurement than NSOM which may provide information that is otherwise inaccessible.

In this letter, the NPOM probe is utilized for the first time to perform nanometer scale molecular characterization. Spectroscopic characterization of dyed polystyrene spheres on a transparent, insulating surface (glass) is accomplished by near-field absorption spectroscopy [Fig. 1(a)]. The dyed spheres are illuminated through the glass. The NPOM photodiode probe is brought into the optical near field of a single-dyed polystyrene sphere on the cantilever surface where it detects the modification of the illumination fields due to the presence of the sphere. The illumination beam is scanned in wavelength and the NPOM probe photocurrent is used to record the spectroscopic response of the particle.

The experimental setup is illustrated in Fig. 1. A noncontact AFM technique is used to control the height of the

a)Corresponding author.

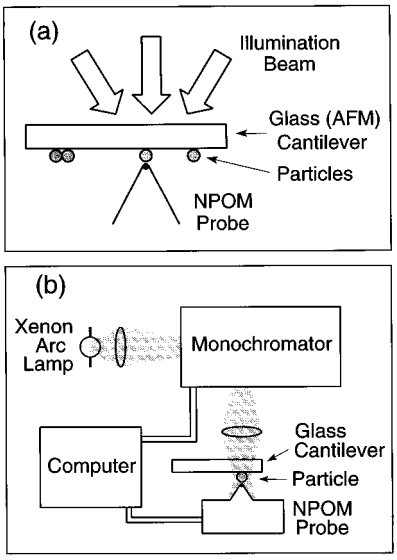

FIG. 1. (a) Near-field absorption experimental setup. (b) Near-field absorption spectroscopy optical setup.

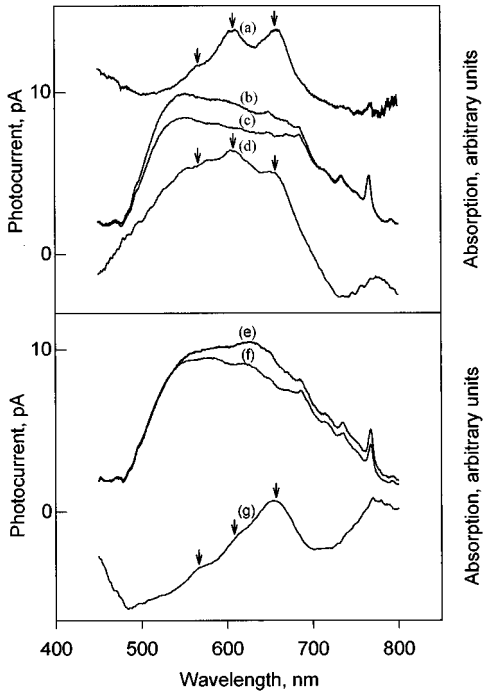

FIG. 2. Near-field absorption spectra of two separate dyed polystyrene spheres. (a) The far-field absorption spectrum of a monolayer of dyed spheres (shown for comparison). (b) The photocurrent response with the probe tip on the surface of the glass cantilever but away from a dyed sphere (system response). (c) The photocurrent response with the probe tip in the near field of a single polystyrene sphere (scaled). (d) The near-field absorption spectrum of the dyed plystyrene spheres. obtained from curves (b) and (c). (e)–(g) The corresponding system response, near-field response, and near-field absorption spectrum for a different 300 nm particle.

probe above the sample surface. While in conventional AFM the probe tip is mounted on a cantilever, in our current experiment, the *sample* is placed on a glass AFM cantilever.[15] A similar setup has been used for NSOM.[16] The sample consists of dye molecules embedded in 300 nm polystyrene spheres. These are ''blue dyed latex spheres, Mfg. Lot No. 3132,'' obtained from Seradyne, Inc.[17] Seradyne will not provide the chemical identity of the dye molecule as the dye is proprietary. The spheres are dispersed on the surface of the 1 mm $\times$ 100 μm $\times$ 20 μm glass cantilever. The NPOM probe is mounted on a piezoelectric scanning tube. The illumination source consists of a 75 W xenon arc lamp source and a 0.32 m scanning monochromator. The monochromator is used to pass a narrowband of wavelengths from the broadband arc lamp illumination source. This light is focused through the glass cantilever to a 50 μm spot on the AFM cantilever surface. This illuminates the dyed spheres, dispersed on the cantilever surface. A computer is used to scan the monochromator wavelength and record the photocurrent of the NPOM probe.

Far-field absorption spectra of the dyed polystyrene spheres are obtained for comparison with near-field results. A monolayer of dyed spheres is distributed on a glass microscope cover slip and placed in the beam path before the beam is focused onto the NPOM detector. Spectra are taken with and without the monolayer in the beam path to separate the response of the particles from the optical system response. Without the monolayer in the beam path, the wavelength is scanned from 450 to 800 nm and the photocurrent is recorded. This spectrum is the system response, $I(\lambda)$, consisting of the output spectrum of the arc lamp source multiplied by the responses of the monochromator and the NPOM probe. The monolayer is then placed in the beam path (in the far field) and another spectrum is taken. With the monolayer in the beam path, the product of the system response, $I(\lambda)$, and the transmission through the monolayer, $T(\lambda)$, is measured. The system response $I(\lambda)$ is divided out as follows:

$$\frac{\text{With monolayer}}{\text{Without monolayer}}=\frac{I(\lambda)T(\lambda)}{I(\lambda)}=T(\lambda)=1-A(\lambda).$$

Subtracting this from unity gives the absorption, $A(\lambda)$, by the monolayer, displayed in Fig. 2(a). We do not expect any spectral signature from scattering, and neglect it in this treatment. Peaks are observed at 567, 608, and 657 nm. This absorption curve is in excellent agreement with an absorption measurement performed on the dyed spheres with a commercial spectrophotometer (Varian model 17D).

To demonstrate the high spatial resolution of the spectroscopy measurement, the NPOM probe is brought into the near field of the dyed spheres distributed on the glass AFM cantilever. The spatial distribution of the optical power in the near field of the spheres is obtained by raster scanning the probe to generate an image (Fig. 3). The image size is 3.5 μm $\times$ 3.5 μm. The illumination wavelength is fixed at 550 nm. The image displayed on the left side is a noncontact AFM image, representing topography. The image on the right is NPOM photocurrent. One of the dyed spheres is located near the center of the image. In this region, the optical image shows a bright spot surrounded by a dark ring. When the absorption spectrum is taken in the near field of the sphere, the probe is centered on the top of the sphere. The noncontact AFM image shows structure containing multiple bumps centered on the sphere. We can attribute this structure to the finite size and shape of the NPOM probe, as the multiple bump shape and orientation are repeated at other places in the AFM image. Another confirmation that we are looking

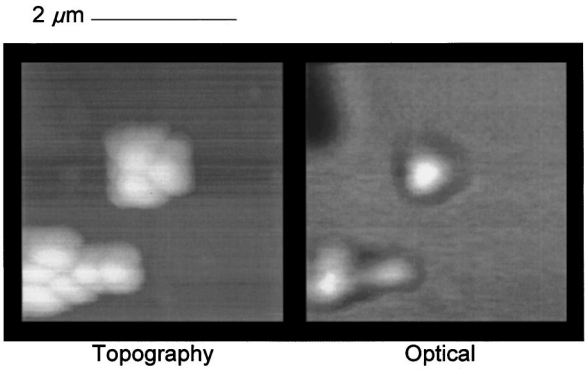

FIG. 3. An NPOM image of a 300 nm dyed polystyrene sphere. The left image is noncontact AFM. And the right image is NPOM photocurrent.

at a single-dyed sphere is that the spatial extent of the AFM structure is significantly larger than the width of the structure in the NPOM image. The spatial half width of this structure in the NPOM image (300 nm) corresponds to the known size of the polystyrene spheres. This image (Fig. 3) is characteristic of the many polystyrene spheres we have imaged.

Near-field spectroscopy is performed with the probe in the near field of a dyed sphere. As in the far-field measurement, two spectra are taken to separate the spectral response of the dyed sphere from that of the rest of the optical system. To measure the system spectral response, the NPOM probe is moved away from the sphere of interest a distance of two micrometers. The wavelength is scanned from 450 to 800 nm and the photocurrent is recorded [Fig. 2(b)]. The probe is then centered on the top of the sphere and the photocurrent is again recorded as the wavelength is scanned [Fig. 2(c), scaled by 0.7 to plot with Fig. 2(b)]. Curve 2(c) is divided by curve 2(b) and subtracted from unity. The result is scaled and shifted to plot with the other curves in Fig. 2. We call the result the near-field absorption spectrum [Fig. 2(d)]. Peaks in the near-field absorption spectrum of this sphere are observed at 610 and 660 nm. The positions of these peaks are in good agreement with the far-field measurement. There are however several differences in Fig. 2(d) when compared to the far-field spectrum [2(a)]. The shoulder seen at 570 nm in the far field is not observed here and the relative amplitudes of the observed peaks differ as well. The differences between near-field and far-field spectra are not understood and require further study.

Not all dyed spheres exhibit exactly the same near-field absorption spectrum. Figures 2(e)–2(g) display the spectrum of a particle at a different location on the AFM cantilever surface. Photocurrent curves are obtained with the NPOM probe located two micrometers away from the particle [Fig. 2(f)] and centered above the particle [Fig. 2(e), scaled by 0.7]. Repeating the procedure described above, the system response is removed yielding the near-field absorption spectrum of the dyed sphere [Fig. 2(g)]. the peak at 660 nm is clearly visible in the near-field spectrum. The peak at 610 nm is now seen as a shoulder at that wavelength. The shoulder at 570 nm is also observed. The position of all three peaks are in excellent agreement with the far-field spectrum. The measurement of the spectra on and off this particle was repeated three times to confirm that we were measuring the true spectral response of the particle and not the convolution of its spectral response with some system drift. The repeatability of the measurement was excellent. This particle is exhibiting a clear spectral difference from the first particle [Figs. 2(b)–2(d)]. Other particles studied, likewise, showed good agreement in peak position. They also exhibited variations in peak amplitude. We attribute these spectral differences from particle to particle to the local optical environment of the particle relative to the reference spectrum location. The reference spectrum is taken with the probe moved laterally across the surface a distance of 2 μm. The differences are due to interference effects that we observe near the sample surface.

Note that these measurements were performed with an incoherent source (<1 W/cm^2). If tunable laser sources are used, spectroscopy of much smaller single particles can be performed provided the spacing between the particles is not smaller than the resolution of the probe.

In summary, we have performed near-field absorption spectroscopy on dye molecules embedded in a single 300 nm polystyrene sphere using a 100 nm NPOM detector. Positive identification of the dye was made by comparison to far-field absorption measurements on the dye. This is the first absorption spectroscopy performed by near-field photodetection optical microscopy.

We thank Pavel Neuzil for contributions to the fabrication of NPOM detectors used in this work. We also thank John Worlock for useful discussion regarding the measurement results. This work was supported by the National Science Foundation (Grant No. ECS-9212407).

[1] E. Betzig and J. K. Trautman, Science **257**, 189 (1992).
[2] H. F. Hess, E. Betzig, T. D. Harris, L. N. Pfeiffer, and K. W. West, Science **264**, 1740 (1994).
[3] J. K. Trautman, J. J. Macklin, L. E. Brus, and E. Betzig, Nature **369**, 40 (1994).
[4] H. Heinzelmann and D. W. Pohl, Appl. Phys. A **59**, 89 (1994).
[5] F. Zenhausen, M. P. O'Boyle, and H. K. Wickramasinghe, Appl. Phys. Lett. **65**, 1623 (1994),
[6] F. Zenhausen, Y. Martin, and H. K. Wickramasinghe, Science **269**, 1083 (1995).
[7] J. M. R. Weaver, L. M. Walpita, and H. K. Wickramasinghe, Nature **342**, 783 (1989).
[8] D. R. Busath, R. C. Davis, and C. C. Williams, in *Scanning Probe Microscopies II*, edited by C. C. Williams, Proc. SPIE **1855** (SPIE, Bellingham, 1993), p. 75.
[9] H. U. Danzebrink, U. C. Fischer, in *Near Field Optics*, edited by D. W. Pohl and D. Courjon (Kluwer, Netherlands, 1993), pp. 303–308.
[10] D. R. Busath, thesis, University of Utah, 1994.
[11] H.-U. Danzebrink, J. Microsc. **167**, 276 (1994).
[12] R. C. Davis, C. C. Williams, and P. Neuzil, Appl. Phys. Lett. **66**, 2309 (1995).
[13] H.-U. Danzebrink, G. Wilkening, and O. Ohlsson, Appl. Phys. Lett. **67**, 1981 (1995).
[14] S. Akamine, H. Kuwano, and H. Yamada, Appl. Phys. Lett. **68**, 579 (1996).
[15] R. C. Davis, C. C. Williams, and P. Neuzil, Opt. Lett. **21**, 447 (1996).
[16] R. J. Stephenson and M. E. Welland, Appl. Phys. Lett. **68**, 1607 (1996).
[17] Seradyn, Inc., 1200 Madison Avenue, P.O. Box 1210, Indianapolis, IN 46206.