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Valentin Lulevich and William A. Ducker

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Scanning near-field optical microscopy utilizing silicon nitride probe photoluminescence

Valentin Lulevich
Department of Chemistry, Virginia Tech, Virginia 24061

William A. Ducker[a)]
Department of Chemical and Biomolecular Engineering, University of Melbourne, Australia and Department of Chemistry, Virginia Tech, Virginia 24061

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We describe a simple method for performing high-resolution scanning near-field optical microscopy (SNOM). A commercial Si_3N_4 tip is illuminated by an intense light source, which causes the tip to emit redshifted (inelastically scattered) light. Part of the redshifted light passes through a sample, allowing transmission light microscopy. By simple modification of a commercial atomic force microscopes (AFM), we are able to image many different samples with high-resolution optical microscopy, achieving 20–30 nm lateral resolution for the best samples. The high resolution of the technique is not only due to the high curvature of the AFM tip, but also to the fact that the intensity of inelastically scattered light transmitted through the sample decays exponentially with the separation between the tip and the sample (decay length ~100 nm). We envisage applications to transmission SNOM, spectroscopic imaging, and imaging of fluorescently labeled bioconjugates. The collection of the optical image does not interfere with the normal operation of the AFM, so deflection, height, or other modes of operation can be captured simultaneously. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2136216]

Scanning near-field optical microscopy (SNOM) (Refs. 1 and 2), is an exciting optical technique in which the "diffraction limit" of far-field optics is overcome by positioning a sharp tip (10–100 nm) near the sample. This sharp tip is used to either emit or collect light. The advantage of SNOM over other high-resolution scanning microscopes, such as atomic force microscope (AFM) (Ref. 3), is that the contrast mechanism involves the interaction between light and matter and therefore there are opportunities to identify adsorbed molecules via spectroscopy.

SNOMs can be classified into two groups:[4,5] (1) waveguide SNOMs, in which the sharp probes act as a waveguide for the collection or emission of light,[2] and (2) "apertureless" SNOMs, in which the sharp probe is used either to scatter light that is generated from an evanescent wave,[5–7] or to detect the coupling of dipoles in the probe and the sample.[8]

In this letter, we present a new approach to SNOM, in which we use a regular AFM tip to scatter light (as in apertureless SNOM) but we use the property of inelastic light scattering by Si_3N_4 AFM tips. We find that when a Si_3N_4 AFM tip is illuminated by an intense 532-nm light source, the tip emits light with a maximum intensity of about 650 nm (orange). We do not observe any photobleaching of the tip over a period of hours. The intensity of light that is coupled from the tip into a glass plate decays exponentially with distance to the plate. This phenomenon offers the promise of a good imaging mechanism because the exponential signal localizes the optical output near the apex of the tip, and the frequency shift should offer a high signal-to-noise ratio because the stimulating light source can be removed by filtration. Thus, the AFM tip is easily turned into a tiny light source that can be scanned to produce an image. This principle is similar to that described by Kopelman *et al.*[9] for the use of an organic fluorophore as a scanning light source, and implemented by Göttlich and Heckl[10] using a fluorescent porous silicon particle as a light source. The advantages of our system are that (1) a mass-produced commercial probe can be used and (2) a much higher resolution was obtained in our experiments, most likely because of a smaller emitting probe and the use of feedback on cantilever deflection allowed closer proximity to the sample. Bouhelier *et al.* have demonstrated photoemission from a gold tip.[11]

The schematic of the experiment is shown in Fig. 1. An AFM (Asylum 3D, Santa Barbara) was mounted above a conventional inverted optical microscope Zeiss Axiovert (Carl Zeiss, Thornwood, NY). The optical microscope was equipped with an oil immersion objective lens (NA 1.45, 60× TIRFM objective, Olympus). Laser light, reflected from a dichroic mirror, was focused on the AFM tip (1–5 μm focus diameter) by the objective lens. A high numerical aperture lens was used because it gives a high optical magnification of the tip and provides the ability to use a high angle of refraction (relative to the normal). After the objective, the beam passes through a thin-bottom (0.1–0.15mm) glass dish (MatTec, US) or a freshly cleaved mica sheet. A small drop of index matching liquid (microscope oil type B, refractive index 1.515, Cargille, US) was placed between the lens and the surface. A thermoelectrically cooled diode laser (532 nm, 10 mW, TECGL-10, World Star Tech., Canada) was used as a light source. We used commercial silicon nitride AFM cantilevers (Veeco, US) with integrated, hollow square-pyramidal Si_3N_4 tips (spring constant 0.3–0.6 N/m). The cantilevers were coated with 10 nm Cr and 30 nm Au on the side opposite the protruding tip. We found that luminescence occurred with or without the metallic coating but was greater with the metallic coating. This shows that the silicon nitride

[a)]Electronic mail: wducker@unimelb.edu.au

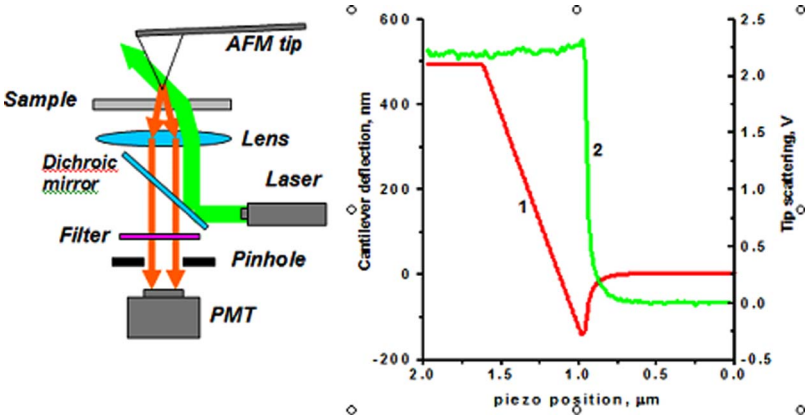

FIG. 1. (Color online) Schematic of the apparatus (left) and signal as a function of tip travel (right). The red (1) curve is the cantilever deflection measured as the tip approaches the sample and the green (2) is the intensity of inelastically scattered light.

itself is photoluminescent but that gold enhances the luminescence.

Light scattered from the tip was collected by the microscope objective and the incident green light was removed with a dichroic mirror and long-pass filter; the orange light was collected by a photomultiplier tube (PMT) (Hitachi H5784-01). Resolution was improved by the addition of a small aperture placed before the PMT. All images presented here were captured in air, but images can also be captured in water.

The intensity of orange light that passes back through the sample and is captured by a photomultiplier tube decays exponentially with the separation between the tip and the sample, as shown in Fig. 1. The best lateral resolution in optical imaging was recorded when the incident laser light was focused onto the tip and the beam angle was adjusted to give the largest gradient of the inelastically -scattered intensity as a function of separation. We note that the high power-density beam causes a large force that pulls the tip toward the sample. The rapid decay of the intensity (decay length ~100 nm) keeps the emitted orange light localized to a small region, thereby providing high resolution. We find that silicon nitride tips from several batches and a variety of types produce this inelastic scattering effect. Under the conditions of our experiments, when the AFM is removed, the green light passes through the sample and illuminates the ceiling of our laboratory, clearly indicating that the beam that illuminates the tip is not evanescent. This suggests that the exponential decay of the optical signal is due to a near-field interaction between the tip and the sample. The photoluminescent effect itself is not due to a near-field interaction because there is a component of the photoluminescence that is present at large (millimeter) separations. At this point we do not understand the molecular origin of the photoluminescence in silicon nitride.

We use the inelastic scattering to obtain high-resolution images of samples. While all the other optical components are kept stationary, the sample is scanned under the tip, so that different positions on the sample come into the path of the intense part of the orange light emitted from the tip. Figure 2 shows images of tobacco mosaic virus in which the AFM is used with feedback to the cantilever Z displacement to maintain constant cantilever deflection. At the same time that we collect the high-resolution AFM image, we also record the intensity of light that is captured by a PMT positioned below the sample to obtain the optical image. Note that the virus is revealed as regions of low light intensity. This is in contrast to the commonly observed imaging artifact where sharp, high features produce higher intensity due to failure of the feedback loop to maintain a constant height above the sample.[12] The optical contrast mechanism is made clear by imaging opaque carbon particles in constant height mode, where the tip stays at an approximately constant height above the glass slide (Fig. 3). Particles as small as 20–30 nm in diameter can be resolved. In earlier work by Azoulay *et al.*,[13] apertureless optical images of (opaque) metal islands showed the islands as regions of high optical signal. This was interpreted as arising from interference between the optical signal from the AFM tip and the specular-reflection field. In Fig. 3, the contrast is reversed compared to that observed by Azoulay *et al.*: a large optical signal arises from the gaps between the opaque particles. This contrast is consistent with contrast arising through absorption, as with transmission light microscopy. The different contrast obtained here is explicable because we are filtering out the

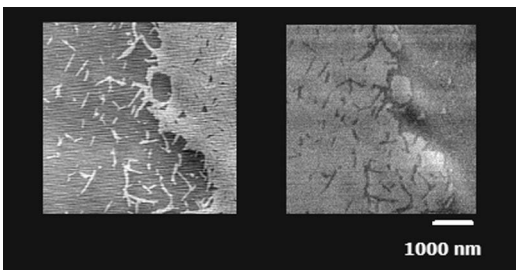

FIG. 2. Simultaneously recorded image of AFM cantilever Z displacement (left) and near-field optical image (right) of tobacco mosaic virus adsorbed on mica, and recorded in air. Images were acquired with strong feedback to maintain constant cantilever deflection through cantilever Z displacement. The SNOM image is in positive contrast (low intensity = black).

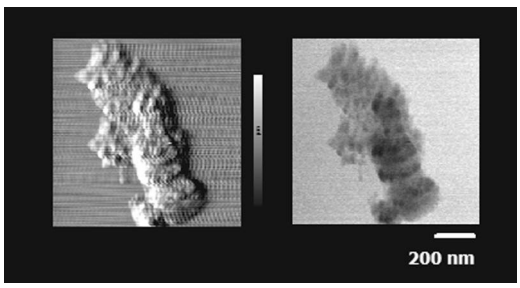

FIG. 3. Simultaneously recorded AFM cantilever deflection (left) and near-field optical images (right) of graphite particles adsorbed on glass and recorded in air. Images were acquired with weak feedback to maintain an approximately constant height above the glass. The SNOM image is in positive contrast (low intensity = black).

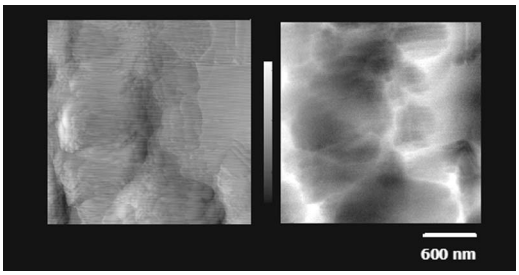

FIG. 4. Simultaneously recorded constant-height AFM (left) and near-field optical images (right) of KCl polycrystalline particles adsorbed on glass and recorded in air. Images were acquired with weak feedback. The SNOM image is in positive contrast (low intensity = black).

incident 532-nm light and collecting only light that is inelastically scattered from the tip. Therefore our optical scheme is very similar to the regular fiber-probe SNOM, where light is emitted from an aperture. This is further clarified in Fig. 4, an image of KCl crystals, where the large optical signal corresponds to the gaps between the crystals. For optically transparent samples such as the virus and KCl, the diminished intensity of transmitted light cannot arise by absorption, so the contrast must arise from the near-field interaction of the dipolar field of the sample with the tip.[8] Note also that in Fig. 4 there is not a perfect correlation between the optical and deflection images: the optical image is not simply a record of the cantilever deflection.

In conclusion, we present a simple, novel approach to high-resolution optical imaging based on the photoluminescence of commercial silicon nitride AFM tips. After stimulation with intense green light, emitted orange light from the tip can be used to probe the sample. The intensity of this orange light decays exponentially with distance from the sample. We achieve 20–30 nm resolution parallel to a surface and 2–5 nm normal to the surface for different samples. At present our tests of resolution are limited by sample feature size. Our images always produce a large optical signal when the tip is above gaps between adsorbed features, and a lower intensity for adsorbed materials that block light to the tip. We have shown that we can vary the frequency of the scattered light, so spectroscopic imaging is also possible. One can also envisage other modes where the tip is scanned at a constant optical signal, or oscillatory modes.

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