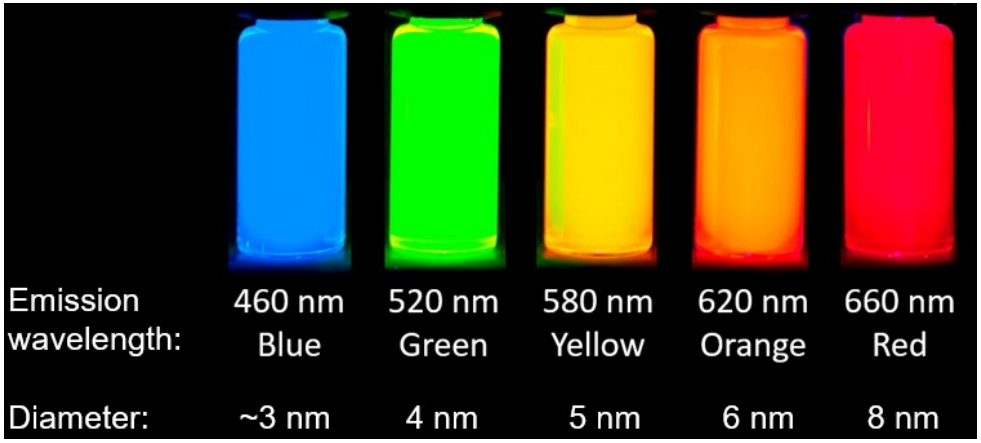
AFM, STM

Nanofeatures: size, morphology, location, interaction …

NSOM

Quantum Dots (behind QLED TV)



Light

Absorption → Color

Luminescence → LED device

Band gap → Electronics

Optoelectronics

Photovoltaics, photoelectric, LED, sensors …

Lecture 16: Near-field Scanning Optical Microscopy (NSOM)

- Background of NSOM;
- Basic principles and mechanisms of NSOM;
- Basic components of a NSOM;
- Different scanning modes and systems of NSOM;
- General applications and advantages of NSOM.

Some people call it Scanning Near-field Optical Microscopy (SNOM)

Scanning probe microscopies

STM

Atomic resolution;
Molecular bonding.

AFM

Atomic Interaction:
- Contact mode
- Non-contact mode
- Tapping (intermittent) mode

Other Interactions:
- Electrostatic mode (scanning electrostatic potential microscope)
- Magnetic mode
- Chemical Force mode

NSOM

Direct correlation between nanostructures and optical properties

tunable

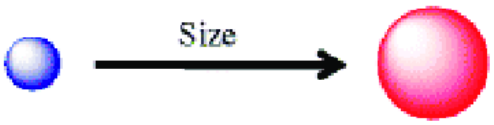
SCM
(scanning confocal microscope)
Single-molecule spectroscopy

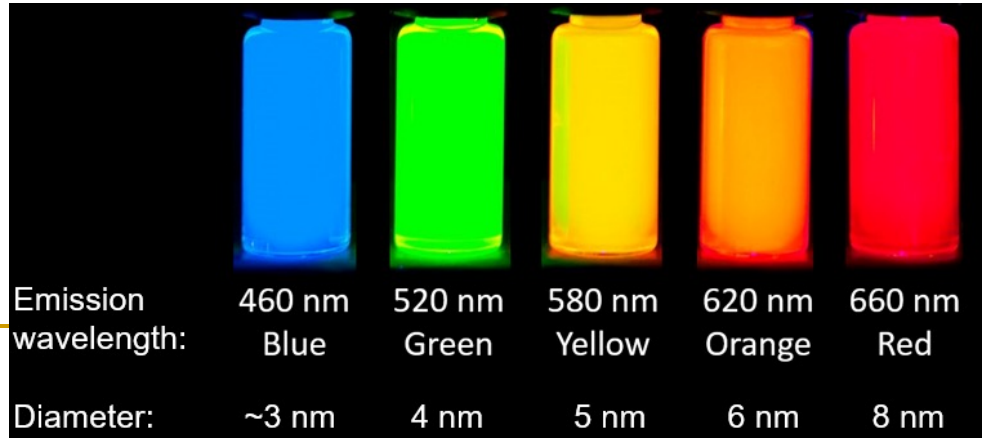
What can NSOM do?

- STM measures electric current, and AFM measures forces, neither deals with light;
- Light is a crucial excitation source in both scientific research and mother nature systems (e.g. photosynthetic system).
- Scientific research fields: absorption, fluorescence, photoinduced electron transfer, light-emitting devices, photovoltaic cells.

Why NSOM?

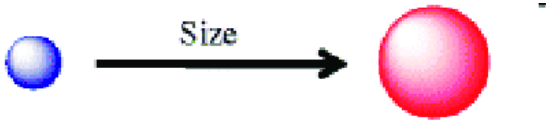
- Light diffraction limit of conventional optical microscopy: λ/2, ~ 250 nm. Actually, in real cases, the optical resolution ~λ, 500 nm; in contrast, NSOM offers higher resolution around 50 nm (or even < 30 nm), depending on tip aperture size.
- NSOM provides simultaneous measurements of the topography and optical properties (fluorescence) --- *direct correlation* between surface nanofeatures and optical/electronic properties.
- This is especially useful for the studying the inhomogeneous materials or surfaces, like nanoparticles, polymer blends, porous silicon, biological systems. Next slide

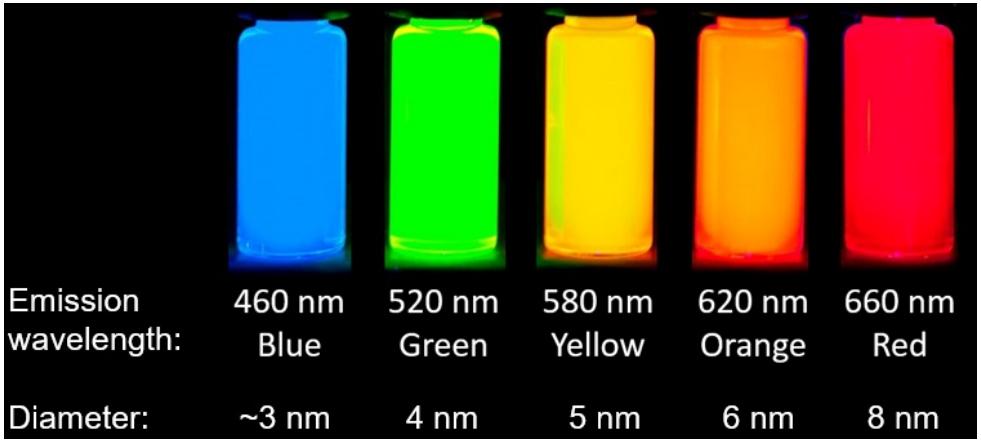




NSOM imaging:

Direct correlation between size and optical/ electronic properties

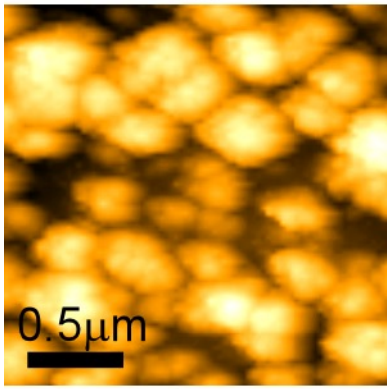




NSOM imaging:

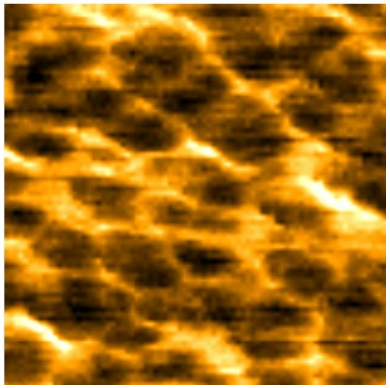
Direct correlation between locations and optical/ electronic properties

NSOM topgraphy



TiO_2 particles wrapped in PPV film

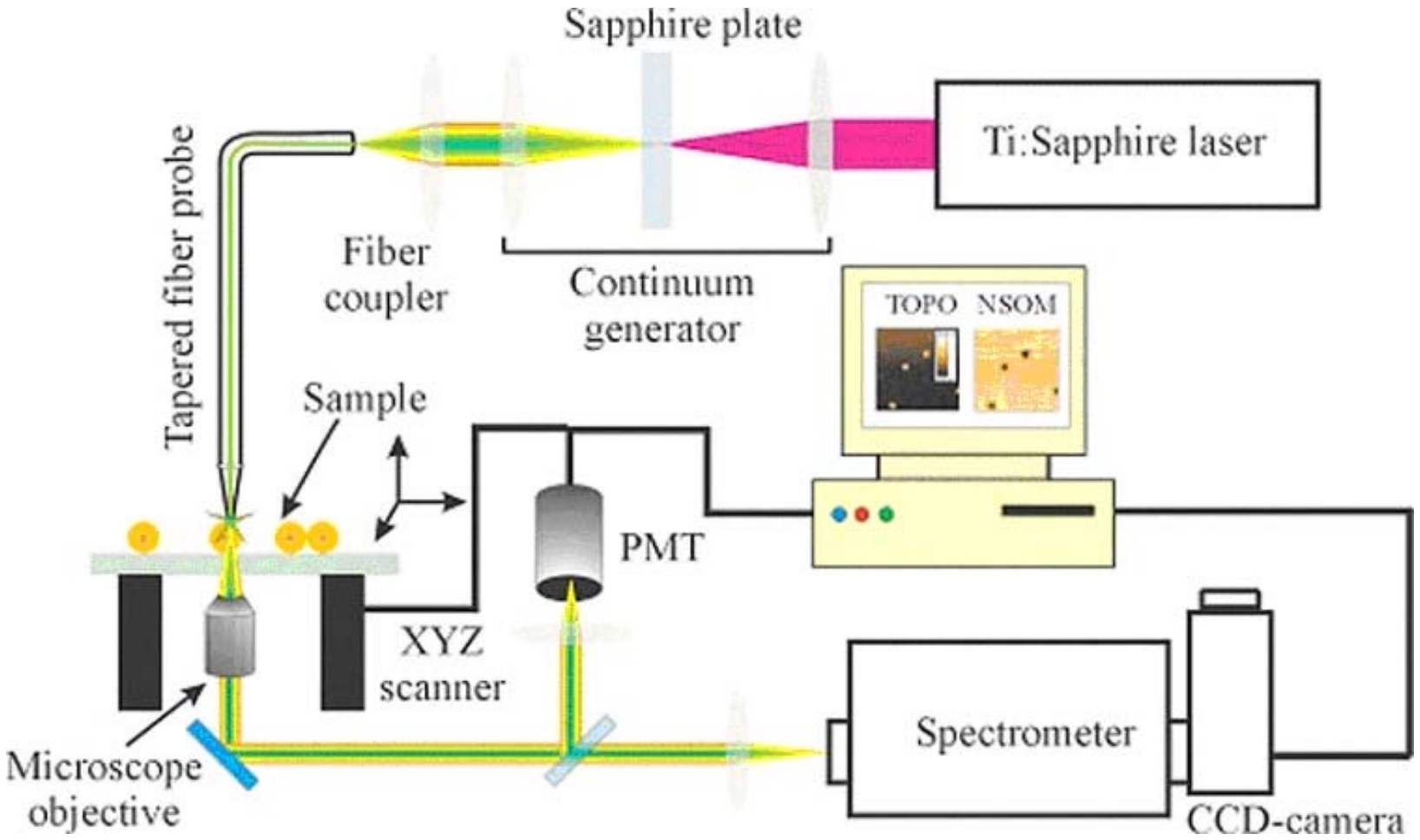
NSOM fluorescence



Fluorescence quenching by TiO_2 particles

Liu, J. Phys. Chem. C 2009, 113, 9368–9374

NSOM Operation System: feedback based on AFM



Major components of NSOM

Optical:

- Light source (lasers: CW and pulsed), Fibers, Mirrors, Lenses, Objectives (oil, large NA)
- Photon detectors (Photon-Multiplier, Avalanche Diode)
- Probe (tip)

Mechanical:

- Translation stage, Piezo scanner
- Anti-vibration optical table

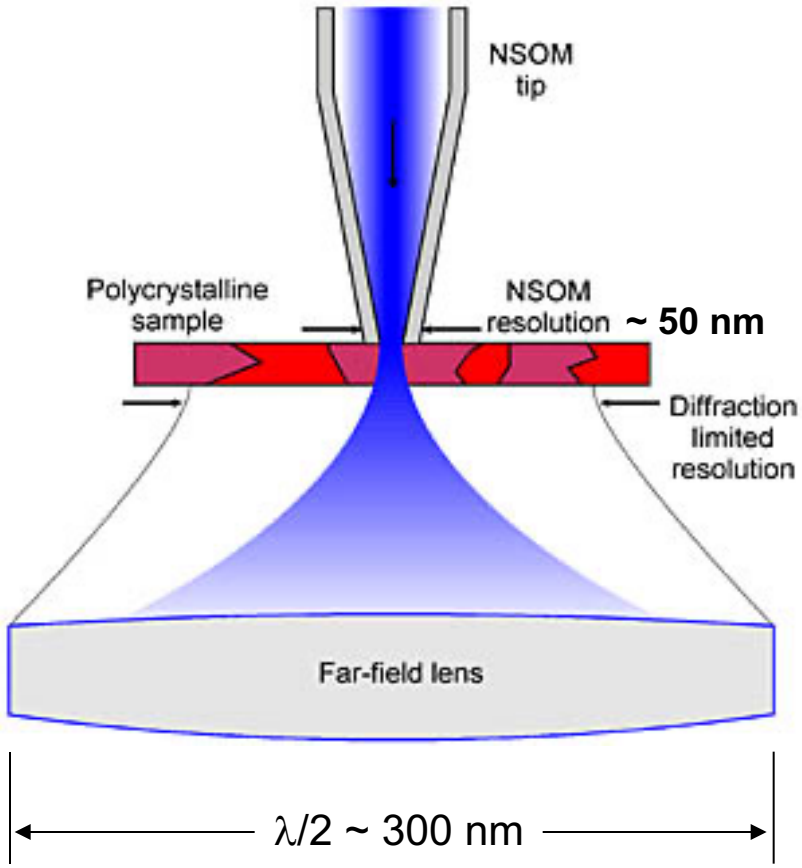
Electrical:

- Scanning drivers for piezo scanner
- z distance control (feedback system)
- Amplifiers, Signal processors
- Software and Computer

What is Near-Field?

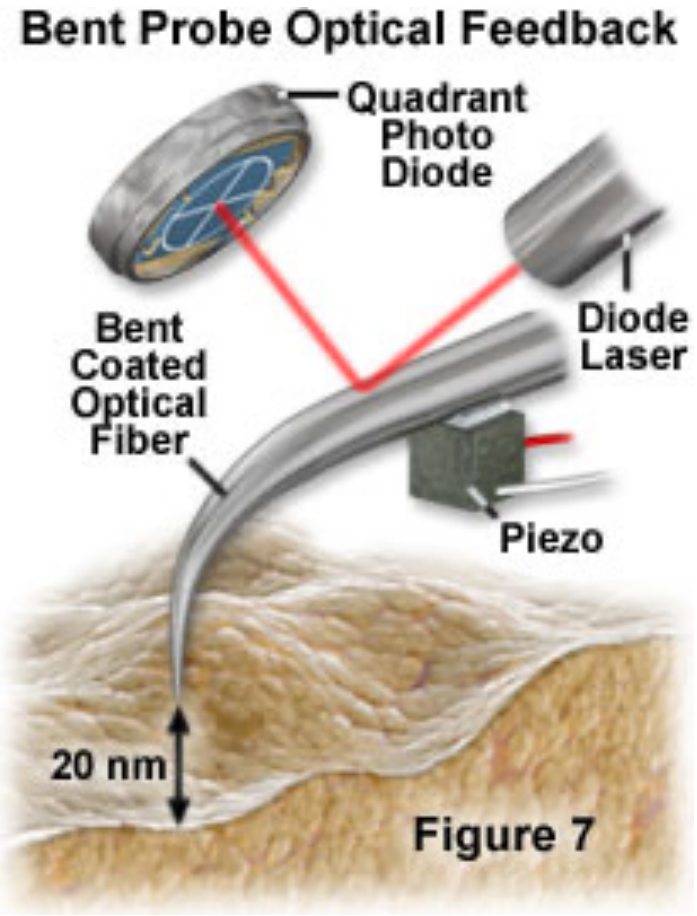
- requires a nanometer sized aperture (much smaller than the light wavelength).
- A specimen is scanned very close to the aperture.
- As long as the specimen remains within a distance less than the aperture diameter, an image with sub-wavelength resolution (aperture size) can be generated.
- There is a tradeoff between resolution and sensitivity (light intensity) --- aperture size cannot be too small.

What is Near-Field?

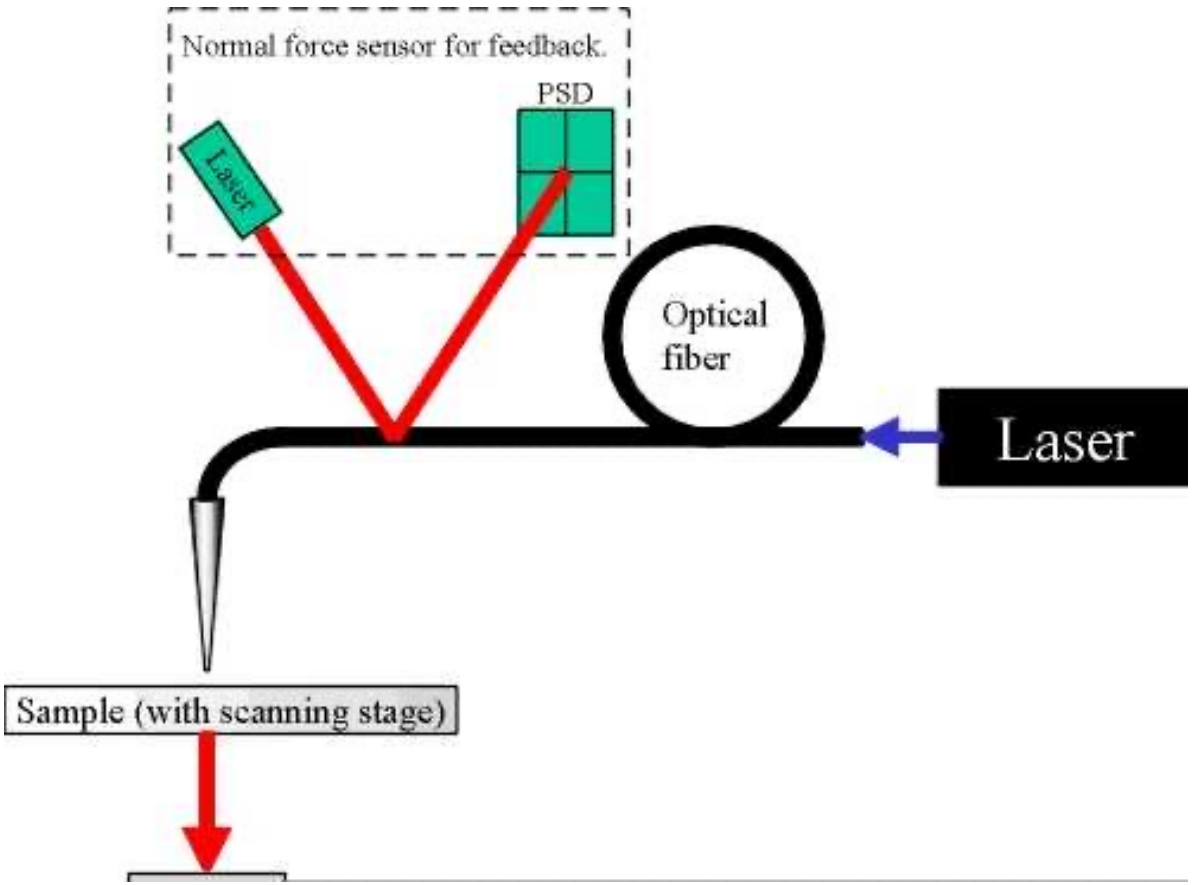


- For high spatial resolution, the probe must be close to the sample

Feedback Mechanism 1: *AFM force sensor*



Feedback Mechanism 1: *AFM force sensor*

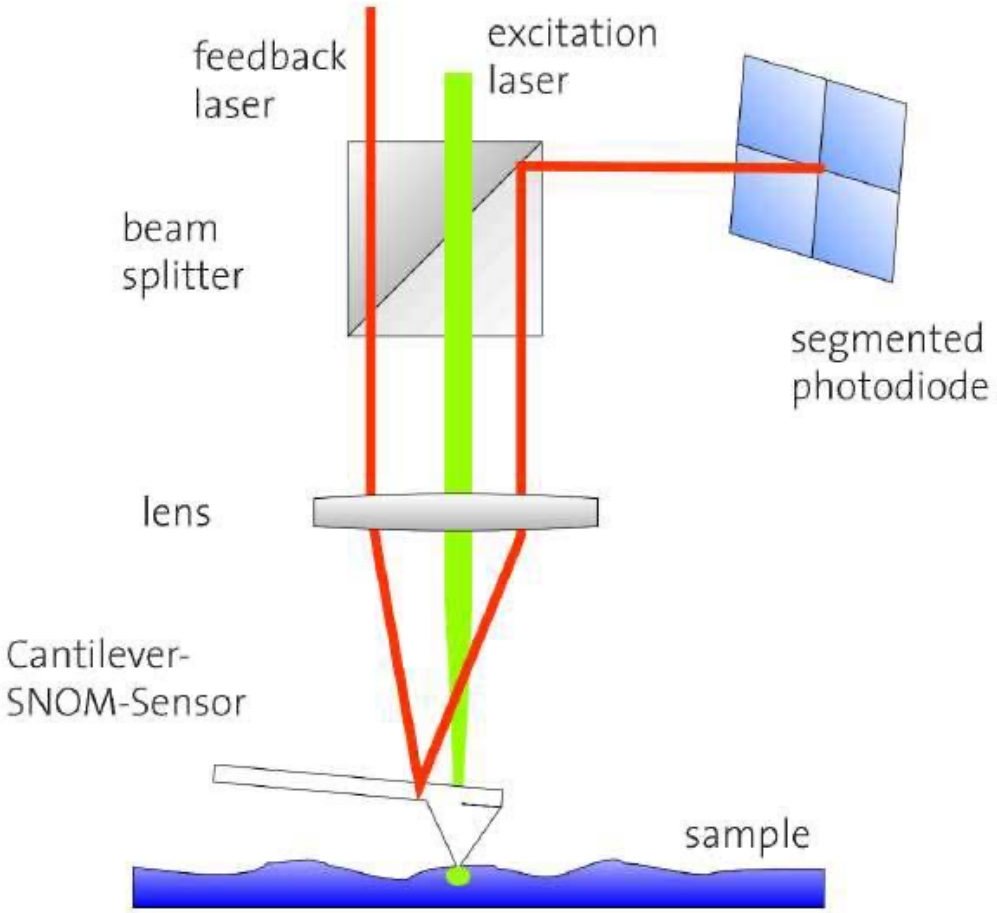


comments:

- Poor spatial resolution due to the fiber cantilever (reflection and spring constant);
- Damage to sample due to tapping scanning.

Nanonics Imaging Ltd.

Feedback Mechanism 2: *Modified AFM*

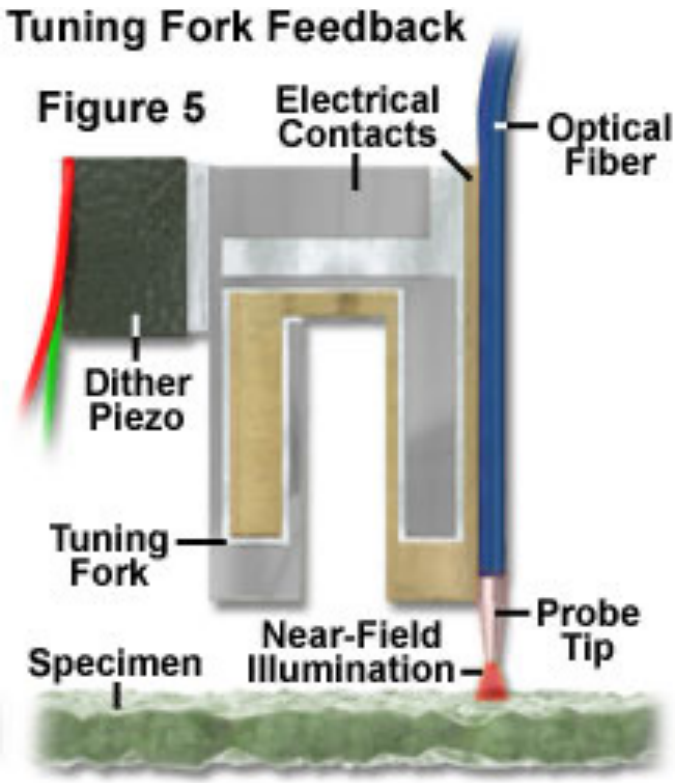


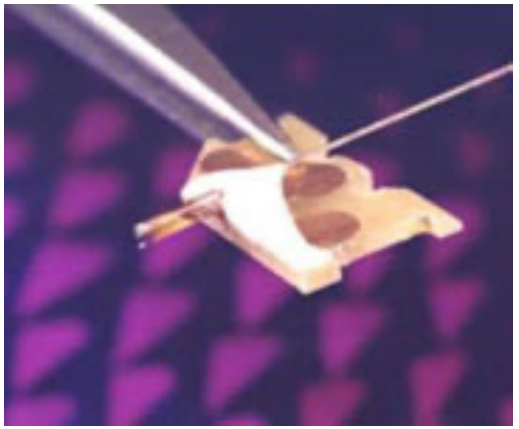
Comments:

- Difficult for optical alignment, two laser beams involved.

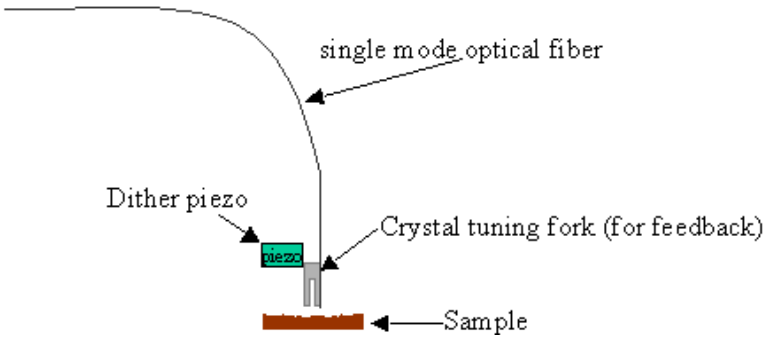
WITec AlphaSNOM

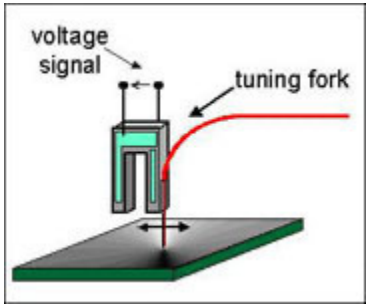
Feedback Mechanism 3: *Shear Force with Tuning Fork*

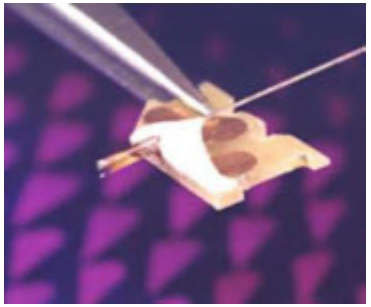




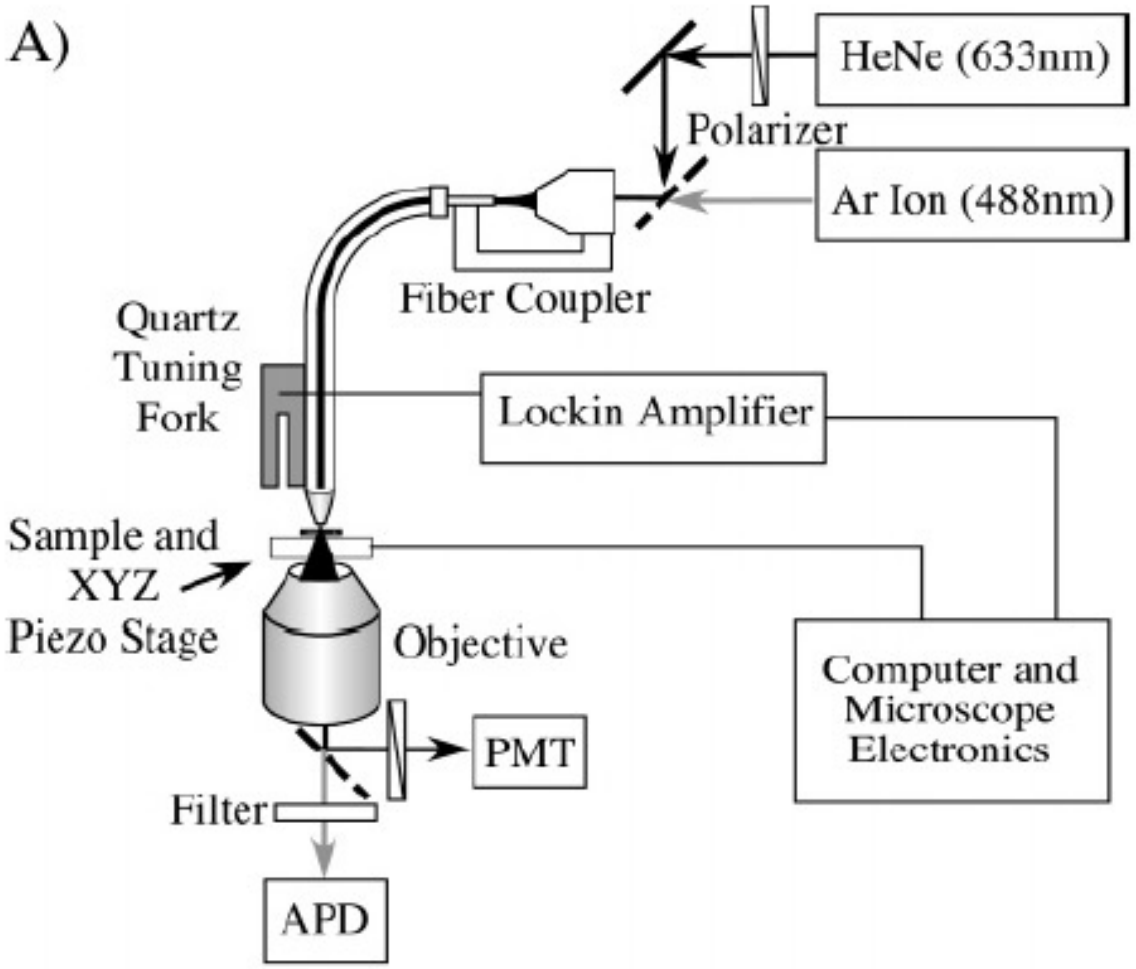
Feedback Mechanism 3: *Shear Force with Tuning Fork*





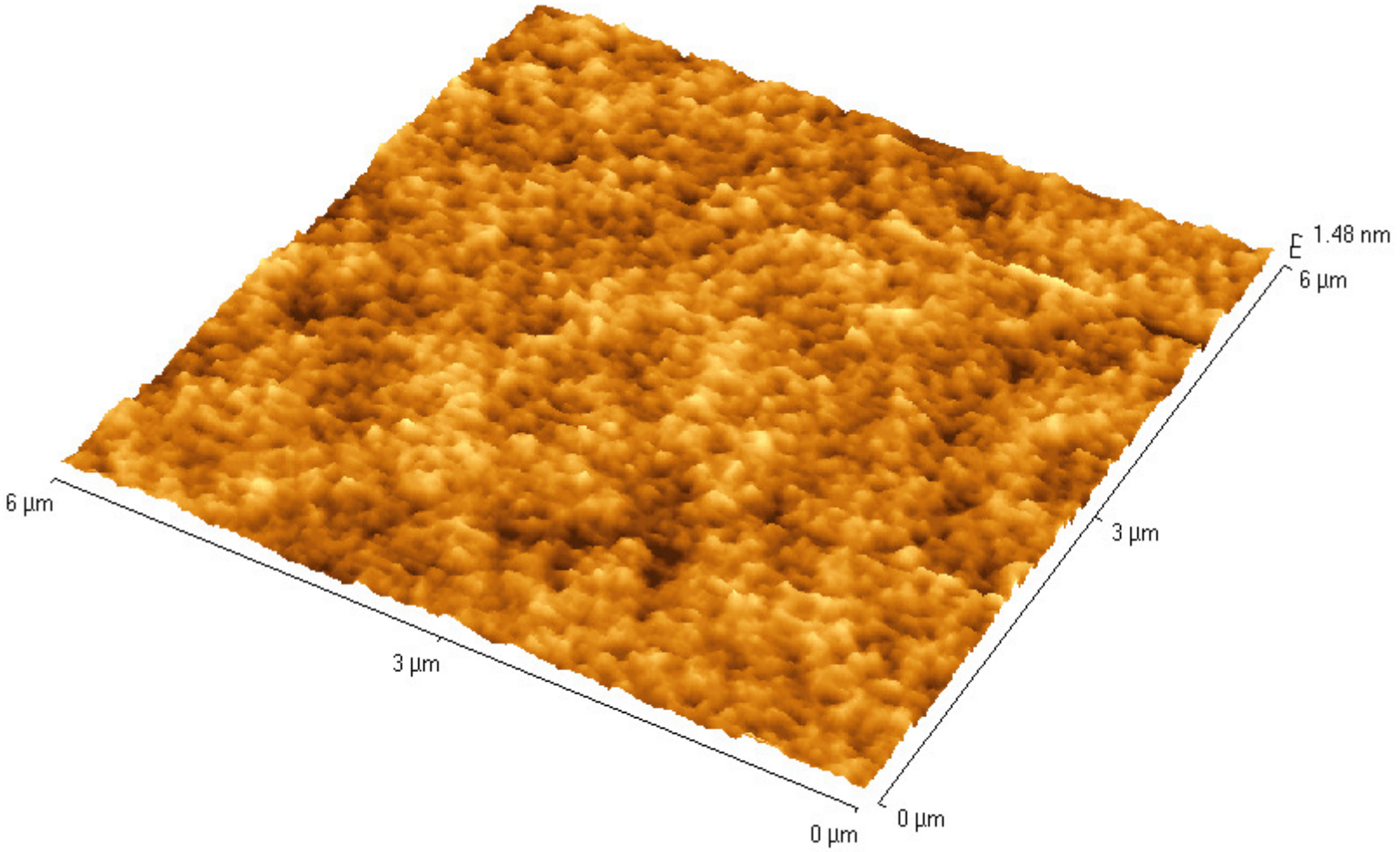


NSOM based on shear force mode



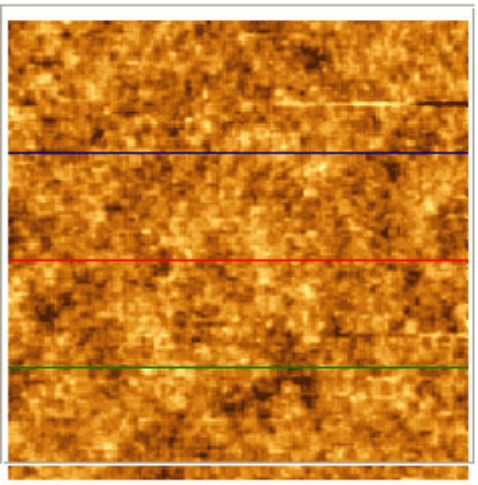
Dan Higgins, Acc. Chem. Res. **2005,** 38, 137-145

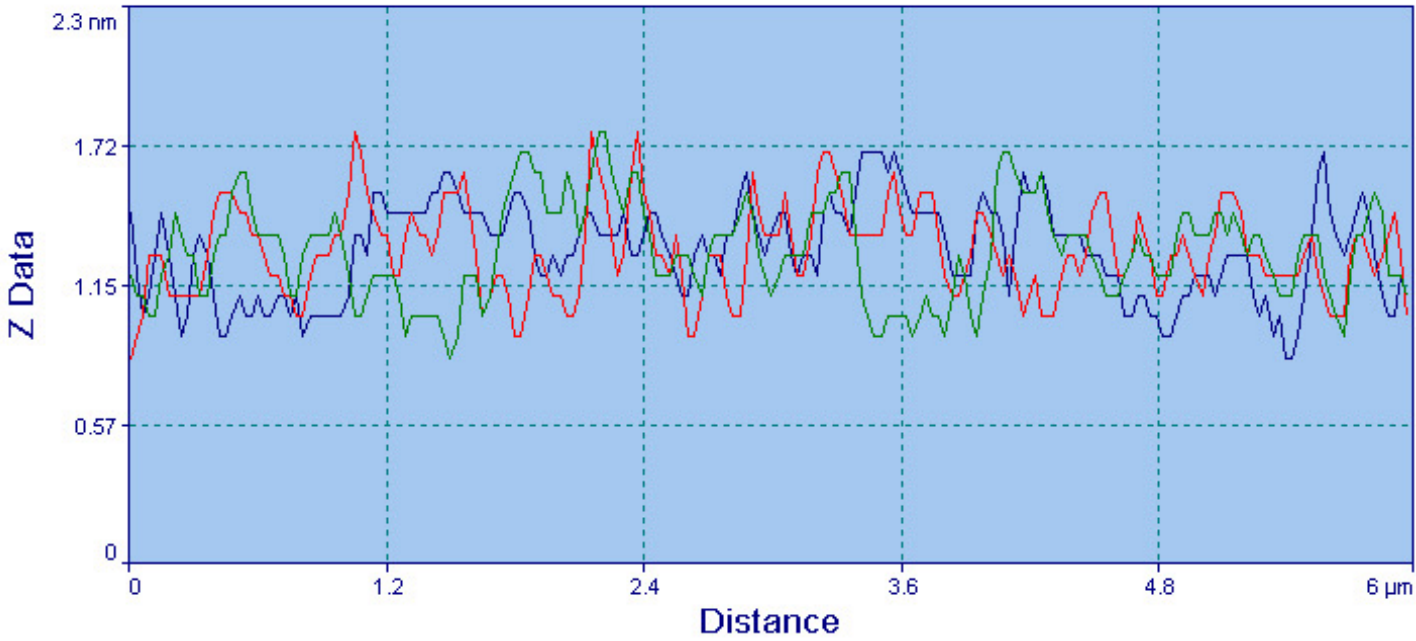
NSOM imaging of cleaned glass



NESMI Lab data

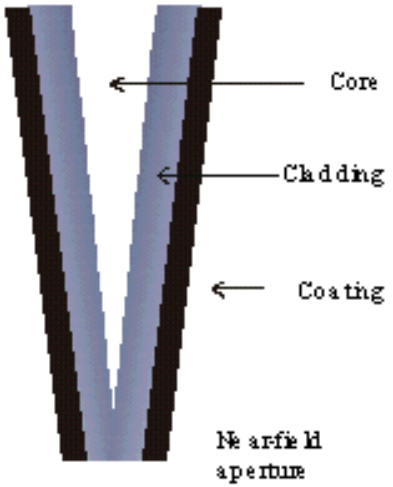
NSOM imaging of cleaned glass

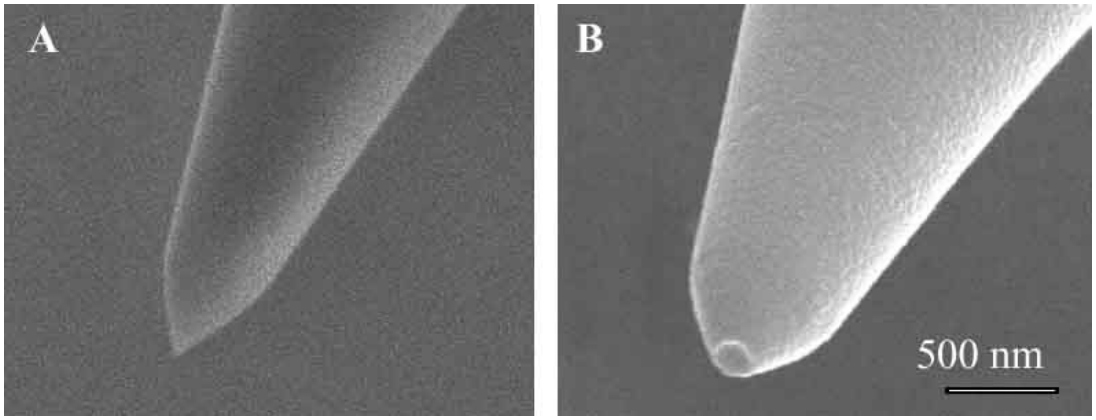


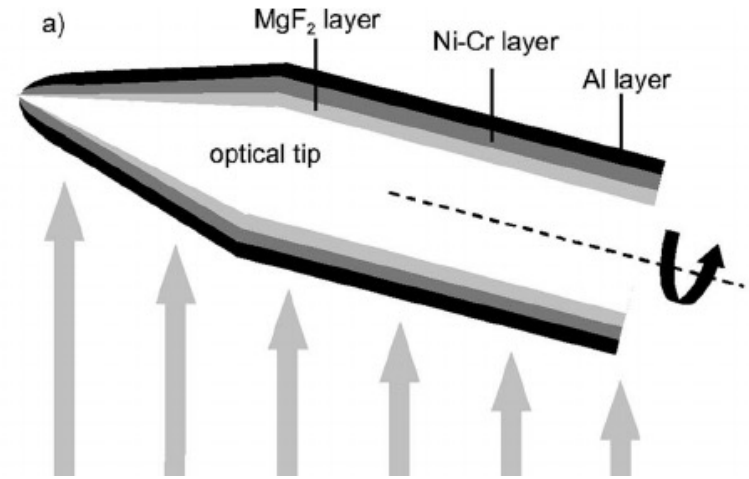


NESMI Lab data

Structure of a NSOM Tip?



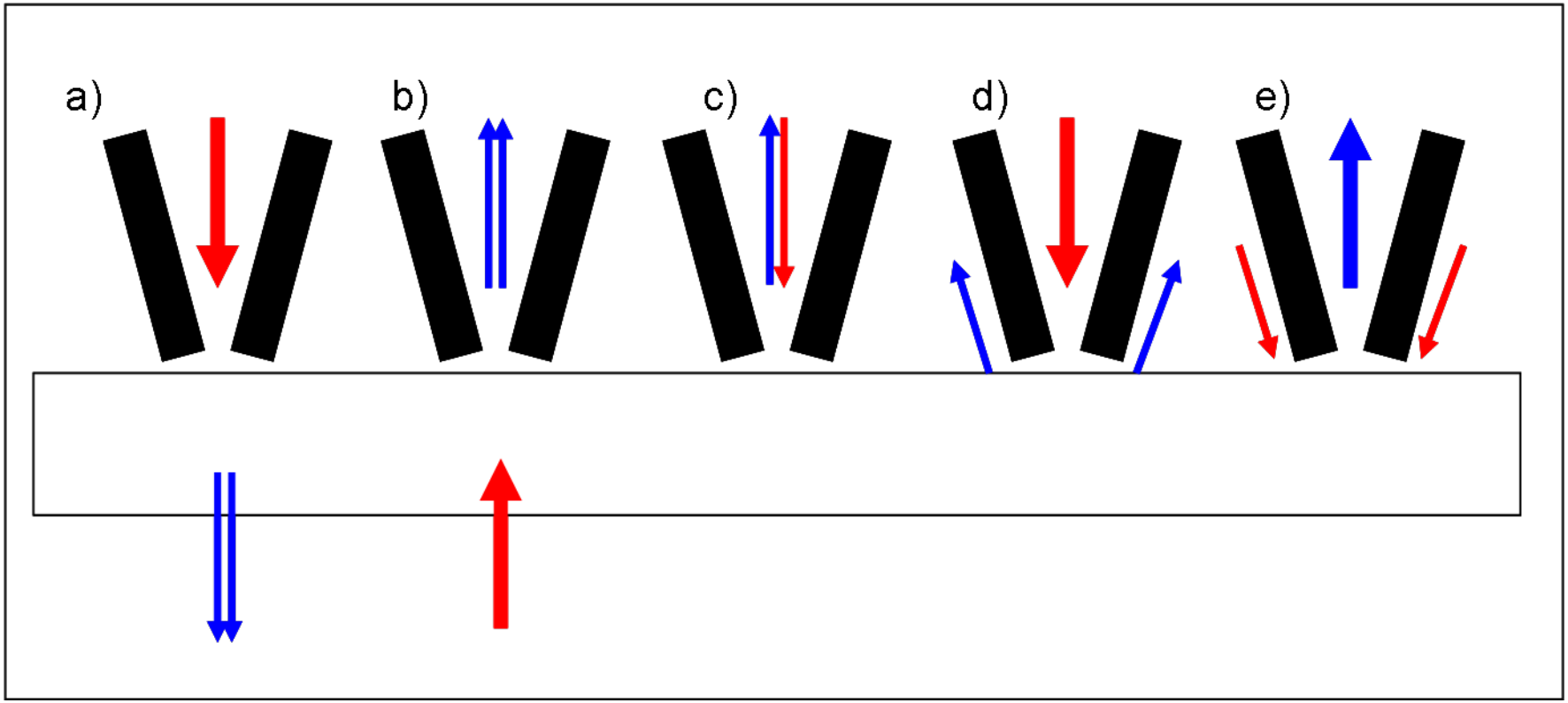




Different Operation Modes

- Illumination by the tip is probably the easiest to operate and interpret, and gives the most signal. It requires a transparent sample, so is limited for application in many samples like silicons and bio-species.
- Reflection modes give less light, and are more dependent on the details of the probe tip, but allow one to study opaque samples.
- The illumination/collection mode provides a complement to the reflection modes, but the signal contains a large background.

Different Operation Modes



a) illumination, b) collection, c) illumination/collection, d) reflection and e) reflection collection.

Brief History of NSOM

- Ideas started in mid-1980's;

  D.W. Pohl, W. Denk, and M. Lanz, *Appl. Phys. Lett.* 44, 651-3 (1984).

  Aaron Lewis, M. Isaacson, A. Harootunian, and A. Murray, *Ultramicroscopy* 13, 227 (1984); --- *even before the AFM concept got proposed and proven in 1986 by* ***Gerd Binnig (Nobel prize in 1986)***

- Technology developed in 1990's;

  Eric Betzig, R. J. Chichester, Single molecules observed by near-field scanning optical microscopy, *Science*, 262, 1422-1425 (1993).

  Cited 1863 times as of Oct. 30 2022

  Eric Betzig, J Trautman, Near-field optics- Microscopy, spectroscopy, and surface modification beyond the diffraction limit, *Science*, 257 (1992), 189-195.

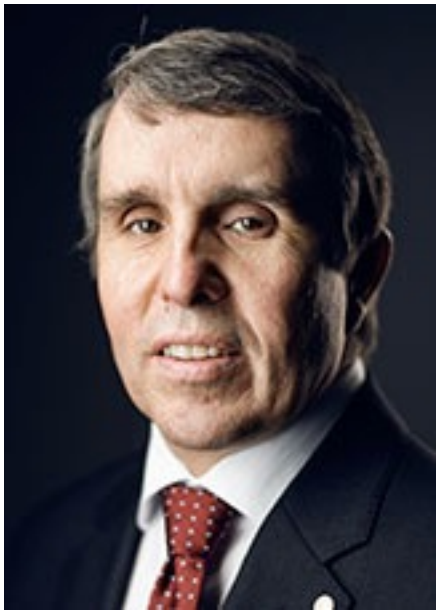
  Cited 2532 times as of Oct. 30 2022

  Eric Betzig was a PhD student of Aaron Lewis at Connell.

- Prototype commercial available since 2000's

The Nobel Prize in Chemistry 2014

"for the development of super-resolved fluorescence microscopy"



Eric Betzig

NSOM

Lecture 16-19

Stefan W. Hell

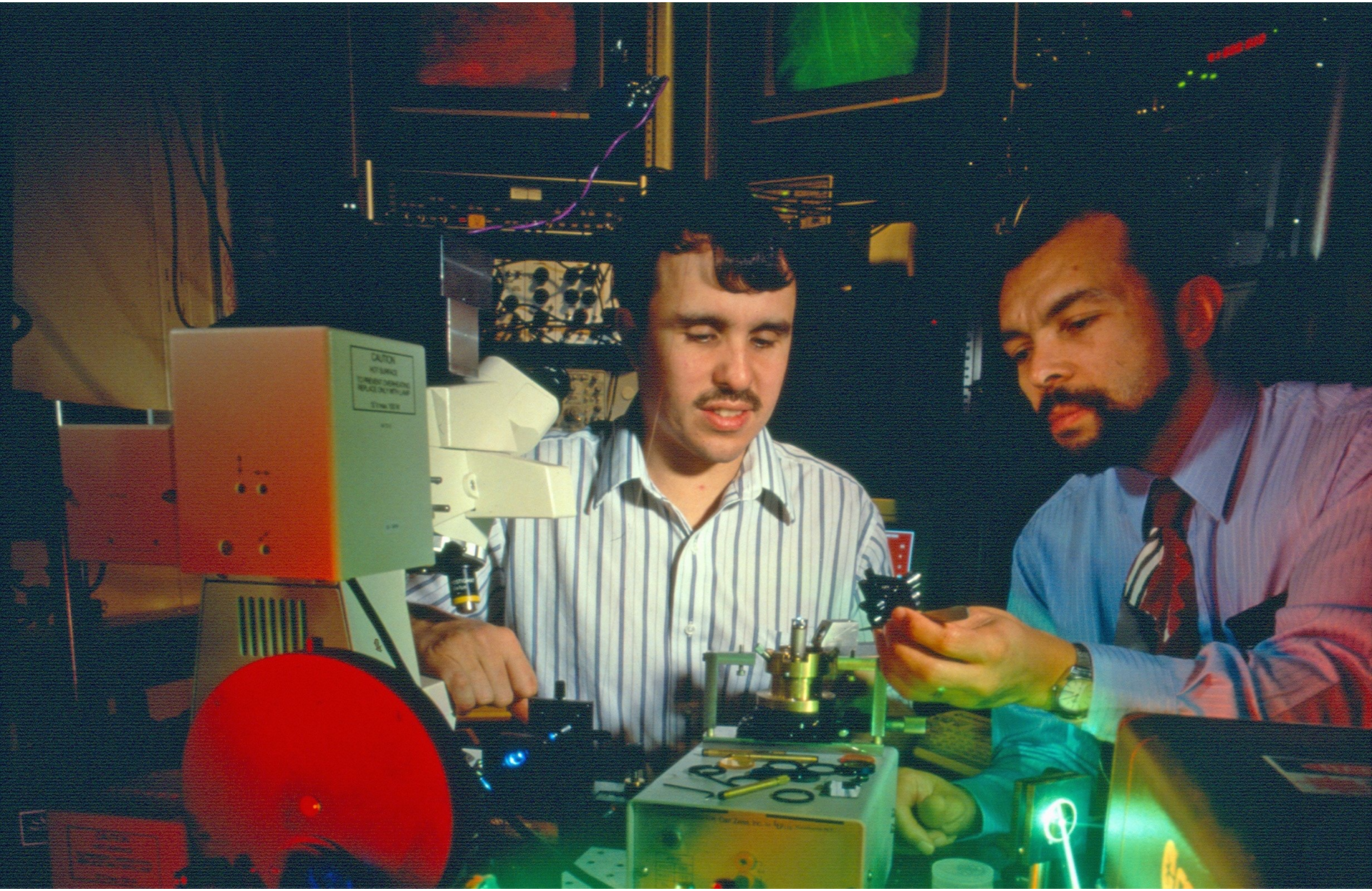
William E. Moerner

SCM

Lecture 20-22

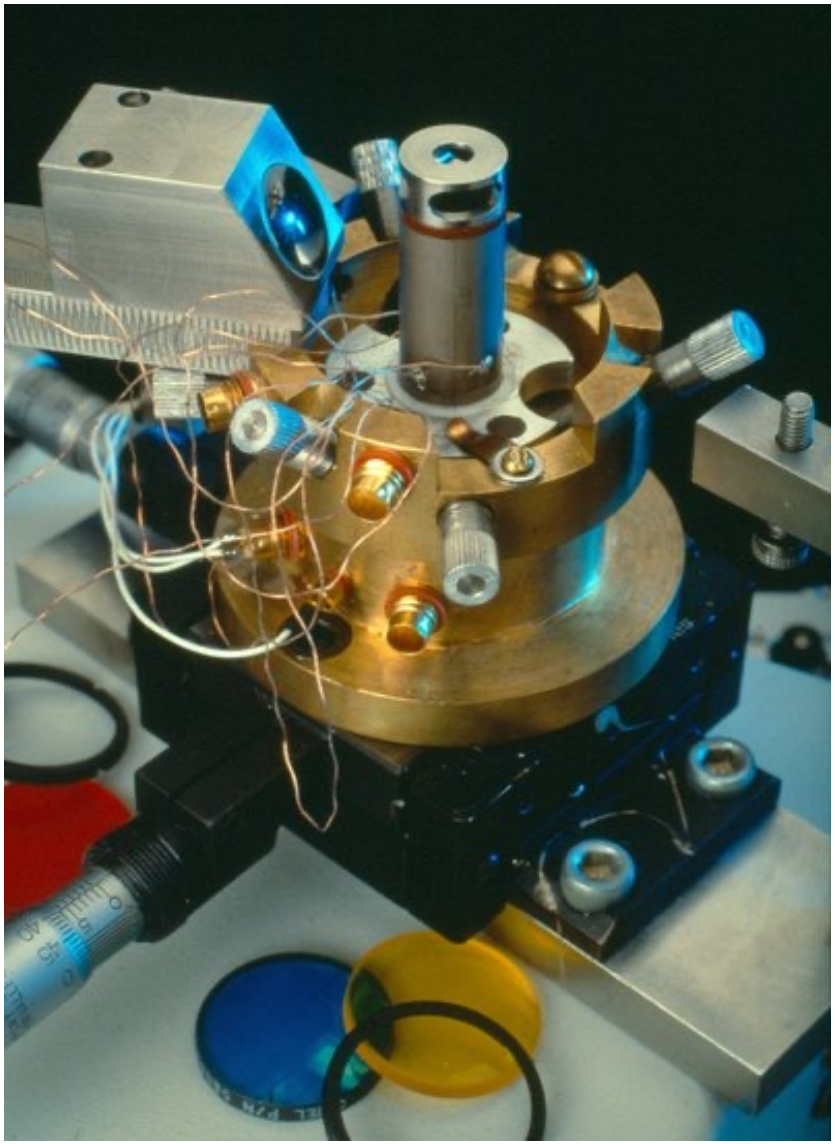
Nine Nobel Prizes have been awarded for work completed at Bell Laboratories

Eric Betzig developed NSOM at Bell Lab



https://www.bell-labs.com/about/history/innovation-stories/super-resolved-fluorescence-microscopy/#gref

Eric Betzig developed NSOM at Bell Lab



“Because of Bell Labs' history and the brilliance of everyone around me, I felt like I was on probation from the time I got there. Two years in, I wrote in my self-evaluation that if I didn’t have a breakthrough in the next year, they wouldn’t need to fire me because I would quit.”
— Eric Betzig

https://www.bell-labs.com/about/history/innovation-stories/super-resolved-fluorescence-microscopy/#gref

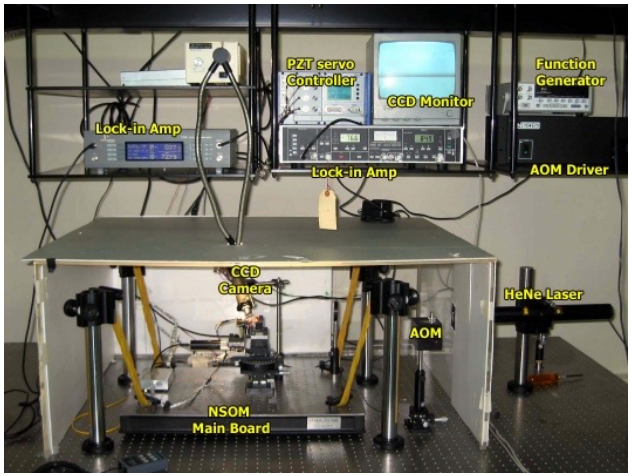
Eric Betzig

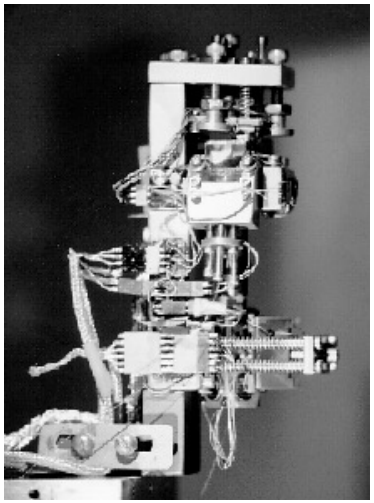
https://en.wikipedia.org/wiki/Eric_Betzig

The Nobel Prize in Chemistry 2014

- 1983, B.S. in Physics from Caltech,
- 1988, Ph.D. from Cornell, with **Aaron Lewis** (initiator of concept of NOSM, and founded **Nanonics Imaging** Ltd, a NSOM manufacturing company)
- 1989, joined AT&T Bell Labs, invented NSOM to image single molecules in 1993
- 1994, tiring of academia and the uncertainty of the corporate structure of Bell Lab (to be spun off AT&T to form Lucent Technologies), he quitted both, becoming a house husband.
- 1996, became VP of R&D of his father's machine company in Ann Arbor, where he developed Flexible Adaptive Servohydraulic Technology (FAST). After spending millions of dollars on development, he sold a total of two devices which did not allow him to achieve commercial success. "Commercial failure of the technology left me unemployed and looking for new directions."
- 2002, returned to the field of microscopy by founding a firm known as New Millennium Research, in Okemos, Michigan. Inspired by the work of Mike Davidson and his fluorescent proteins, he developed photoactivated localization microscopy (PALM), a method of controlling fluorescent proteins using pulses of light to create images of a higher resolution than previously thought possible. In the living room of his old Bell Labs collaborator, Harald Hess, they developed the first optical microscope based on this technology. They built their first prototype in less than two months, gathering widespread attention.
- 2005, joined HHMI's Janelia Farm Research Campus as a group leader to work on developing super high-resolution fluorescence microscopy techniques.
- 2010, he was offered the Max Delbruck Prize, but he declined it, allowing Xiaowei Zhuang to receive the award.
- 2014, jointly awarded the Nobel Prize in Chemistry along with Stefan Hell and William E. Moerner.
- 2017, joined the faculty of UC Berkeley

Quick Looking back : Home Build NSOMs





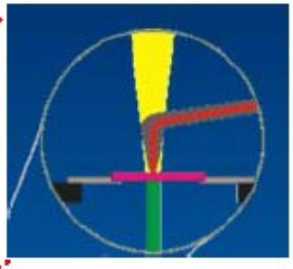
New versions of NSOM

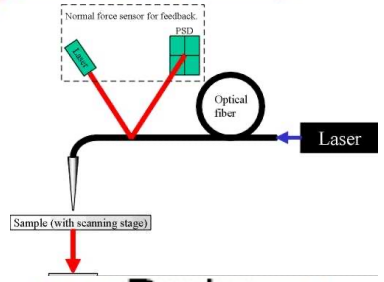
- 4 companies over the world produce good NSOM systems.
- The picture shows the model of Veeco Aurora III (DI, Thermomicro).
- Veeco is now part of Bruker

This one is based on shear force feedback.

Commercial NSOM: Nanonics MultiView 2000

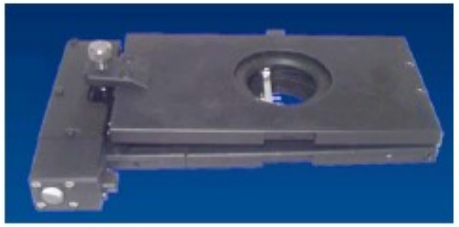
APD





Probe

Laser

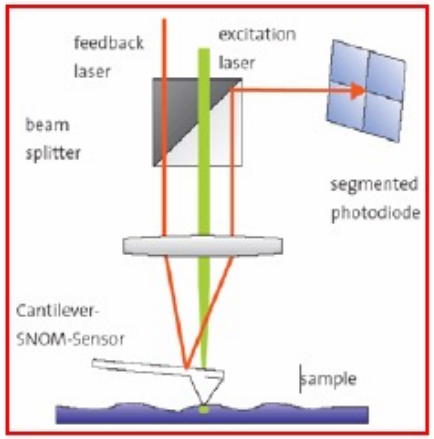


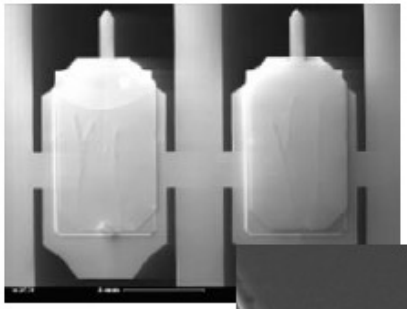
Scanner

Pictures taken from Nanonics

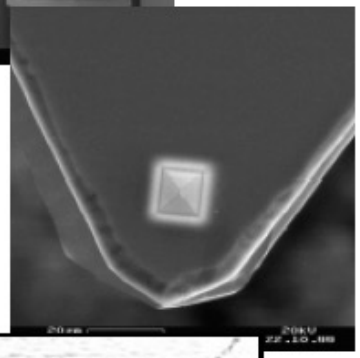
Aaron Lewis: Founder, was a professor at Cornell, Ph.D. advisor of Nobel Laureate Eric Betzig

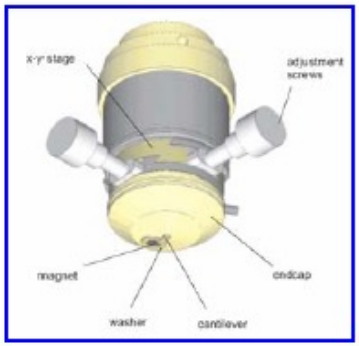
Commercial NSOM: Witec ALphaSNOM



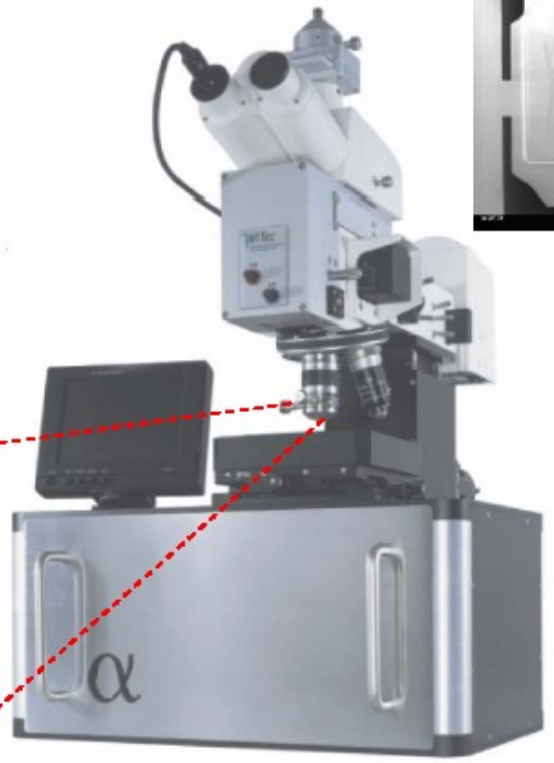


Cantilevered probe

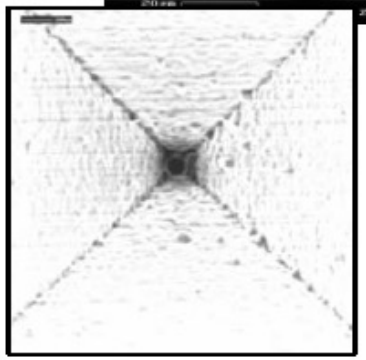




Probe Mounting



Pictures taken from Witec



Aperture

Analytical Chemistry,
2003, vol.75, page **2 2 3 A**

Shedding light on NSOM

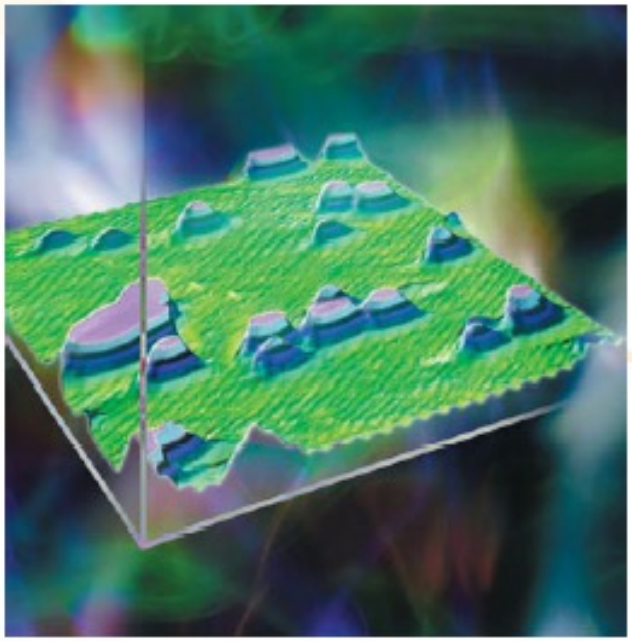
Years ago, NSOM had a slow start. Now, scientists are taking full advantage of its technological edge over other scanning probe techniques.

Cheryl M. Harris

It took patience and hard work. Now, finally, researchers are seeing some sunshine break through what was once a cloudy beginning for near-field scanning optical microscopy (NSOM). Paul Barbara of the University of Texas–Austin (UT–Austin) is among a group of analytical chemists who have a deep respect for this tool and see it as a technique ripe with potential, ranging from chemistry to physics.

NSOM, or SNOM, is steadily finding an important place in analytical chemistry, and company representatives are enthusiastic about its future in nanotechnology. Experts describe it as a bridge between atomic force microscopy (AFM) and optical microscopy. "The great thing about NSOM is that it gives you topographic information online with optics. This is something people could never do in the past," says Aaron Lewis of Nanonics, who in the mid-1980s led a group of researchers at Cornell University that published the first papers on the applications of NSOM.

Lewis still recalls a grant administrator at British Petroleum who in 1982 wrote him a letter that all but dismissed NSOM when the technique was still in its infancy. "The research you describe certainly meets the 'fundamental' criterion," wrote the administrator, "but I have had some difficulty in imagining an outcome of sufficient magnitude to justify an involvement." With that, the administrator told Lewis's group that the research didn't qualify for funding. "Many people in those days were not even taught that near-field optics could, in fact, be anything," recalls Lewis, who now teaches applied physics at Hebrew University in Jerusalem. "Now with all this nanotechnology revolution, people are looking deeper and deeper into how you look at light, how you concentrate light, how you analyze light, [and] how you manipulate light in very small domains."



Researchers and company representatives recall that during the early to mid-1990s, when NSOM instruments started appearing in laboratories, the technique presented many challenges

Optics in the Nano-World

S. W. Koch and A. Knorr

Applications of optical microscopy are generally limited by the standard resolution limit set by the wavelength of visible light. The invention of near-field scanning optical microscopy (NSOM) first enabled this limit to be overcome, opening up many systems, from physics to biology, to investigation by optical microscopy. NSOM offered greatly improved spatial resolution compared with conventional optical microscopy, and the use of tunable excitation sources allowed basic spectroscopic information to be obtained. On page 2224 of this issue, Guest *et al.* (*1*) report the next major step forward in this field. The authors describe a technique that combines the high spatial resolution of NSOM with the high spectral resolution of coherent nonlinear optical spectroscopy.

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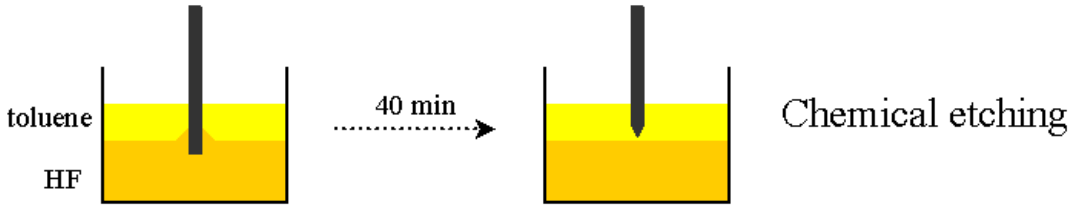
Optical measurements at the nanometer scale require a light source with an illumination spot in the nanometer range. For visible-light frequencies, where the wavelength is a few hundred nanometers, conventional optical microscopy fails because the resolution is restricted to half the wavelength of the used light (*2*). To overcome this problem, the light must be localized in a spot with a diameter much smaller than the wavelength of the light. Ideally, the spot should have nanometer-scale dimensions. This can be done by applying small apertures (*3*).

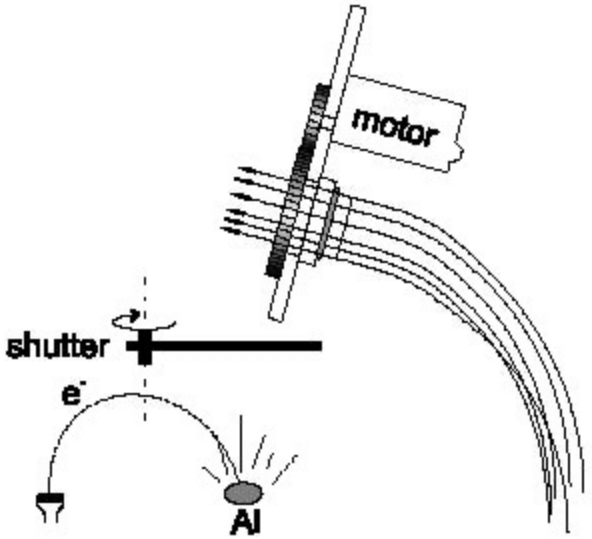
The price for this high resolution is that the character of the light changes drastically when it propagates through the aperture. The localization of the light waves results in the formation of evanescent waves, which have an imaginary wave number and decay exponentially in space (in contrast to conventional light waves, which propagate freely). The intensity of an evanescent wave thus decays rapidly as the distance from the aperture increases. Therefore, the aperture has to be close to the object, often only a fraction of the wavelength away. This is the regime of near-field optics.

NSOM techniques have many applications in solid state physics, where substantial efforts are made to design electronic devices with features on the nanometer scale. Electrons can be confined in nanometer-scale structures, called quantum dots (*4*). In these structures, the matter-wave properties of the electrons are changed drastically because the spatial confinement of the electrons approaches the deBroglie wavelength. Their electronic and optical properties therefore differ qualitatively from those of the bulk material.

The atomic landscape encountered by electrons in a quantum dot can be mapped and analyzed with tunneling spectroscopy

Fabrication of NSOM Tip: *chemical etching*





Fabrication of NSOM Tip: *mechanical pulling*

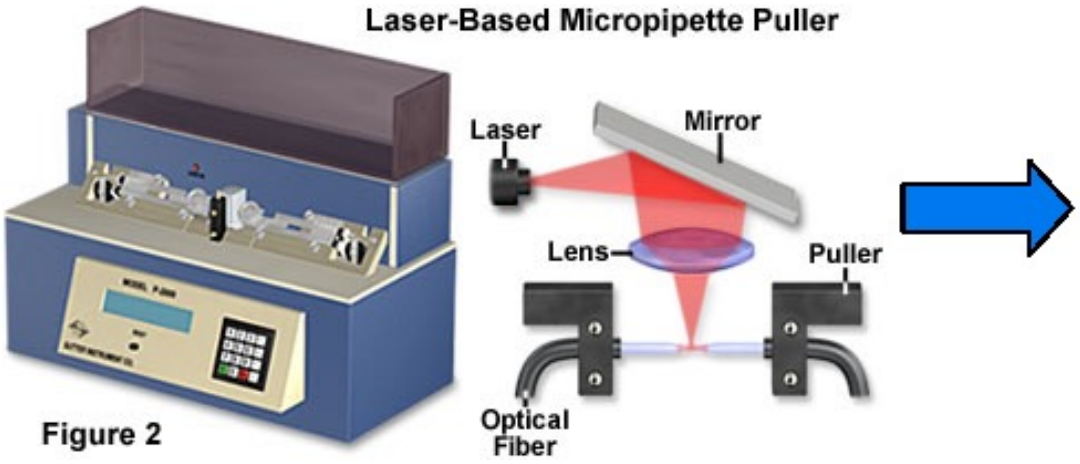
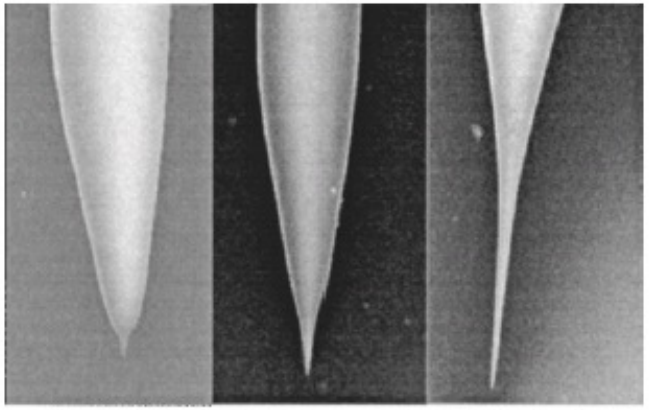


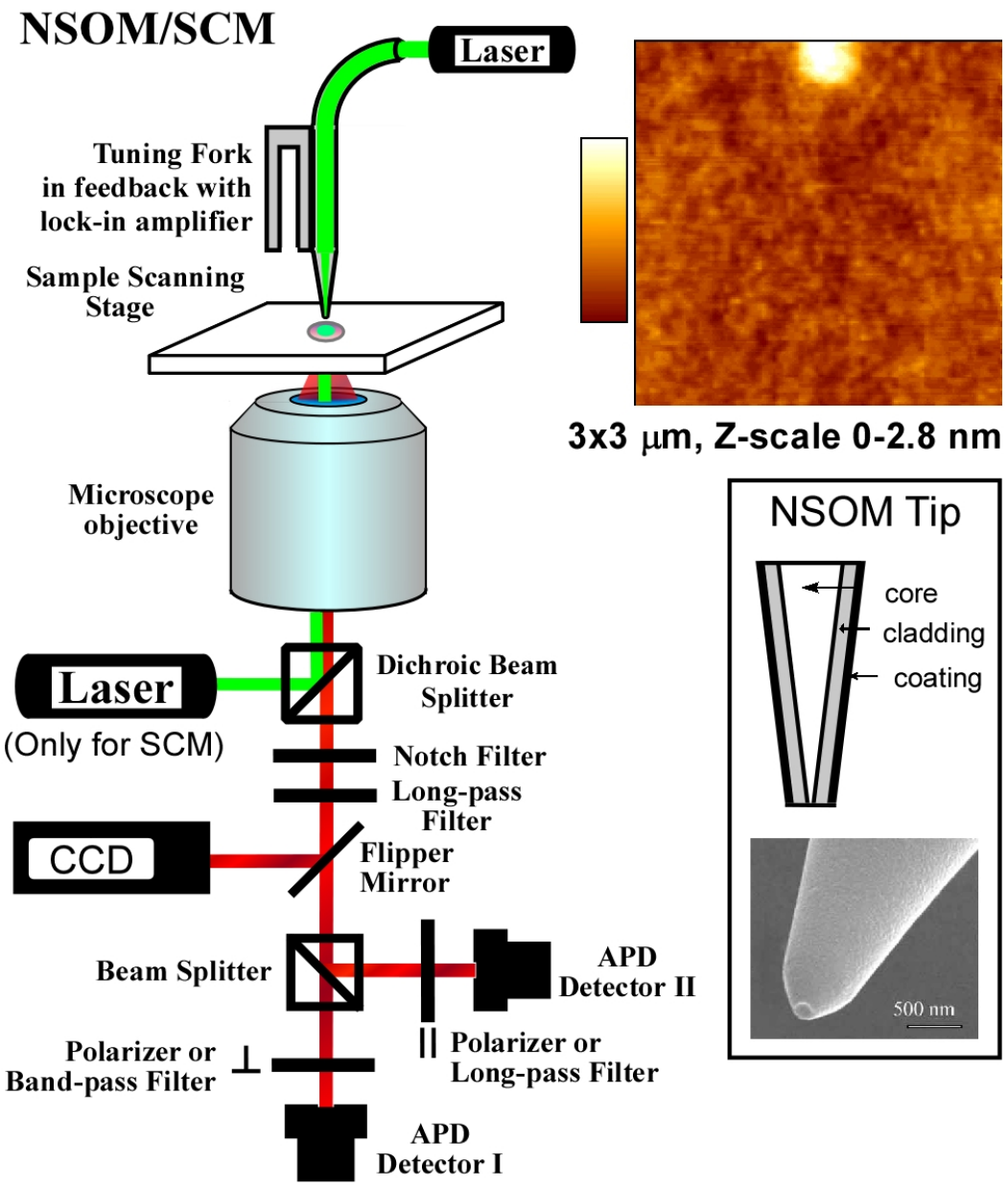
Figure 2



Major applications of NSOM: *highly adaptable to be integrated with other spectroscopy methods*

- Ultrahigh resolution OPTICAL Imaging
- Spectroscopy
  - Nearfield Surface Enhanced Raman Spectroscopy
  - Local Spectroscopy of Semiconductor Devices
- Modification of Surfaces
  - Subwavelength photolithography
  - Ultra High Density data storage
  - Laser Ablation
- Nearfield femtosecond studies

Extended NSOM system spectral and optical imaging



HORIBA Scientific

AIST-NT
Advanced Integrated Scanning Tools for Nano Technology

The platform allows AFM, STM, NSOM, and confocal optical spectroscopy (Raman and fluorescence imaging).

Typical examples of NSOM research

- Quantum size effect for semiconductor nanocrystals;
- Self-organized nanostructures: thin film dewetting, phase separation;
- Self-assembly or self-alignment: nanospheres, nanorods, nanowires;
- Heterogeneous biological systems: cells, proteins, enzymes, membranes;
- Real optoelectronic devices: solar cells, optical switches, LEDs;
- Imaging single-molecules (research of SMS was initiated by NSOM);
- High resolution studies of charge transfer in DNA and polymer chains.

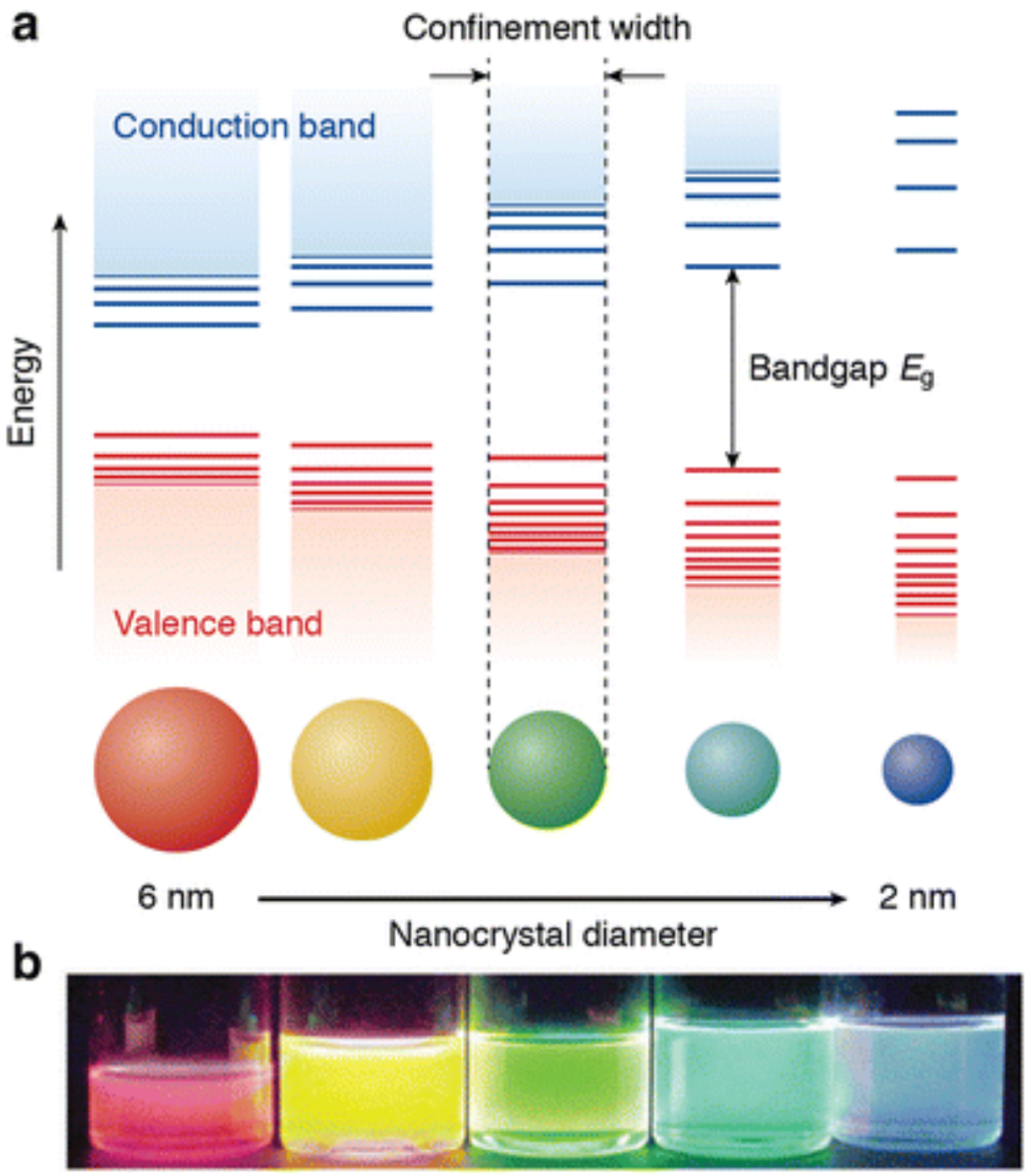
To be discussed in the coming lectures …

Nanoparticles: a unique manifestation

- Semiconductor nanospheres represent one of the most attractive nanostructures, and have a wide variety of applications in optoelectronics, magnetics, and biological applications.
- The size of nanoparticles can be tuned between individual molecules and the bulk counterparts.
- The nanosphere remains the same crystalline structure as the bulk crystal, but it shows unique size dependent physical and chemical properties, so called *quantum size effect*. See next slide.
- Conventional spectroscopy measurements of nanoparticles require uniform size distribution of the particle system, which is normally hard to attain.
- However, NSOM measurement removes such a need by focusing on only one particle a time.

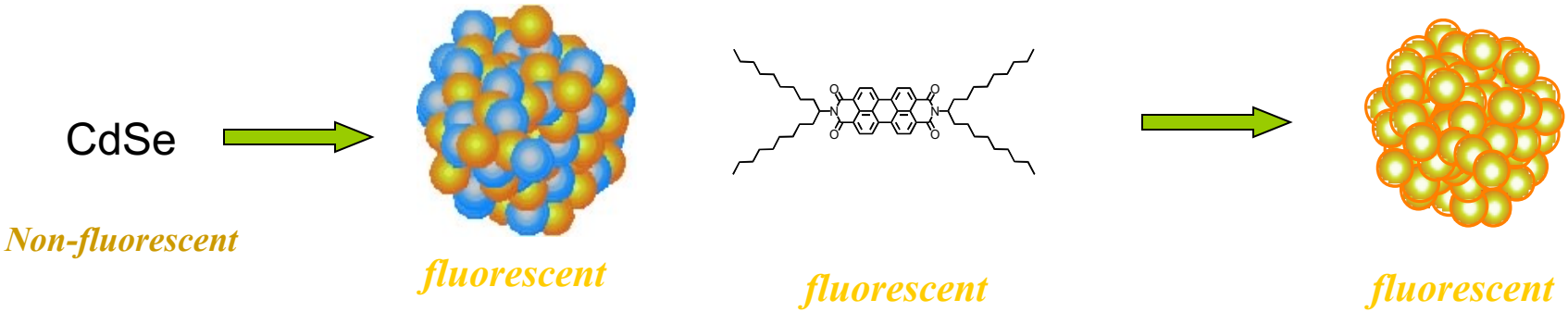
Quantum Size Effect of Semiconductor Materials

1. As particle decreases in size, the bandgap increases, approaching the energy difference between LUOM and HOMO for the individual molecules;
2. For fluorescent semiconductor materials, like **CdS**, the different bandgap leads to different emission wavelength;
3. By making different sizes of the particles, people can tune the emission color across the whole visible region.



Organic Semiconductor Nanocrystals: *Q-effect*

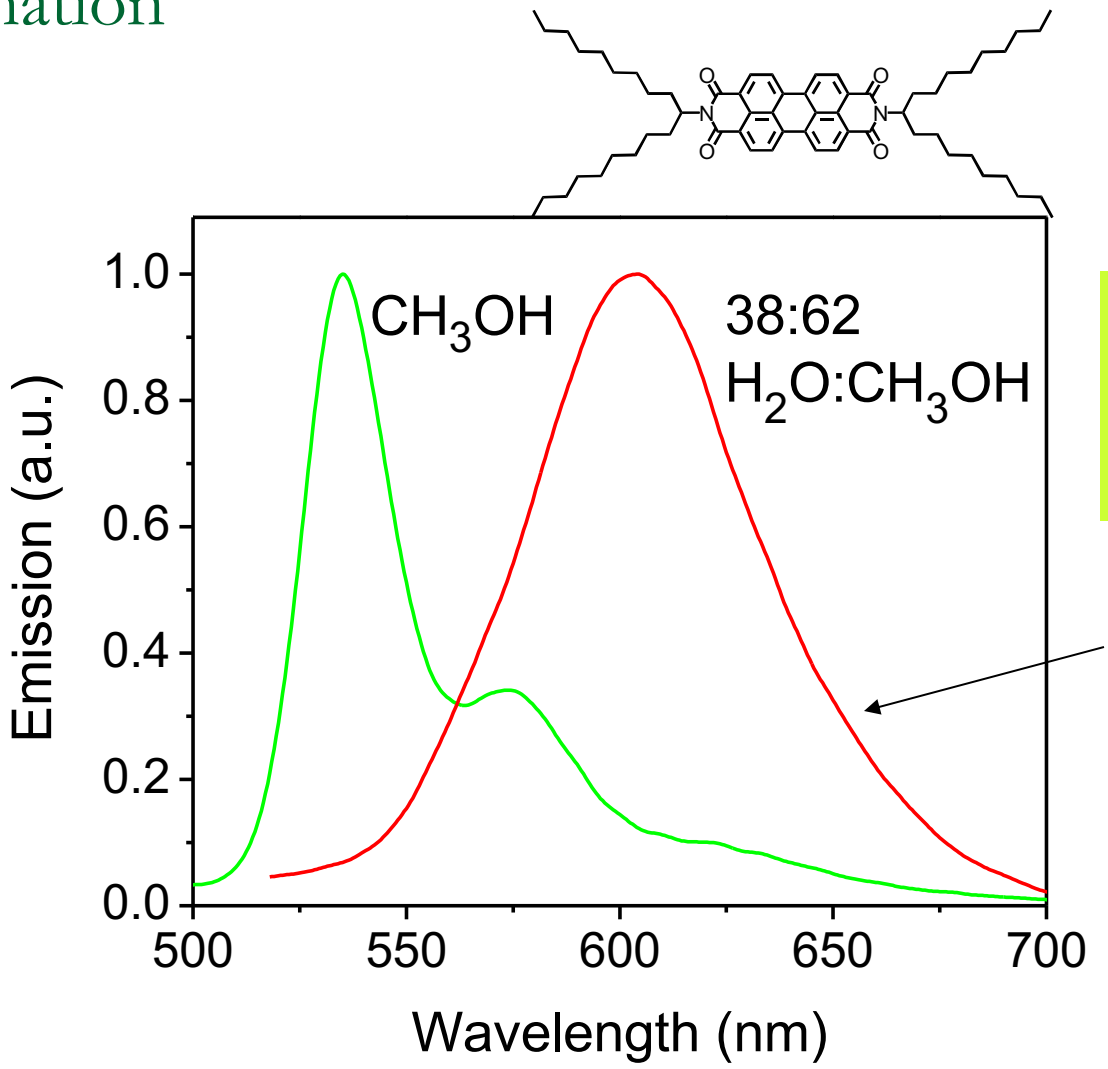
- less papers on *organic* nanoparticles, while thousands on *inorganic* counterparts.
- Why?



Inorganic Nanoparticle

Organic Nanoparticle

Emission shift of PTCDI molecules upon crystal formation

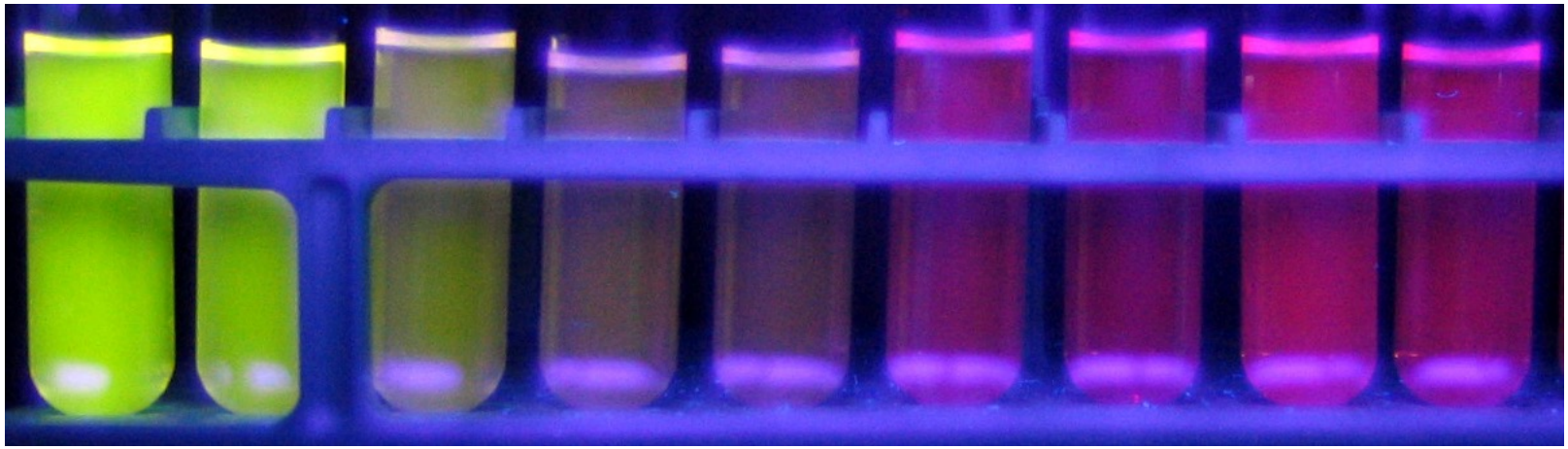


Quantum size effect is expected for the transition state between the two.

crystal

NESMI Lab data

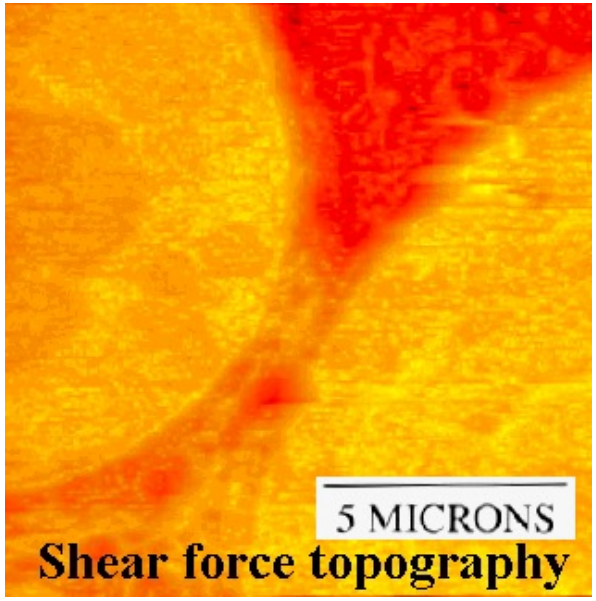
Tuning Emission of PTCDI materials

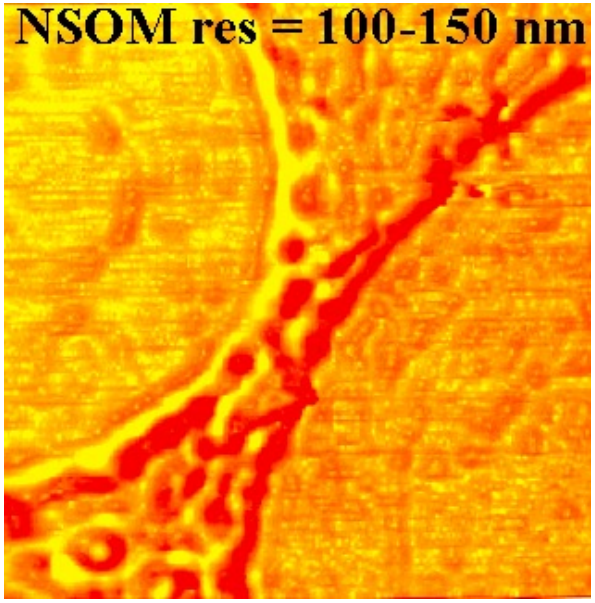


Free molecules ----------→ crystals

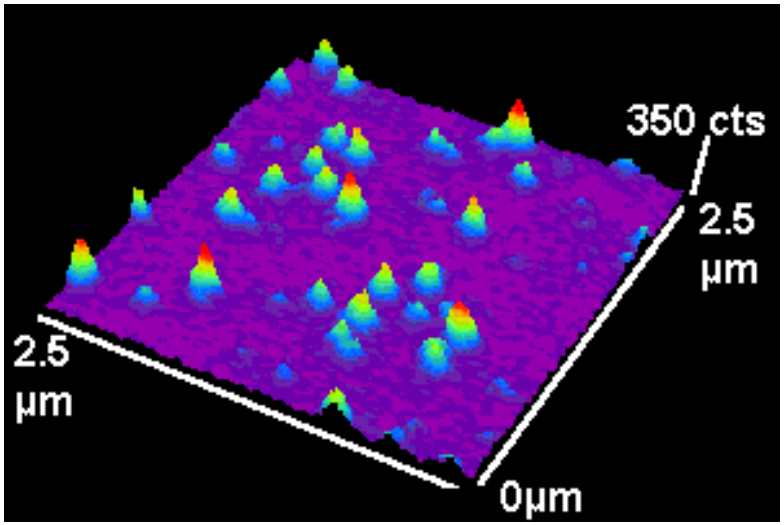
NESMI Lab data

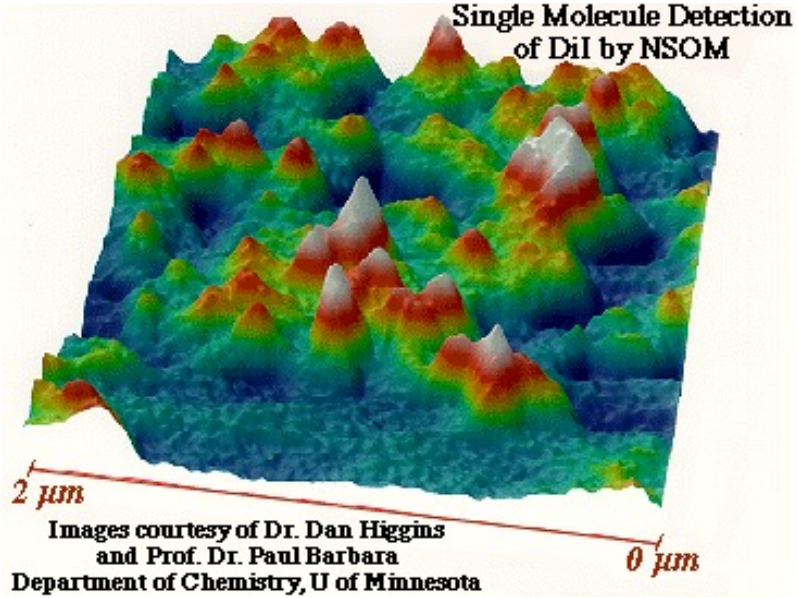
Typical NSOM Examples: Muscle Tissues





Typical NSOM Examples: Single-Molecules Embedded in Polymer Films





Revealing double strands of DNA: *fluorescence dye YOYO-1 only combines with the double-strand*

DNA double helix is 2.0 nm wide

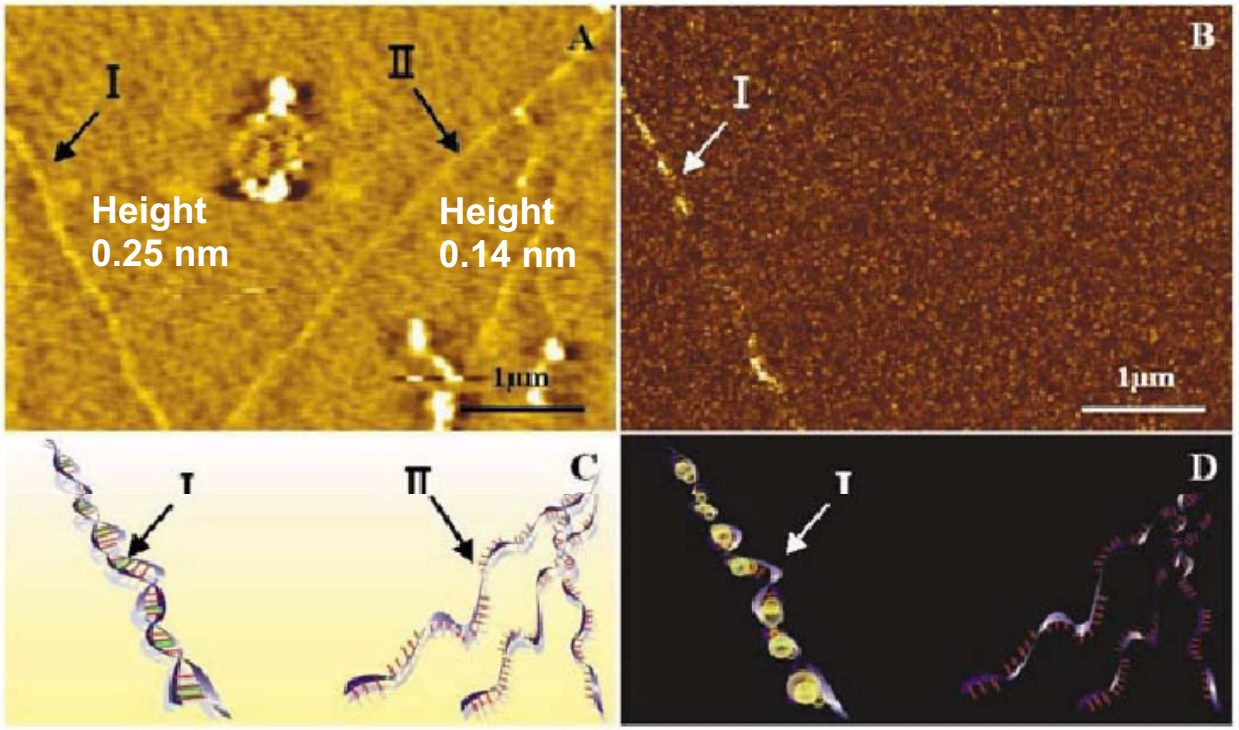
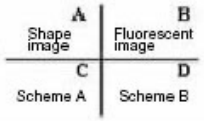


Fig. 2 Distinction between Single-Strand DNA and Double-Strand DNA Using SNOM/AFM



A strict distinction between single-strand and double-strand DNA was made possible for the first time by comparing the obtained shape and fluorescence data.

Explanation of the figure:

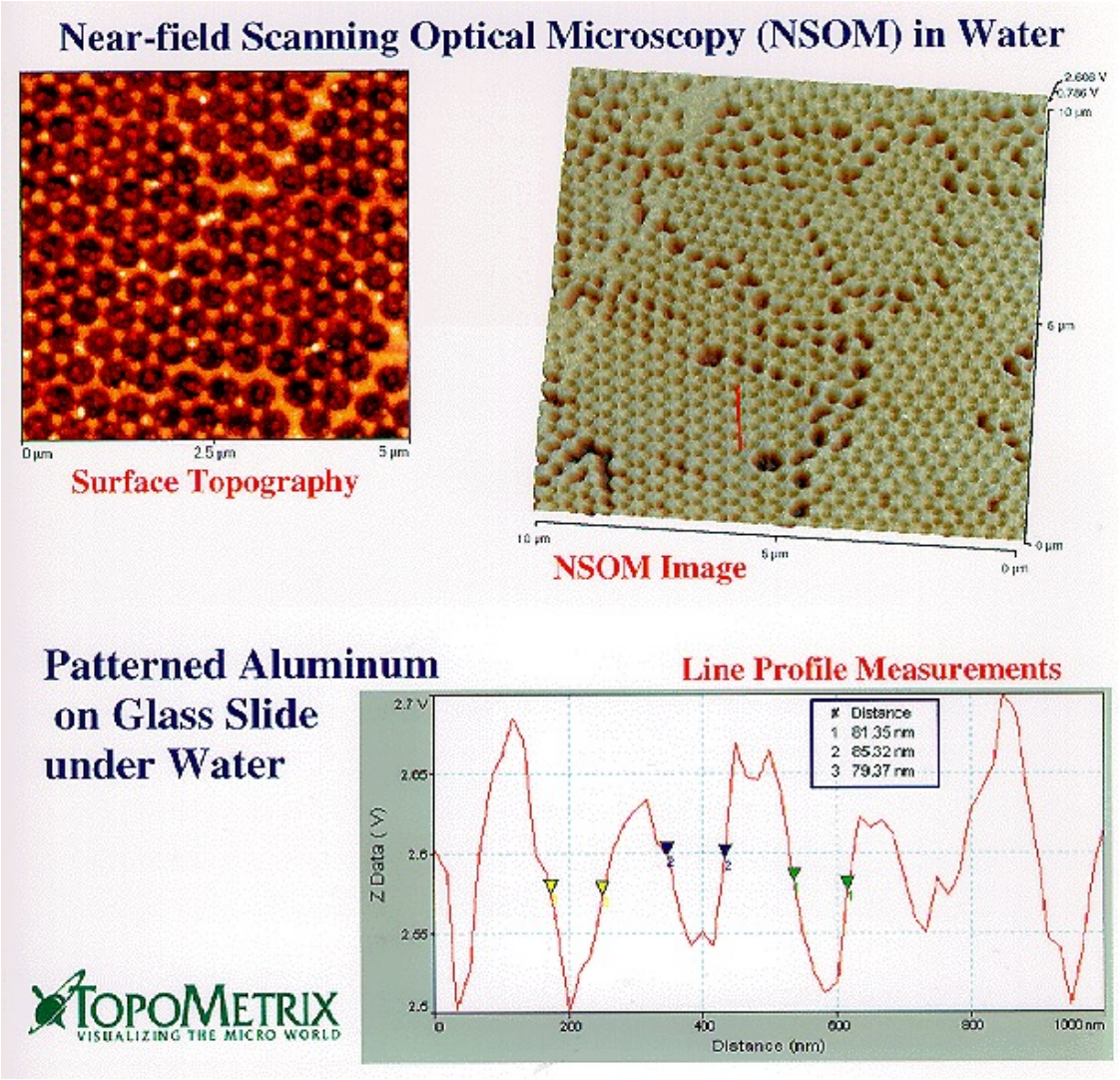
A is the DNA shape image. It shows that the height of DNA (I) is 0.25 nm, that of DNA (II) is 0.14 nm and DNA (I) is wider than DNA (II).

B is the fluorescence image captured at the same time as A. It shows the fluorescence image of only DNA (I).

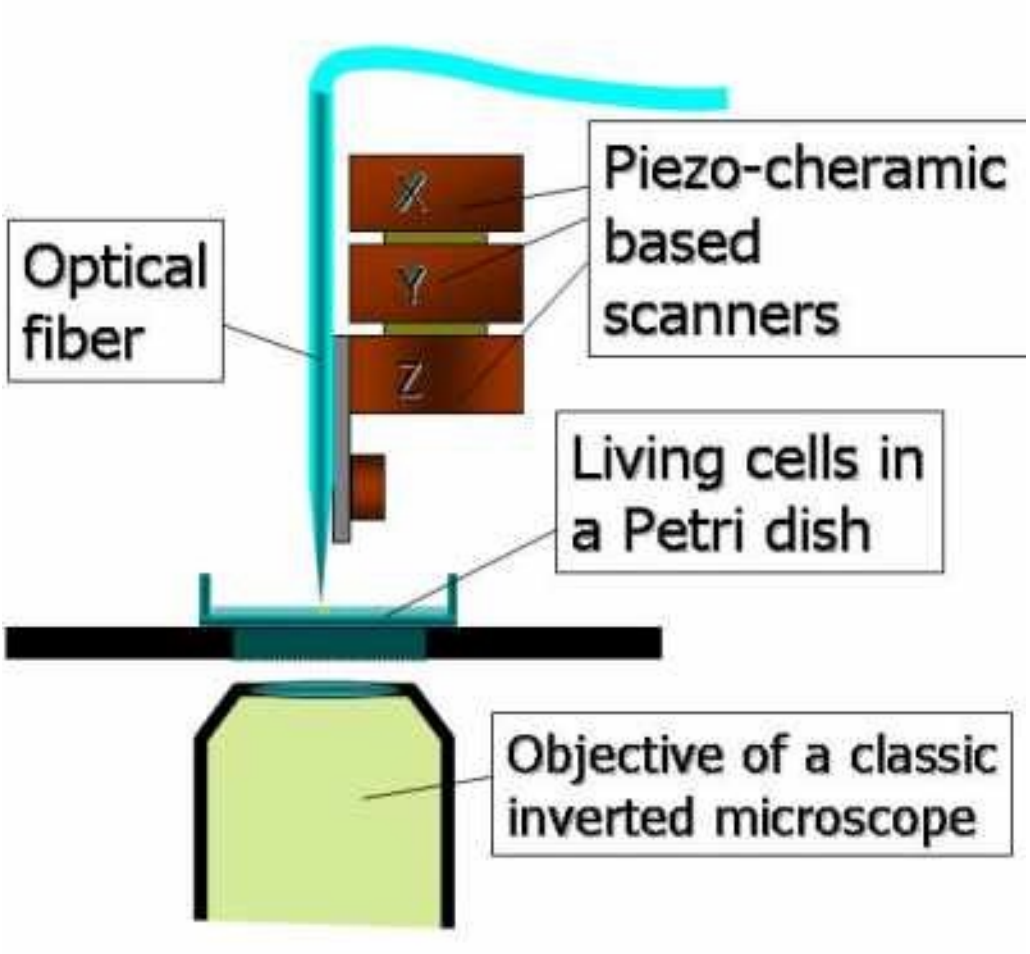
C and D are schematic diagrams of A and B respectively. The fluorescent dye (YOYO-I) combines only with the double-strand DNA. In consequence, it can be estimated that DNA (I) presenting the fluorescence image is the double-strand DNA and DNA (II) without the fluorescence image is the single-strand DNA.

It might be difficult to distinguish between single and double strands of DNA by topography imaging. But combination of fluorescence with NSOM provides a powerful way to do this.

NSOM imaging in water: an approach to living cells

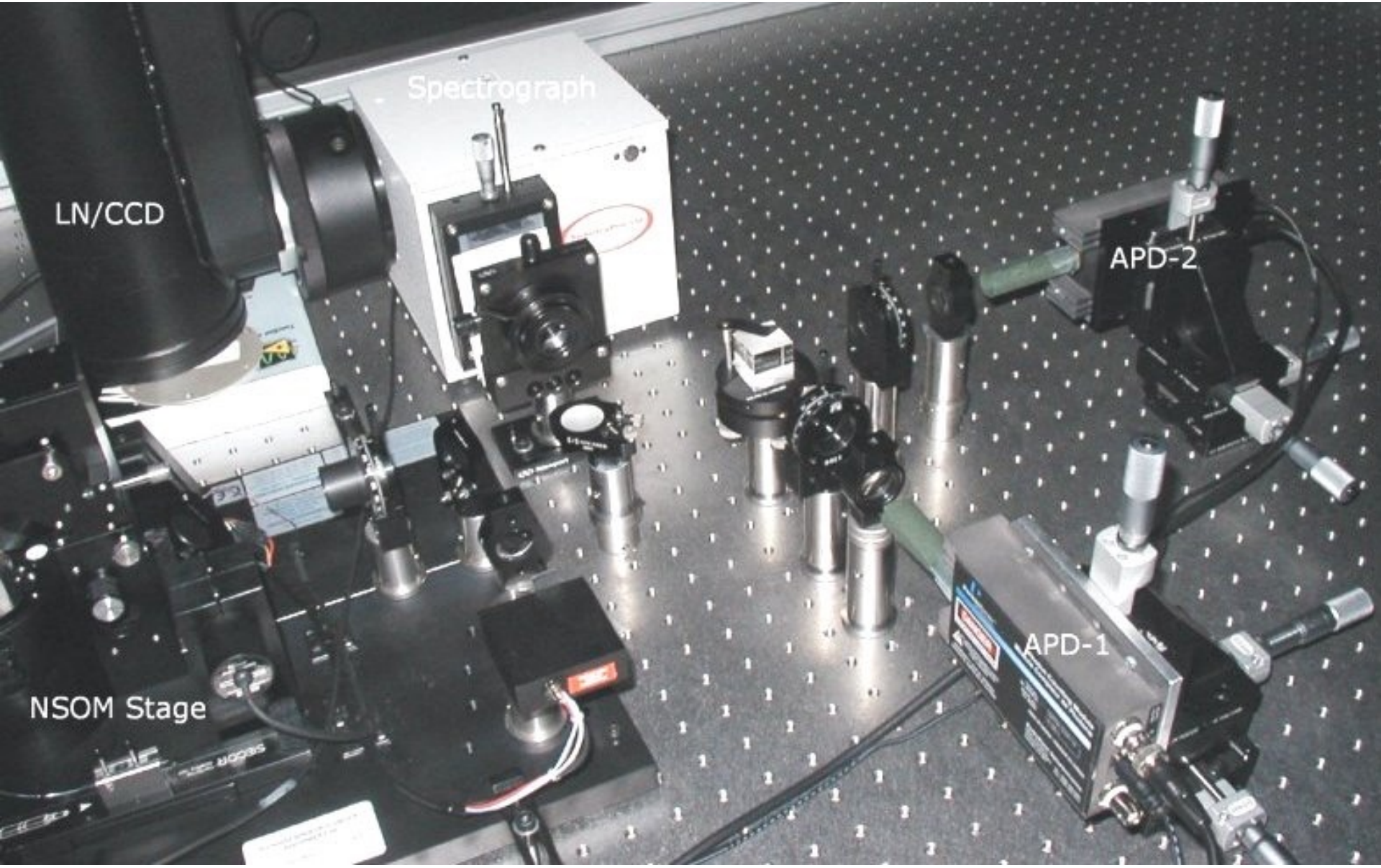


NSOM imaging of living cells



Some limitations (disadvantages) of NSOM

- Practically zero working distance (for objective) and an extremely small depth of field (for tip).
- Extremely long scan times for high resolution images or large specimen areas.
- Very low transmissivity of apertures smaller than the incident light wavelength --- low intensity of incident light for excitation, a problem for weak fluorescent molecules.
- Only surface features can be imaged and studied.
- Fiber optic probes are somewhat problematic for imaging soft materials due to their high spring constants, especially in shear-force mode


Spectrograph
LN/CCD
APD-2
APD-1
NSOM Stage

Near-field Scanning Optical Microscopy (NSOM)