Scanning Probe Studies of Single Nanostructures

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Paul S. Weiss is an Associate Professor of Chemistry at The Pennsylvania State University, where he began his academic career as Assistant Professor in 1989. He received his S.B. and S.M. degrees in chemistry from MIT in 1980 and his Ph.D. in chemistry from the University of California at Berkeley in 1986. He was a postdoctoral member of technical staff at Bell Laboratories from 1986 to 1988 and a Visiting Scientist at IBM Almaden Research Center from 1988 to 1989. He was a Visiting Professor at the University of Washington Department of Molecular Biotechnology from 1996 to 1997 and at the Kyoto University Electronic Science and Engineering Department and Venture Business Laboratory in 1998. He and his group investigate the chemistry and physics of surfaces at the atomic scale using scanning tunneling microscopy and spectroscopy. They have developed new techniques to expand the applicability and chemical specificity of scanning probe microscopies. They also use fluorescence microscopy and multibeam optical tweezers to control the local composition in real and model biological membranes in order to mediate uptake and adhesion.

I. Introduction

Scanning probe microscopies are ideally suited for isolating and probing nanostructures. Great difficulties remain in interpreting both spatial and spectral data from these probes. In this review, we focus on attempts to couple nanometer-scale imaging with spectroscopic techniques in order to understand what it is that is "seen" with scanning probe microscopes and to glean useful insight into the properties of the nanostructures under study. Additional capabilities unique to these microscopes are also discussed in the creation and measurement of nanostructures.

We limit the nanostructures discussed to nanometer-scale particles or distributed structures deposited or created on surfaces. We exclude such single-molecule measurements as single carbon nanotubes, single DNA chains, or single antigen−antibody complexes.

Nanostructures show great promise as materials with chemical, physical, and electronic properties that can be tailored and thus enhanced through variations in composition, size, shape, functionalization, and environment. A difficulty comes in deciding which materials and forms to target among the myriad variations possible. Current synthetic capabilities typically do not allow facile creation of a specific nanostructure in bulk. The approaches that have been taken to characterize specific nanostructures include systematic syntheses of ranges of particles, separation by size or other property after

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synthesis, modeling, and measurement of selected fractions of nanostructure product distributions.

In this last category, scanning probe microscopy uniquely allows the study of single, identifiable particles.[1,2] The heterogeneity of nanoparticle distributions can be eliminated by studying them one at a time with SPMs. Studying nanoparticles individually also serves to make it difficult or impossible to verify or to calibrate results by independent means. Trends or specific spectral features can provide key insights into the properties of nanometer-scale particles and structures. By combining topographic and spectroscopic measurements, SPMs are ideally positioned to elucidate these structure−property relationships. This review will focus on current examples of such simultaneous structural and spectroscopic measurements. We also point out opportunities for other combinations of measurements in areas where the spectroscopies are now first being demonstrated.

After less than 20 years in existence, scanning probe microscopies still remain very much under development.[3−7] Advances in measuring the properties of nanoparticles with scanning probe microscopes (SPMs) have been hindered by our inability to interpret the images and spectra obtained. To date, most surface studies involving SPMs have focused on morphology or have characterized systems with known structures or spectra. As these measurements become better understood and more routine, they will be applied to nanoparticles and nanostructures.

Another unique aspect of scanning probe microscopies is their ability to manipulate atoms and molecules so as to construct nanostructures for study.[8−16] We will describe several extraordinary and revealing studies where SPMs were used to construct the structures to be probed. In this sense, SPMs are unique in being able to assemble what we shall call "distributed nanostructures" in which the atoms need not be bound directly to one another. Such efforts have resulted in new abilities to explore and to control the atomic-scale world. Such experiments can serve to guide later synthetic or lithographic (or other) efforts to create particular structures of value.

II. Required Elements of Scanning Probe Microscopes

We first review the essential elements of all SPMs. This will allow us to discuss the additional information that can be obtained by collecting more information while scanning or by interrupting scanning for specific local measurements. Scanning probe microscopes all have three elements in common. First, in each, scanning is done by piezoelectric elements. Second, a feedback mechanism and, third, a means of recording are also required; the specifics of these aspects will be sketched for each SPM next. As then discussed in the sections below, additional capabilities can be added by simultaneous acquisition of multiple signals.

For scanning tunneling microscopes (STMs), the feedback is based on keeping the tunneling current constant. In vacuum, this current typically changes by an order of magnitude for each ∼1 Å change in probe tip−sample separation. In the most common operating mode, recording is done by monitoring the voltage supplied to the piezoelectric transducer to maintain a constant current.

For atomic force microscopes (AFMs), feedback is based on the force vs separation characteristic of the tip and sample surface. As this function goes through a minimum close to where the tip makes contact with the surface, the AFM can operate in two basic modes: in and out of contact with the surface. In contact, the AFM uses the repulsive force between the probe and sample surface but may disturb the sample under study. The force varies rapidly with changes in separation, and feedback is thus straightforward. Other related methods, such as "tapping mode", try to minimize contact and thus damage but still rely on the in-contact time to dominate the feedback signal. Out of contact, the AFM uses the more weakly varying attractive force between the tip and sample but has much less chance of unintentionally changing the sample surface. Recording in AFMs requires that the deflection of the probe tip cantilever (in the most common geometry) be measured. This can be done by tunneling to it, by monitoring interference fringes from reflecting light off it, by monitoring the deflection of light reflected from it, or by making the cantilever itself into a sensing element by incorporating piezoresistive elements into it. These latter two recording methods allow an additional valuable measurement of lateral and/or shear force to be made in a straightforward way. This can be measured by monitoring the twist of the cantilever while scanning. This can be used to measure the attractive, adhesive, and/or frictional forces between the tip and sample while recording images.

For near-field scanning optical microscopes (NSOMs), the feedback mechanism is most typically based on the force felt by the probe. This is often the shear force which varies as the probe approaches the sample.[17] This is analogous to AFM feedback described above, but the vibration of the optical fiber probe laterally reduces the resolution of force images simultaneously obtained. Variations in probe geometry may allow NSOM with more conventional AFM-style feedback.

With each of these techniques, one can do more by recording additional signals simultaneously or by freezing the feedback loop with a sample-and-hold circuit and then by doing local measurements. Synopses of selected additional capabilities for scanning probe microscopes are given below. It is these additional capabilities that are sure to impact the selection, measurement, and thus usefulness of nanostructures in the coming years.

III. Scanning Tunneling Microscopy

A. Scanning Tunneling Spectroscopy

The simplest and earliest spectroscopy using STM focuses on measuring the local electronic spectra of the sample.[18] The tunneling electron energies are varied simply by changing the bias voltage applied between STM tip and sample. Both filled and empty electronic states can be probed since at positive sample bias electrons tunnel from the tip to empty states

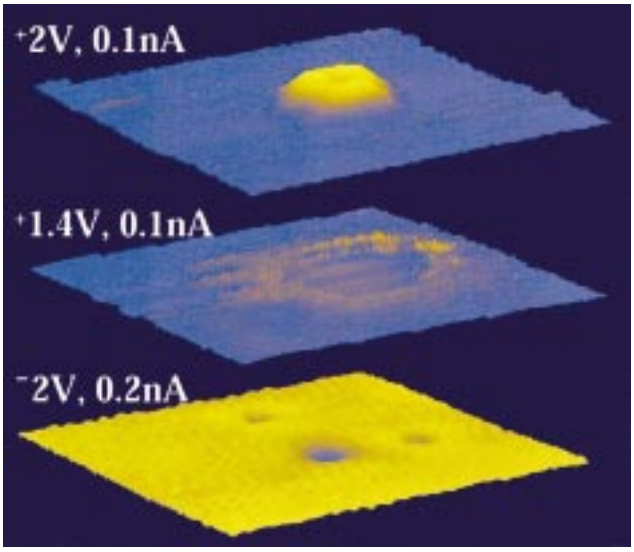

Figure 1. Three STM images of a Ni_3 cluster adsorbed on the basal plane of MoS_2 at 4 K. All three images show the same 60 Å × 60 Å area of the surface. The images were acquired with sample biases of +2 (A), +1.4 (B), and −2 V (C). Adapted from Figure 3 of ref 16.

of the sample and at negative sample bias electrons from filled sample states tunnel to the probe tip.

STM images are convolutions of the electronic and topographic structures of the surfaces under study. Recent reviews have addressed the theoretical interpretation of STM images of molecular adsorbates.[19−21] While this complicates the interpretation of images and can hamper unambiguous identification of features, it gives the chemically relevant view of the surface−energy-resolved local electronic structure. It is this that mobile atoms and molecules "see" as they traverse the surface. By selecting one or more particular energies for study, we are able to view the same electronic surface experienced by mobile reactants or intermediates.[16,22−24]

Spectroscopic information can be obtained by recording multiple images at different bias voltages as in Figure 1 for a Ni_3 cluster on MoS_2.[16] Alternatively, spectra can be acquired at one or more selected locations or at each imaged point by holding the probe tip still and sweeping the bias voltage. In this way, spatial variations of the electronic structure can be mapped with exquisite detail.

The electronic properties of nanoparticles vary with size, composition, and structure. Scanning probe microscopes are uniquely able to determine aspects of all of these properties simultaneously. Banin et al. have used a low-temperature STM to elucidate the electronic properties of individual semiconductor nanoparticles.[25] They were able to correlate the detailed structure in the measured tunneling spectra they measured with photoluminescence spectroscopy of ensembles of such particles.

Electron scattering can be observed from many surface features including adatoms, impurities, step edges, and grain boundaries. Eigler, Avouris, and their co-workers have observed long-range oscillations in the electronic surface structure from adatoms, step edges, and vacancy islands.[9,26−30] An example is shown below in the discussion of distributed nanostructures.

Photons produced by tunneling electrons provide another source of information about the species in the tunneling junction. Both the integrated intensity and emission spectra provide more interpretable forms of local information, with subnanometer spatial resolution. Photons are produced by inelastic processes. Tunneling electrons excite species or plasmons in the tunneling junction, and the excitation decays via photon emission in a process similar to cathodoluminescence. The first reported work on photon emission scanning tunneling microscopy (PESTM) was done by Gimzewski and co-workers and Alvarado and co-workers, both of the IBM Research Division.[31−33]

Many nanostructures have very similar topographic features, typically appearing as protrusions. Emitted photons provide an additional channel of information, interpretable in analogy to UV−vis spectroscopy. Such spectral information has been used to differentiate between nanoparticles of different composition. Downes and Welland used the threshold voltage, the minimum bias voltage magnitude required for photon emission, to differentiate between Au and Ag nanoparticles.[34] The threshold voltage is dependent on the tip and the sample material, for Au and Ag samples with a W tip the threshold voltage was found to be $V_{sample} = +2.1$ and +3.3 V, respectively. An example of reaching this threshold bias voltage is shown in Figure 2 in which emission from nanoparticles occurs at the higher magnitude of the bias voltage shown in the lower frames (B). Photon emission can also give insight into the local chemical environment. Varying the functionalization capping a nanoparticle can induce vastly different efficiency in photon emission.[35] One of the strengths of SPMs is also the extremely high spatial resolution. McCarty and Weiss found strongly enhanced photon emission from asperities on Au nanoparticles as shown in Figure 3.[35]

As for electronic spectra, the SPM tip can be positioned over a particle of interest and the local optical spectrum and/or the photon emission efficiency vs bias voltage can be recorded. By monitoring the local optical emission spectrum, Lindahl et al. observed Stark shifts in the photon emission spectra for InP quantum dots.[36]

Other scanning tunneling spectroscopies have recently been developed that show great promise for measuring nanoparticles and nanostructures but have not yet been applied for this purpose. We bring them up here because these techniques are certain to have an impact in this field.

Inelastic electron tunneling spectroscopy (IETS) enables direct chemical identification of adsorbed species via vibrational spectroscopy with the full lateral resolution of the STM. Ho and co-workers have demonstrated this for small molecules on metal surfaces at low temperature.[37] This spectroscopy is analogous to the sandwich tunneling junction measurements done over the last 30 years.[38] Observing excitations in this way may allow the identification of more complicated adsorbed species and complexes, but the spectroscopy has not yet developed to this point.

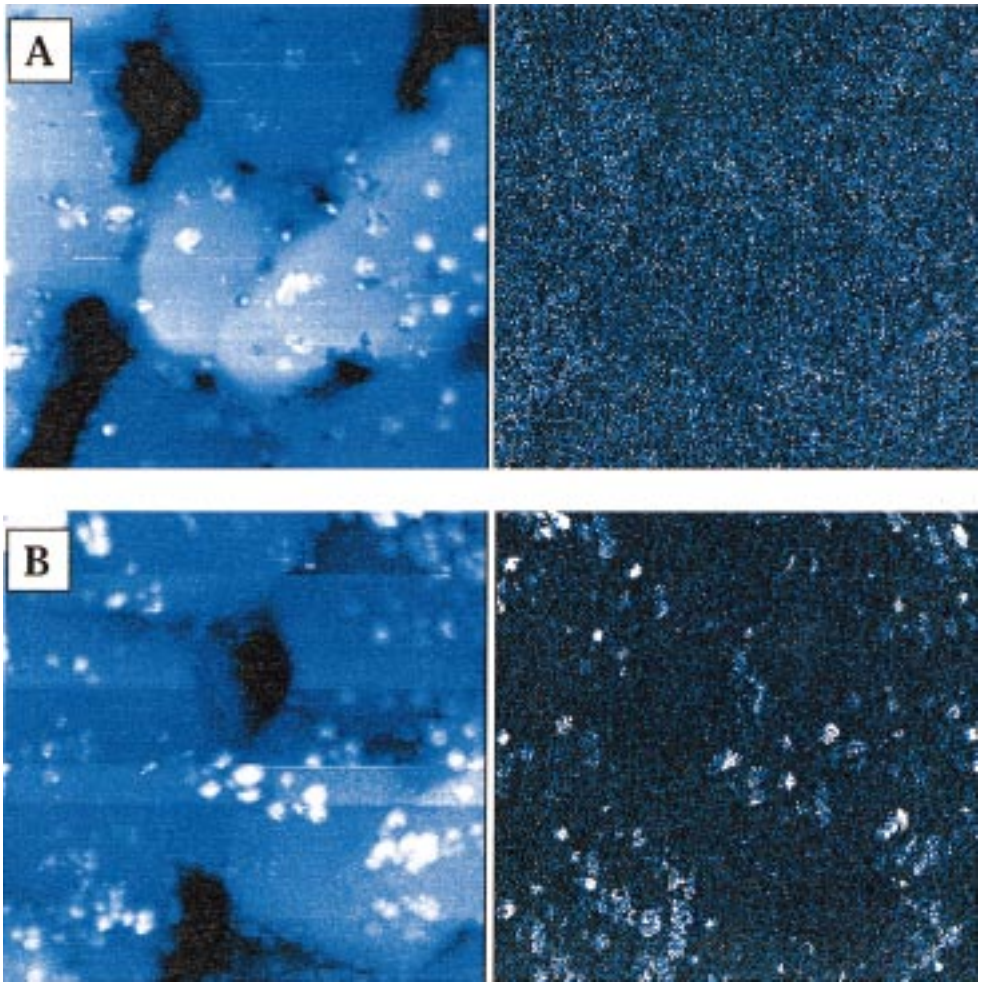

Figure 2. Two PESTM images of Au nanoparticles showing the onset of photon emission. Photon emission turns on at a bias voltage of 1.8 V. (A, left) STM image 2000 Å × 2000 Å, $V_{sample} = 1.7$ V, $I_{tunnel} = 2.2$ nA. (A, right) Simultaneously recorded photon emission map. (B, left) STM image 2000 Å × 2000 Å, $V_{sample} = 2.0$ V, $I_{tunnel} = 2.2$ nA. (B, right) Simultaneously recorded photon emission map.

B. Constructing and Probing Structures with the Scanning Tunneling Microscope

Scanning probe microscopes have the unique capability of changing the structure probed.[39] This has been used to build structures that could not be formed by any other means. One aspect of this is the ability to build "distributed nanostructures" in which atoms or molecules are positioned with atomic precision.

Nanostructures can literally be built atom by atom. Figure 4 shows an example where a single Ni atom is being purposefully dragged across the basal plane of MoS_2.[16] Weiss and Eigler rearranged Xe atoms on Pt{111} by this means.[39] Eigler and co-workers positioned 48 Fe atoms in a circle on a Cu{111} surface to build a "quantum corral" as shown in Figure 5.[9,26,27] The surface state electrons of the Cu{111} substrate surface scatter off the iron adatoms, producing interference patterns as shown in the figure. Other structures were built as well to understand the effects of multiple scattering and of the shape of the distributed nanostructure.[26]

Hashizume and co-workers have made nanostructures by a novel STM-based method.[40] First, they used the technique developed by Lyding employing energetic electrons from the STM tip to remove selected H locally from H-terminated Si(100) surfaces.[41] They then examined the electronic structure of these one-atom-wide bare Si lines and measured the resulting electronic wave functions using the STM.

IV. Atomic Force Microscopy

A. Measuring Nanoparticles and Nanostructures Using the Atomic Force Microscope

Despite many opportunities for simultaneous measurements, only limited measurements providing new insight have been done with the AFM. Among the measurements likely to be useful are the chemical functionalization of the probe tip[42] and the ability to measure specific forces such as magnetism.[43] More progress has been made in constructing nanostructures and then probing their properties, as described in the section below and in section VI.

B. Constructing and Probing Structures with the Atomic Force Microscope

An atomic force microscope with a conducting probe tip is able to measure currents on samples that are not accessible to a STM. In this section we highlight three uses to which such instruments have been put.

Figure 3. Photon emission comes exclusively from an asperity on a gold nanoparticle adsorbed on a mercaptoethylamine-functionalized Au{111} terrace. Topography acquired by STM (top) and simultaneously acquired photon emission map (bottom). Image size 180 Å × 180 Å, $V_{sample} = -2.0$ V, $I_{tunnel} = 5.0$nA.

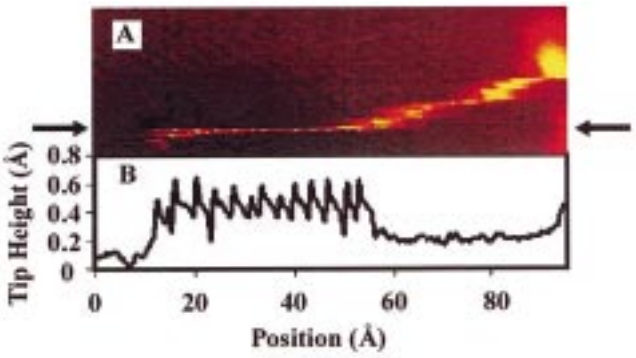

Figure 4. (A) STM image showing the manipulation of a Ni adatom by the probe tip at 4 K (30 Å × 95 Å image area, $V_{sample} = 1.5$ V, $I_{tunnel} = 100$ pA). Images are acquired line by line, from the bottom to the top as shown here. Data were collected as the tip moved from left to right in this image, and the tip was quickly moved back to the start of the next line. (B) Tip−sample separation during Ni motion is plotted. The line is indicated by the two arrows in A. The motion of the tip indicates that the Ni adsorbate hops to neighboring lattice sites owing to an attractive interaction with the STM probe tip. (Reprinted with permission from ref 16. Copyright 1998 American Chemical Society.)

A key advantage is that a sample can be imaged for which most or all is insulating. Then current, surface potential, or other measurements can be made on the areas where possible, but no dc current is required. Likewise, such an instrument can be used to apply an electric field to a film in an area selected using the AFM.

The SPM probe tip can be used to oxidize locally as a means to fabricate nanoscale structures.[44,45] Many conducting and semiconducting materials have been patterned using direct oxidation. The simultaneous ability to test *during* fabrication enables creation of devices with exquisitely tailored electronic properties. Snow and Campbell have oxidized areas of Ti films to produce precise metal-oxide−metal junctions.[44] Avouris and co-workers have oxidized areas of a Si surface to produce thin oxide films for use as gates in nanoscale devices.[45] The high electric fields between SPM tip and sample oxidize Si with nanometer resolution in all three spatial dimensions. The ability to control oxidation has allowed model electronic nanostructures to be built and explored. Both reduced size conventional devices and components can be built and novel structures explored. Study of these nanostructures has already revealed several key concerns to address before nanoscale electronic devices will be viable, including current density limitation within the device.

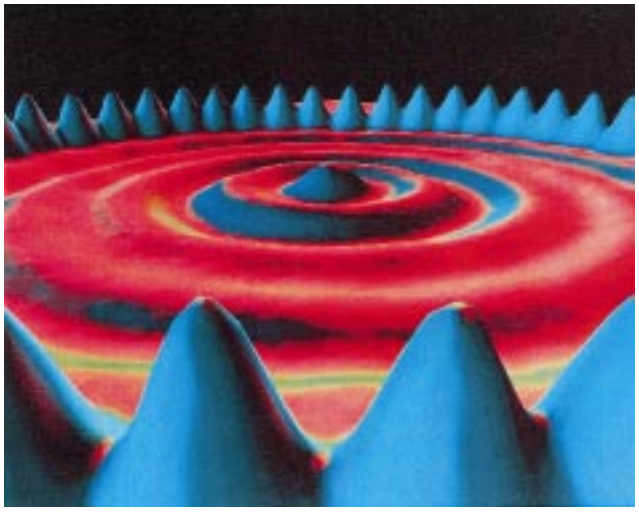

Figure 5. Spatial image of the eigenstates of a quantum corral—a distributed nanostructure made of a 48-atom Fe ring constructed on the Cu(111) surface. (Adapted from ref 9.)

Gimzewski and co-workers constructed an "electromechanical amplifier" by positioning a single C_{60} molecule under the tip of a probe microscope.[46] At low bias voltage, the resistance of the C_{60} molecule decreased as it was compressed. The separation between the tip and sample could be varied by changing the amount of current passing through the C_{60} molecule.

A number of groups have poled ferroelectrics locally with conducting AFM and then have followed the surface charge or patterned ferroelectric with AFM measurements.[47,48] An example is shown in Figure 6, which shows the local poling of a copolymer ferroelectric ultrathin film.[48] A conducting AFM cantilever was used to pole the pattern into the film by orienting the polymer using an applied electric field. Here the topography shows no variation in a film which has been locally poled, and yet complex structures can be written by orienting dipoles within the film and read back using the AFM.

V. Near-Field Scanning Optical Microscopy

The development of the near-field optical microscope (NSOM) enabled optical spectroscopies with subwavelength lateral resolution. By using force feedback, the NSOM combines topographic information and local optical spectra. The gains in resolution

Figure 6. Local piezoelectric effect of a locally poled ferroelectric ultrathin copolymer film is imaged by applying an oscillating electric field between the conducting cantilever of an AFM tip and a conducting substrate. The resulting vibration of the piezoresistive cantilever is recorded and displayed here. The imaged area is 8 μm × 8 μm. This pattern was previously made by poling the ferroelectric film by applying a potential to the area shown. Simultaneously acquired topographic AFM measurements (not shown) indicate no disruption of the film morphology (from ref 48).

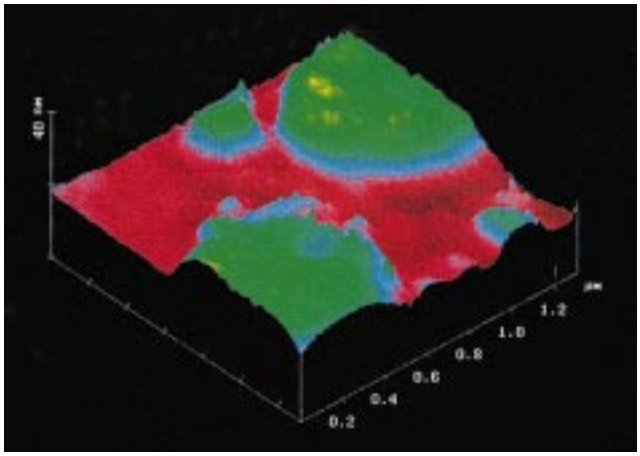

Figure 7. Fluorescence emission near-field scanning optical microscope image (1.3 μm × 1.3 μm) of the light-harvesting complexes within a photosynthetic membrane fragment. (Reprinted with permission from ref 53. Copyright 1994 American Chemial Society.)

from far-field microscopies are not great but for some samples can be significant. Where isolated particles can be spaced apart at will, near-field measurements are not required to obtain individual particle spectra.[49] Many nanoparticle studies fall within this category. Other samples require the extra resolution possible with the NSOM. Examples are biological membranes with included nanostructures and semiconductor materials with inclusions such as dopants whose density determines the overall material properties. Several reviews of far-field single-molecule measurements address this issue.[50−52]

Figure 7 shows an NSOM image of light-harvesting complexes in a photosynthetic membrane recorded by Xie and co-workers.[53] The brighter spots are assigned as the light-harvesting complex on the basis of their fluorescence spectra. Simultaneously acquired shear force images (not shown) correspond to the topography and to the feedback signal discussed in section II.

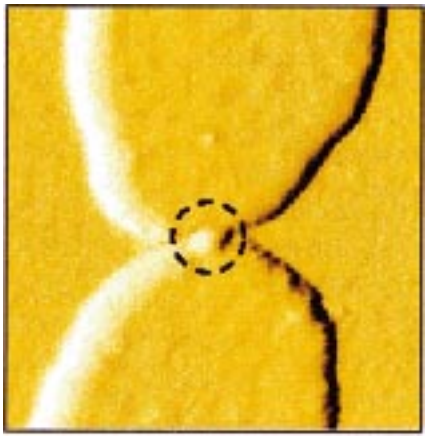

Figure 8. Single-particle device fabricated by AFM-assisted manipulation of a 20 nm sized Au nanoparticle between two metallic leads. Image size: 400 nm × 400 nm (from ref 15).

Relatively few studies have compared images or spectra of the same nanometer-scale features using scanning probe microscopes and other techniques. Natan, Stranick, and co-workers have done this for Au colloid monolayers using AFM, NSOM, and electron microscopy.[54] Many more such studies will be required to work out the limits, advantages, and idiosyncrasies of the various scanning probe techniques.

Recently, NSOMs have been developed capable of vibrational infrared and Raman spectroscopies.[55,56] Near-field Raman scanning optical microscopy yields extremely small signals but useful chemical information.[55] Near-field microscopy has now also been accomplished in the vibrational infrared. Extension of the spectral range to this chemical fingerprint region will certainly soon find application in nanostructures.[56]

VI. Hybrid Devices

By using aspects of SPMs, such as cantilevers and interaction force measurements, new high-sensitivity and high-specificity detectors have been created. As discussed above, an AFM tip can be functionalized with specific chemical groups to measure interactions with molecules or biological species on a surface.[57,58] Colton and co-workers, to describe the chemistry of a surface, modified an AFM tip with oligonucleotides. Colton and co-workers have taken AFM cantilever arrays and set them up as detectors using specific antibody interactions. Gimzewski and co-workers have worked along similar lines to create large parallel and independently addressable arrays of such hybridized cantilevers as sensors.[59]

SPMs cannot only study nanoscale structures, but also build them. Hartmann and co-workers have positioned individual nanoparticles between electrodes using an AFM tip as shown in Figure 8.[15] They then used these devices to measure the electronic properties of the electrode−nanoparticle−electrode junction as a function of temperature and bias. Construction and identification of this system de-

pended upon their AFM measurements. While this may not be a general fabrication technique, it does allow us to glimpse now into the future world of nanometer-scale electronics and devices. As with materials properties, we can then target desired structures for construction by faster parallel methods.

VII. Prospects and Directions

While scanning probe microscopes enable access to single nanoparticles, our ability to interpret the information that we obtain remains primitive. It is only through developing means to gain simultaneous complementary information on the single nanoparticle or nanostructure under study that we can hope to realize the full potential of materials at this scale. The first steps on this path have been taken. Many more spectroscopic and other probes are certain to be developed for SPMs and applied to nanoparticles and nanostructures.

An additional capability sure to be exploited further is our ability to construct or to modify or simply to position structures for study. By making systematic changes in the structures studied, we expect to make rapid progress in elucidating the critical aspects determining the properties associated with those structures. The first such studies have already been done,[9,15] and more are sure to follow.

VIII. Acknowledgments

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IX. References

(1) Kuk, Y.; Jarrold, M. F.; Silverman, P. J.; Bower, J. E.; Brown, W. L. *Phys. Rev. B* **1989**, *39*, 11168−11170.
(2) McCarty, G. S.; Love, J. C.; Kushmerick, J. G.; Charles, L. F.; Keating, C. D.; Toleno, B. J.; Lyn, M. E.; Castleman, A. W., Jr.; Natan, M. J.; Weiss, P. S. *J. Nanoparticle Res.* **1999**, *1*, in press.
(3) Binnig, G.; Rohrer, H.; Gerber, Ch.; Weibel, E. *Phys. Rev. Lett.* **1982**, *49*, 57−61.
(4) Binnig, G.; Quate, C. F.; Gerber, Ch. *Phys. Rev. Lett.* **1986**, *56*, 930−933.
(5) Harootunian, A.; Betzig, E.; Isaacson, M.; Lewis, A. *Appl. Phys. Lett.* **1986**, *49*, 674−676.
(6) Betzig, E.; Harootunian, A.; Lewis, A.; Isaacson, M. *Appl. Opt.* **1986**, *25*, 1890−1900.
(7) Weiss, P. S. *Trends Anal. Chem.* **1994**, *13*, 61−67.
(8) Eigler, D. M.; Schweizer, E. K. *Nature*, **1990**, *344*, 524−526.
(9) Crommie, M. F.; Lutz, C. P.; Eigler, D. M. *Science* **1993**, *262*, 218−220.
(10) Bartels, L.; Meyer, G.; Rieder, K.-H. *Phys. Rev. Lett.* **1997**, *79*, 697−700.
(11) Bartels, L.; Meyer, G.; Rieder, K.-H. *Appl. Phys. Lett.* **1997**, *71*, 213−215.
(12) Bartels, L.; Meyer, G.; Rieder, K.-H.; Velic, D.; Knoesel, E.; Hotzel, A.; Wolf, M.; Ertl, G. *Phys. Rev. Lett.* **1998**, *80*, 2004−2007.
(13) Cuberes, M. T.; Schlittler, R. R.; Gimzewski, J. K. *Appl. Phys. Lett.* **1996**, *69*, 3016−3018.
(14) Tang, H.; Cuberes, M. T.; Joachim, C.; Gimzewski, J. K. *Surf. Sci.* **1997**, *386*, 115−123.
(15) Hartmann, E.; Junno, T.; Carlsson, S.-B.; Cehovin, A.; Kortegaard, C.; Thelander, C.; Ling, T.; Montelius, L.; Samuelson, L. *Proceedings of the 3rd Workshop on Innovative Circuits and Systems for Nanoelectronics*, 1998, A2/1−6.
(16) Kushmerick, J. G.; Weiss, P. S. *J. Phys. Chem. B* **1998**, *102*, 10094−10097.
(17) Betzig, E.; Trautman, J. K. *Science* **1992**, *257*, 198−195.
(18) Hamers, R. J. *Annu. Rev. Phys. Chem.* **1989**, *40*, 531−559.
(19) Sautet, P.; Joachim, C.; Boucquet, M. L.; Salmeron, M. *Ann. Chim. Fr.* **1992**, *17*, 217−227.
(20) Chiang, S. *Chem. Rev.* **1997**, *97*, 1083−1096.
(21) Sautet, P. *Chem. Rev.* **1997**, *97*, 1097−1116.
(22) Kamna, M. M.; Stranick, S. J.; Weiss, P. S. *Science* **1996**, *274*, 118−119.
(23) Kamna, M. M.; Stranick, S. J.; Weiss, P. S. *Isr. J. Chem.* **1996**, *36*, 59−62.
(24) Kandel, S. A.; Weiss, P. S. *Acc. Chem. Res.* Manuscript in preparation.
(25) Banin, U.; Cao, Y. W.; Katz, D.; Millo, O. Submitted for publication.
(26) Heller, E. J.; Crommie, M. F.; Lutz, C. P.; Eigler, D. M. *Nature* **1994**, *369*, 464−466.
(27) Crommie, M. F.; Lutz, C. P.; Eigler, D. M. *Nature* **1993**, *363*, 524−527.
(28) Hasegawa, Y.; Avouris, Ph. *Phys. Rev. Lett.* **1993**, *71*, 1071−1074.
(29) Avouris, Ph.; Lyo, I.-W.; Walkup, R. E. *J. Vac. Sci. Technol. B* **1994**, *12*, 1447−1455.
(30) Avouris, Ph.; Lyo, I.-W.; Molinas-Mata, P. *Chem. Phys. Lett.* **1995**, *240*, 423−428.
(31) Alvarado, S. F.; Renaud, Ph.; Abraham, D. L.; Schonenberger, C. H.; Arent, D. J.; Meier, H. P. *J. Vac. Sci. Technol. B* **1991**, *9*, 409−413.
(32) Berndt, R.; Gimzewski, J. K. *Phys. Rev. Lett.* **1991**, *67*, 3796−3799.
(33) Berndt, R.; Schlittler, R. R.; Gimzewski, J. K. *J. Vac. Sci. Technol. B* **1991**, *9*, 573−577.
(34) Downes, A.; Welland, M. E. *Appl. Phys. Lett.* **1998**, *72*, 2671−2673.
(35) McCarty, G. S.; Weiss, P. S. Unpublished data.
(36) Lindahl, J.; Pistol, M. E.; Montelius, L.; Samuelson, L. *Appl. Phys. Lett.* **1996**, *68*, 60−62.
(37) Stipes, B. C.; Rezaei, M. A.; Ho, W. *Science* **1998**, *280*, 1732−1735.
(38) Jaklevic, R. C.; Lambe, J. *Phys. Rev. Lett.* **1966**, 1139−1142.
(39) Weiss, P. S.; Eigler, D. M. *Nanosources and Manipulations of Atoms Under High Fields and Temperatures: Applications*; Binh, V. T., Garcia, N., Dransfeld, K., Eds.; *NATO ASI Series E: Applied Sciences*; Plenum: New York, 1993; Vol. 235, p 213−217.
(40) Hitosugi, T.; Hashizume, T.; Heike, S.; Watanabe, S.; Wada, Y.; Hasegawa, T.; Kitazawa, K. *Jpn. J. Appl. Phys.* **1997**, *36*, L361−364.
(41) Lyding, J. W.; Shen, T.-C.; Hubacek, J. S.; Tucker, J. R.; Abeln, G. C. *Appl. Phys. Lett.* **1993**, *64*, 2010−2012.
(42) Frisbie, C. D.; Rozsnyai, L. F.; Noy, A.; Wrighton, M. S.; Lieber, C. M. *Science* **1994**, *265*, 2071−2074.
(43) Mamin, H. J.; Rugar, D.; Stern, J. E.; Fontana, R. E., Jr.; Kasiraj, P. *Appl. Phys. Lett.* **1989**, *55*, 318−320.
(44) Snow, E. S.; Campbell, P. M. *Science* **1995**, *270*, 1639−1641.
(45) Avouris, Ph.; Martel, R.; Hertel, T.; Sandstrom, R. *Appl. Phys. A* **1998**, *66*, 659−667.
(46) Joachim, C.; Gimzewski, J. K. *Chem. Phys. Lett.* **1997**, *265*, 353−357.
(47) Gruverman, A.; Auciello, O.; Tokumoto, H. *Int. Ferroelec.* **1998**, *19*, 49−83.
(48) Chen, X. Q.; Terai, Y.; Horiuchi, T.; Yamada, H.; Matsushige, K.; Weiss, P. S. *Thin Solid Films* **1999**, in press.
(49) Nie, S. M.; Chiu, D. T.; Zare, R. N. *Science* **1994**, *266*, 1018−1021.
(50) Wu, M.; Goodwin, P. M.; Ambrose, W. P.; Keller, R. A. *J. Phys. Chem.* **1996**, *100*, 17406−17409.
(51) Goodwin, P. M.; Ambrose, W. P.; Keller, R. A. *Acc. Chem. Res.* **1996**, *29*, 607−613.
(52) Keller, R. A.; Ambrose, W. P.; Goodwin, P. M.; Jett, J. H.; Matrin, J. C.; Wu, M. *Appl. Spectrosc.* **1996**, *50*, 12A−32A.
(53) Dunn, R. C.; Holton, G. C.; Mets, L.; Xie, X. S. *J. Phys. Chem.* **1994**, *98*, 3094−3098.
(54) Grabar, K. C.; Brown, K. R.; Keating, C. D.; Stranick, S. J.; Tang, S.; Natan, M. J. *Anal. Chem.* **1997**, *69*, 471−477.
(55) Jordan, C. J.; Stranick, S. J.; Cavanagh, R. R.; Richter, L. J.; Chase, D. B. *Surf. Sci.*, in press.

(56) Stranick, S. J.; Richter, L. J.; Cavanagh, R. R. *J. Vac. Sci. Technol. B* **1998**, *16*, 1948−1952.
(57) Lee, G. U.; Chrisey, L. A.; O'Ferrall, C. E.; Pilloff, D. E.; Turner, N. H.; Colton, R. J. *Isr. J. Chem.* **1996**, *36*, 81−87.
(58) Lee, G. U.; Chrisey, L. A.; Colton, R. J. *Science* **1994**, *266*, 771−773.
(59) Lang, H. P.; Berger, R.; Battiston, F.; Ramseyer, J.-P.; Meyer, E.; Andreoli, C.; Brugger, J.; Vettiger, P.; Despont, M.; Mezzacasa, T.; Scandella, L.; Güntherodt, H.-J.; Gerber, C.; Gimzewski, J. K. *Appl. Phys. A* **1998**, *66*, S61−S64.

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