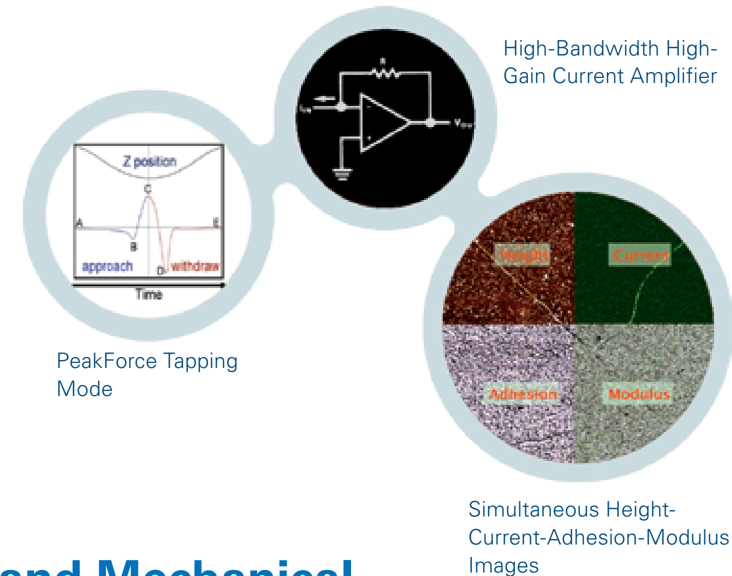

Application Note #132

Simultaneous Electrical and Mechanical Property Mapping at the Nanoscale with PeakForce TUNA

AFM-based conductivity measurements are a powerful technique for nanometer-scale electrical characterization on a wide range of samples. Traditionally, these measurements have been categorized into two classes: Conductive AFM (CAFM), which covers the higher current range (sub-nA up to µA), and Tunneling AFM (TUNA), which covers the lower current range (sub-pA up to nA). Because of practical limitations, most conductive AFM measurements have been restricted to the Contact Mode of AFM operation. As for TUNA, it has become common to use the term to refer to both the sensing module and the measurement technique, regardless of the current-level. As a technique, TUNA has 3 key elements: 1) the current sensor, also known as the TUNA module, 2) the conductive AFM probe, and 3) the base mode of AFM operation. Each of these elements contributes to the technique's capabilities, but also to its limitations. Improvement to any of these areas has the potential to improve the technique's overall performance and applications. Bruker has developed an enhanced TUNA module with its proprietary PeakForce Tapping™ mode of operation[1] that makes significant improvements to all three of these elements to enable 1) exquisite tip-sample force control, which is ideal for soft delicate samples, 2) quantitative nano-mechanical material property mapping through PeakForce QNM™, 3) correlated nanoscale electrical property characterization through TUNA, and 4) extreme ease of use through the ScanAsyst™ image optimization algorithms. A special probe has also been designed for use on particularly challenging samples. This note discusses the basics of PeakForce TUNA, compares it to standard Contact Mode–based TUNA, and provides data demonstrating the unique capabilities and differentiated applications enabled through the combination of PeakForce Tapping and AFM conductivity measurement.

AFM and Conductivity Mapping

The overall performance of AFM-based conductivity mapping parallels the performance of its underlying mode of operation, carrying over both its benefits and its limitations.

Contact Mode Based TUNA (Contact TUNA)

Conductivity measurements at the nanoscale were first enabled with a Contact Mode AFM equipped with a conductive tip and a current-sensing module. Contact-TUNA has been applied in many research and manufacturing laboratories for the analysis of a wide range of materials, for a wide range of applications. For example, traditional Contact Mode TUNA has been used to localize and image electrical defects in semiconductor and data storage devices, to evaluate the uniformity and integrity of thin dielectric films, to characterize piezoelectric and ferroelectric materials, conducting polymers, nanotubes, biomaterials, and others. However, the use of Contact Mode for topographic feedback has proven to be a severe limiting factor. For samples that require low imaging forces in either (or both) the vertical or lateral directions, Contact Mode imaging is not possible, and therefore neither is traditional TUNA imaging. The Contact Mode limitation applies to the study of many conductive polymers, organics or other soft conducting materials, or loosely bound samples such as nanowires.

TappingMode Point Contact IV (Tapping-TUNA)

AFM has achieved tremendous benefits from a variety of oscillating tip modes of operation, most notably TappingMode®. During TappingMode imaging, the AFM cantilever is oscillated at its fundamental flexural resonance. This has the advantage of largely eliminating lateral forces that tend to damage the tip and/or sample when imaging in Contact Mode. The vertical interaction force is also substantially reduced due to the high mechanical Q of the cantilever, permitting imaging of soft or delicate samples. When imaging in TappingMode, the AFM tip oscillates relative to the sample by tens of nanometers, and only spends a few percent of that oscillation in contact with the surface. This is advantageous for eliminating tip wear and sample damage, but presents a problem for conductivity measurements. In order to measure the current signal in such a short time duration (~microseconds) with reasonable signal-to-noise ratio, the current amplifier would need a bandwidth in the MHz range at a high gain (10^9~10^{11} V/A). This is beyond the reach of the current technology. To circumvent this challenge, point-contact current imaging was introduced. In this configuration, TappingMode is used for topographic imaging, and then current-voltage curves are taken at selected points in a Contact Mode fashion.[2]

Torsional Resonance TUNA (TR-TUNA™)

It is known that AFM cantilevers can oscillate in many different modes, including higher order flexural and torsional modes. Imaging with these higher order modes enables the study of a wide range of tip-surface interactions. Consider the case of imaging with the cantilever oscillating in the first torsional resonance mode. In this mode, lateral forces that act on the tip cause a change in the torsional resonant frequency, amplitude, and/or phase of the cantilever. AFM measurements at torsional resonances have many advantages, but the key advantage for TR-TUNA is the ability to achieve low-force scanning while maintaining the tip in the near-field.[3] The use of TR-Mode® extends the sample space available to TUNA to include those samples traditionally believed to be too soft or delicate for Contact Mode (and hence TUNA). This includes conducting polymers, loosely bound nano-materials and organic thin films, as well as more traditional thin film samples such as nano-pillar based low-k materials. However, with TR-TUNA there is concern that the tip-sample contact is changing during each torsional oscillation cycle, and that these deviations are likely to cause variability in the current measurement. To mitigate this, the torsional resonance amplitude is kept very small (less than a few angstroms), but stable operation at these low amplitudes can be extremely challenging. This operational limitation has prevented the wide spread use of TR-TUNA.

PeakForce TUNA Principles

PeakForce TUNA (PF-TUNA) builds on PeakForce Tapping, and in doing so, also acquires the capability of PeakForce quantitative nanomechanical measurements (PeakForce QNM).

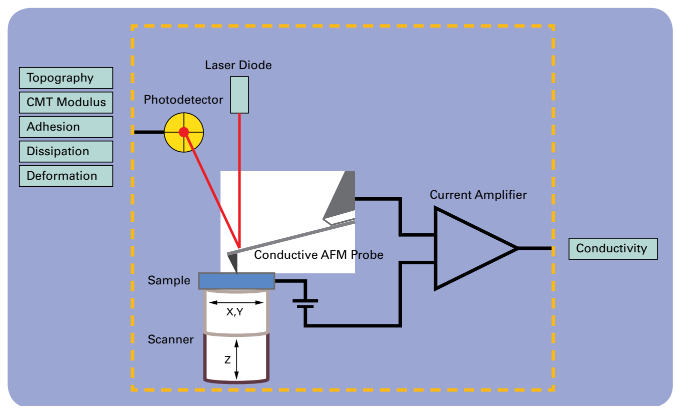

Figure 1. Illustration of PeakForce TUNA setup for simultaneous topography, mechanical and electrical property mapping.

PeakForce Tapping

As in TappingMode, in PeakForce Tapping, the probe and sample are intermittently brought into contact while the tip is scanned across the sample. This eliminates lateral forces during imaging. Unlike TappingMode, where the feedback loop keeps the average cantilever vibration amplitude constant, in PeakForce Tapping the feedback loop controls the maximum force on the tip (Peak Force) for each individual cycle. Because the force measurement bandwidth of a cantilever is approximately equal to its fundamental resonant frequency, by choosing a modulation frequency significantly lower than the cantilever's resonant frequency, the PeakForce Tapping control algorithm is able to directly respond to the tip-sample force interaction. This direct force control protects the tip and the sample from damage, but more importantly, allows every tip-sample contact to be controlled and recorded for additional mechanical property analysis. In the current implementation, the modulation frequency is 1 to 2kHz.

Quantitative Mechanical Property Mapping

The foundation of material property mapping with PeakForce QNM is the ability of the system to acquire and analyze the individual force curves from each tip-sample interaction that occurs during the imaging process. The curves are analyzed in real-time to obtain quantitative mechanical properties of the sample, including adhesion, modulus, deformation, and dissipation. These material property maps are treated as conventional AFM channels, and can be displayed and analyzed together with topography.

PeakForce TUNA Module

It is important to note that the PeakForce Tapping, oscillation frequency (1kHz–2kHz) falls nicely between the TappingMode (>50kHz), and Contact Mode (DC) interaction cycles. In fact, this mid-band operation is the single most important element for TUNA to work in an intermittent contact mode. In each tapping cycle, the tip is in contact with the sample only for a fraction of the cycle (tens to hundreds of microseconds). The TUNA module must be able to pick up a current signal during this time period with acceptable signal-to-noise ratio. A rule of thumb is that the bandwidth of the TUNA module must be 10x greater than the tapping frequency at the chosen gain. At TappingMode frequencies this is far beyond the reach of current technology. At PeakForce Tapping speeds, it is an attainable challenge. The released PeakForce TUNA module is engineered to have a bandwidth around 15kHz across a range of gains from 10^7 V/A to 10^{10} V/A, with the noise below 100fA on cycle-averaged current.

The PF-TUNA module has 6 gain settings (10^7 V/A, 10^8 V/A, 5 x 10^8 V/A, 10^9 V/A, 10^{10} V/A, 5 x 10^{10} V/A), adjustable through a combination of hardware and software switches. The integration of a wide range of gains on one single module eliminates the need to change modules while searching for the optimal gain to match the conductivity level of a sample, or when different gains are needed to reveal all different conductivity levels present in one single sample. It is noteworthy that the offset at each different gain setting is automatically zeroed out upon each engage, or gain change, to assure measurement accuracy. The PeakForce TUNA module, while designed to work with PeakForce Tapping mode, is compatible with Contact Mode, and provides equal or better noise performance in Contact Mode compared to existing TUNA modules.

PeakForce TUNA Quantities

Figure 2 illustrates what happens when the periodically modulated PeakForce Tapping probe interacts with the surface. The top line represents the Z-position of the cantilever base, as a function of time, as it goes through one period. The middle line represents the force measured by the probe during the approach (blue) and withdraw (red) of the tip to the sample. The bottom line (green) represents the detected current passing through the sample. Since the modulation frequency is about 1kHz, the time from point A to point E is about 1ms.

When the tip is far from the surface (point A), there is little or no force on the tip. As the tip approaches the surface, the cantilever is pulled down toward the surface by attractive forces (usually van der Waals, electrostatic, or capillary forces) as represented by the negative force (below the horizontal axis). At point B, the attractive forces overcome the cantilever stiffness and the tip is pulled to the surface. The tip then stays on the surface and the force increases until the Z position of the modulation reaches its bottom-most position at point C. This is where the peak force occurs. The peak force (force at point C) during the interaction period is kept constant by the system feedback. The probe then starts to withdraw and the force decreases until it reaches a minimum at point D. Adhesion is measured by the force at this point. The point where the tip comes off the surface is called the pull-off point. This often coincides with the minimum force. Once the tip has come off the surface, only long range forces affect the tip, so once again, the force is very small or zero when the tip-sample separation is at its maximum (point E).

From the current-time plot, the PeakForce TUNA algorithm extracts three measurements: 1) peak current, 2) cycle-averaged current, and 3) contact-averaged current. Peak current is the instantaneous current at point C, coinciding with peak force. This corresponds to the current measured at a defined force. Peak current may be, but is not necessarily, the maximum current, since the limited rise time (imposed by the bandwidth of the TUNA module or the resistance-capacitance of the sample) may cause a lag in the current response. Cycle-averaged current is the average current over one full tapping cycle, from point A to point E. This includes both the current measured while tip is in contact with the surface, and while it is off the surface. Contact-averaged current is the average current only when the tip is in contact with the surface, from the snap-in at point B to the pull-off at point D.

The current-time plot usually has different characteristics than the force-time plot. It does not always have a peak (as in the force-time plot); current can reach a plateau after a certain force threshold. There is also an AC current component of the measurement, part of which is capacitive charging, which is removed from the output. The tip (including cantilever) and the sample essentially form a capacitor, and the modulation of z-position causes its capacitance to modulate. At a constant DC bias, charging/discharging current at the tapping frequency will occur. Again, this is considered parasitic, and removed as

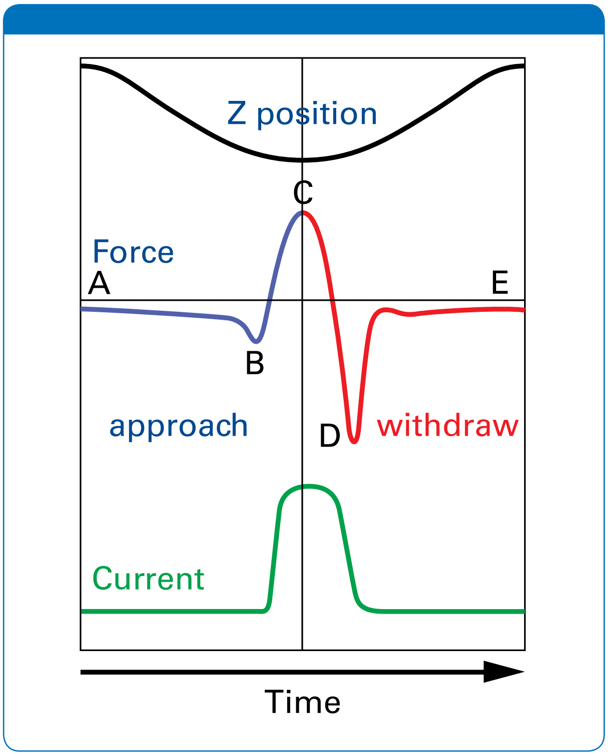

Figure 2. Plots of Z position, Force, and Current as a function of time during one PeakForce Tapping cycle, with critical points including (B) jump-to-contact, (C) peak force, (D) adhesion labeled.

background. The dynamic change of the current (together with deflection) can be captured with NanoScope's "High-Speed Data Capture" function at any time during scanning, and can later be analyzed and correlated (with force for instance).

PeakForce TUNA Operation Mode

PeakForce TUNA can be operated in either imaging or spectroscopy mode. In the imaging mode, maps of the electrical current are obtained with topography and mechanical properties. In the spectroscopy mode, one can collect current-voltage (I-V) curves.

- **Imaging mode**

In the imaging mode, an electrically conductive probe is scanned over the sample surface in PeakForce Tapping mode as the feedback loop keeps the maximum force (peak force) exerted on the tip at a constant value by adjusting the extension of the Z piezo. This protects the tip and sample from damage while allowing the tip sample contact area to be minimized. During scanning, the user can apply a DC bias between the tip and the sample. The TUNA module, a low-noise, high-bandwidth linear current amplifier, senses the resulting current passing through the sample. This data is presented simultaneously with the topography image and mechanical properties maps (when using PeakForce QNM). The observed current can be used as a measure of the local conductivity, or electrical integrity, of the sample under study. Since the system can acquire up to eight channels simultaneously, it is possible to map the major mechanical properties such as deformation, adhesion, DMT modulus, dissipation, and electrical properties such as cycle-averaged current and peak current together with topography in a single pass. Offline analysis functions can calculate statistics of the electrical properties of different regions, sections through the data showing the spatial distribution of the properties, and/or correlation between mechanical, topographic and electrical properties.

Here are several tips for using PeakForce TUNA in the imaging mode: 1) use smaller PeakForce setpoints for soft or delicate samples; 2) PeakForce setpoint will affect all three reported current quantities (peak current, cycle-averaged current and contact-averaged current), 3) Decreasing PeakForce Tapping amplitude will increase contact time within each tapping cycle, resulting in higher cycle-averaged current and higher contact-averaged current. 4) If simultaneous mechanical properties are desired, a PeakForce setpoint sufficient to attain a few nanometers of deformation is necessary for an accurate DMT Modulus reading.

- **I-V Spectroscopy mode**

In addition to the imaging mode, PeakForce TUNA also measures local current-voltage (I-V) spectra using the spectroscopy mode. In order to obtain I-V spectra, the imaging scan is stopped and the tip is held in a fixed location while the sample bias is ramped up or down. In spectroscopy mode, the feedback is switched to Contact Mode, a constant deflection is maintained by the feedback loop while the sample bias is ramped. This assures tip-sample contact is fixed while I-V curve is taken. The resulting current through the sample is plotted versus the applied bias. The software can either record a single spectrum or average over multiple spectra. The higher bandwidth of the PeakForce TUNA module allows I-V curves to be taken at higher speeds; and it expands the bandwidth of AC based dI/dV measurements, for instance, using the "Generic Lock-in" feature offered with the NanoScope® V Controller. I-V curves can also be taken using the "Point & Shoot" feature. The "Point & Shoot" feature offers the option of drawing a line or a box on an image, defining a number of points, and then the AFM tip will automatically move to those locations to capture one or multiple I-V curves at each point. While this is a powerful automation feature, it often can be more useful to "manually" choose a few spots of interest at specific regions on the sample.

	PF-TUNA	Contact-TUNA	Tapping TUNA	TR-TUNA
Conductivity mapping	Yes	Yes	No	Yes
Minimum peak force	<100 pN	<10 nN	<3 nN	—
Quantitative Mechanical Property Mapping	Yes	No	No	No
Ease of use	Yes	Yes	Yes	No

Figure 3. Comparison of AFM-based conductivity measurement techniques.

Summarizing Conductivity Mapping Modes

Figure 3 summarizes the nanoscale conductivity mapping techniques available with AFM. Of the conductivity mapping techniques, PeakForce TUNA has the best capability in force control, quantitative mapping, and ease of use while retaining the current mapping resolution of Contact-TUNA. While Contact-TUNA remains a useful mode for robust samples, PeakForce TUNA is the mode of choice for soft delicate samples, such as conducting polymers and loosely bound nanostructures. Conductivity mapping on hard samples also benefits from the light forces used in PeakForce TUNA. Tips can be preserved from wearing, rupture or break-off, which is in the interest of high resolution and measurement consistency.

Complementary Environmental Control

A glove-box is often a necessity for handling air sensitive materials, such as organic solar cell and lithium battery materials. Bruker provides complete environmental control by integrating Bruker's AFM systems (currently MultiMode® 8, Dimension® Icon, and Dimension Edge™) with M-Braun's glove box. Feed-through ports are engineered to guarantee the performance of the glove box, providing sub-ppm levels of O_2 and H_2O. Vibration isolation is addressed with a custom engineered table, along with an active vibration isolation table in the glove box (passive tables also available). This enables measurement to be done without compromising the integrity of the sample nor the performance of the AFM. The controlled environment also benefits measurement consistency and resolution when no water condenses on the sample or around the tip

Applications in Organic Solar Cells

Organic solar cells have been regarded as a promising candidate in harvesting solar energy due to their great potential of low-cost production, light weight, and mechanical flexibility. However, their widespread adoption is hindered by the efficiency of such organic photovoltaic (OPV) devices, which are now below the threshold for commercial viability. The key component of an organic solar cell is a blend of a donor and an acceptor materials to form bi-continuous networks, named a bulk heterojunction (BHJ).[4] The donor/acceptor pair can comprise of two different conjugated polymers, but more often a conjugated polymer such as poly(2-methoxy-5-(3′,7′-dimethyl-octyloxy))-p-phenylene vinylene (MDMO-PPV) or poly-3(hexylthiophene) (P3HT) as the donor and a soluble fullerene derivative such as [6,6]-phenyl C61 - butyric acid methyl ester (PCBM, a C60-derivative) as the acceptor. To fabricate a device, powders of the donor and the acceptor are dissolved in an organic solvent followed by spin casting this solution onto an indium tin oxide (ITO) coated glass substrate (a semitransparent conductive substrate). Subsequently, aluminum electrodes are deposited atop the active layer using a shadow mask and a thermal evaporator. When light is shined on the device through the ITO side, the active layer absorbs light creating excitons (bound electron-

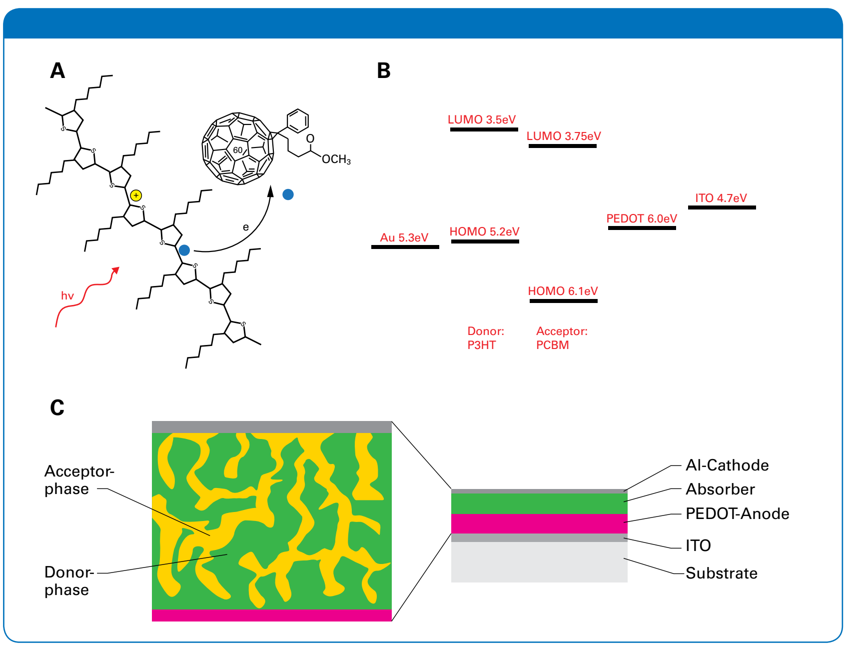

Figure 4. (a) A common donor/acceptor pair used in organic solar cells: poly-3(hexylthiophene) (P3HT) as the donor (p-type) and [6,6]-phenyl C61 - butyric acid methyl ester (PCBM, a C60-derivative) as the acceptor (n-type). (b) HOMO and LUMO levels of P3HT and PCBM in comparison with the work functions of Au, PEDOT and ITO. (c) The stacking of an organic bulk heterojunction solar cell.

hole pairs) which are typically separated into free charges at the donor/acceptor interface (the junction). Although the active layer needs to be 100~200nm thick to capture most of the incident light, the diffusion length of an exciton is only 10~20nm. To yield an efficient energy conversion device, the donor and acceptor domains must be around 20nm. The charge generation and charge transport in organic solar cells depend strongly on the nanoscale morphology and the degree of the donor and acceptor phase separation. The efficiency of the solar cell is largely determined by the morphology of the heterojunction, thus, it is crucial to probe these nanoscale properties.

Conductive AFM has proven to be a useful tool in revealing the morphology on the nanoscale and detecting the conductivity on the same location for direct correlation. It lends unique insight into the underlying heterogeneity of organic solar cell materials or devices, and provides a nanoscale basis for understanding the interplay between its morphology and performance. However, Conductive AFM has been largely based on Contact Mode, which is not well suited for imaging polymer samples. The vertical and lateral forces involved in Contact Mode imaging inevitably cause damage to the sample and jeopardize data integrity. Conductive tips with small spring constant (~0.2N/m) and small setpoint value are often used to minimize destruction of the polymer layer while keeping the conductive coating free from surface contamination. Even with all these measures taken, reliable traditional Contact-TUNA remains a challenge. As pointed out by Ginger, who coined photo-current AFM (pcAFM), which is derived from Contact Mode-based Conductive AFM, "Perhaps one of the most significant practical challenges to using pcAFM is obtaining a good electrical image without causing significant damage to the sample. Patience and a willingness to sacrifice many AFM cantilevers in the name of science, are often necessary."[5]

Example 1: Thermal Annealing Effect on P3HT Thin Film

Figure 5 shows PeakForce TUNA data taken on a P3HT deposited atop poly(3,4-ethylenedioxythiophene) (PEDOT) and ITO. In this example, the effect of thermal annealing on P3HT (a common donor) thin film was examined. The substrate was a glass slide coated with transparent ITO and modified by spin-coating a PEDOT layer. A thin film of P3HT was spin-cast on top in a N2-filled glove box (<1 ppm O_2 and H_2O) and annealed at 120°C. Various annealing approaches have been reported to affect the polymer ordering, resulting in changes in morphology and charge transport behavior. The taller features in topography, with associated higher modulus, may be an indication of areas with more order. It is not surprising that most of those

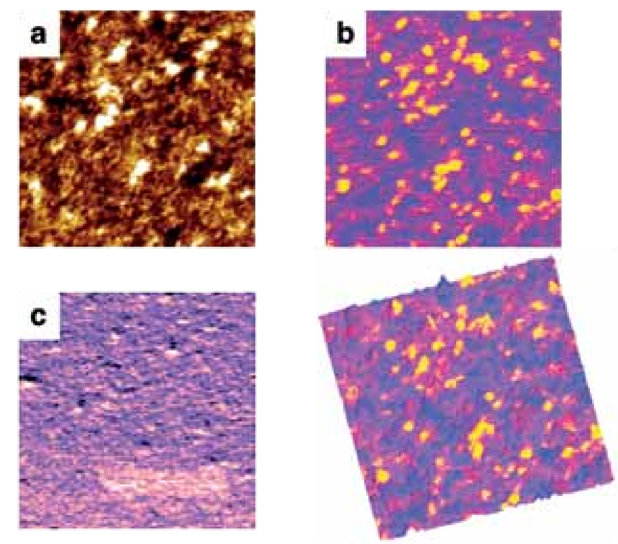

Figure 5. PeakForce TUNA images of P3HT thin film spin-coated on glass/ITO/PEDOT substrate, and annealed at 120 °C. Shown are (a) topography, scale 10nm; (b) peak current, scale 300pA; (c) DMT modulus, scale 15MPa (d) the overlay of conductivity map on topography. Image size is 2 µm × 2 µm, taken at 1 nN PeakForce, 3V DC bias, using Bruker's PeakForce TUNA probe (Au coating, spring constant of 0.4N/m) on a MultiMode 8 AFM in a glove box with below 1 ppm O_2 and H_2O. Sample courtesy of Prof. Nguyen, UCSB.

ordered areas show higher conductivity. Some of them, however, are poorly conductive, implying there may be a poorly ordered layer underneath that act as traps. Some "hot" spots from flat areas on the surface may have some conductivity enhancing ordered structure lying underneath. Note the conductive spots have similar round shapes, suggesting ordered aggregates tend to be cylindrical.

Example 2: P3HT:PCBM Organic Solar Cell

Figure 6 shows PeakForce TUNA data taken on a P3HT:PCBM bulk heterojunction solar cell with the AFM tip in place of the cathode. P3HT:PCBM thin films (~100nm thick) were prepared by spin coating from a toluene solution of the polymers onto ITO-coated glass substrates modified with a thin PEDOT layer. PF-TUNA was used to image the P3HT:PCBM BHJ networks, and their respective domains. Variations in conductivity (Figure 6b) can be clearly seen in Cycle-averaged Current. The closer match of the workfunction of Au (tip coating) and ITO to the HOMO of P3HT (p-type) determines that the majority of the current comes from hole transport along the P3HT phase. Thus it is postulated the higher conductivity regions are P3HT rich, whereas the poorer conductive regions are PCBM rich. The conductivity through the active layer indicates the

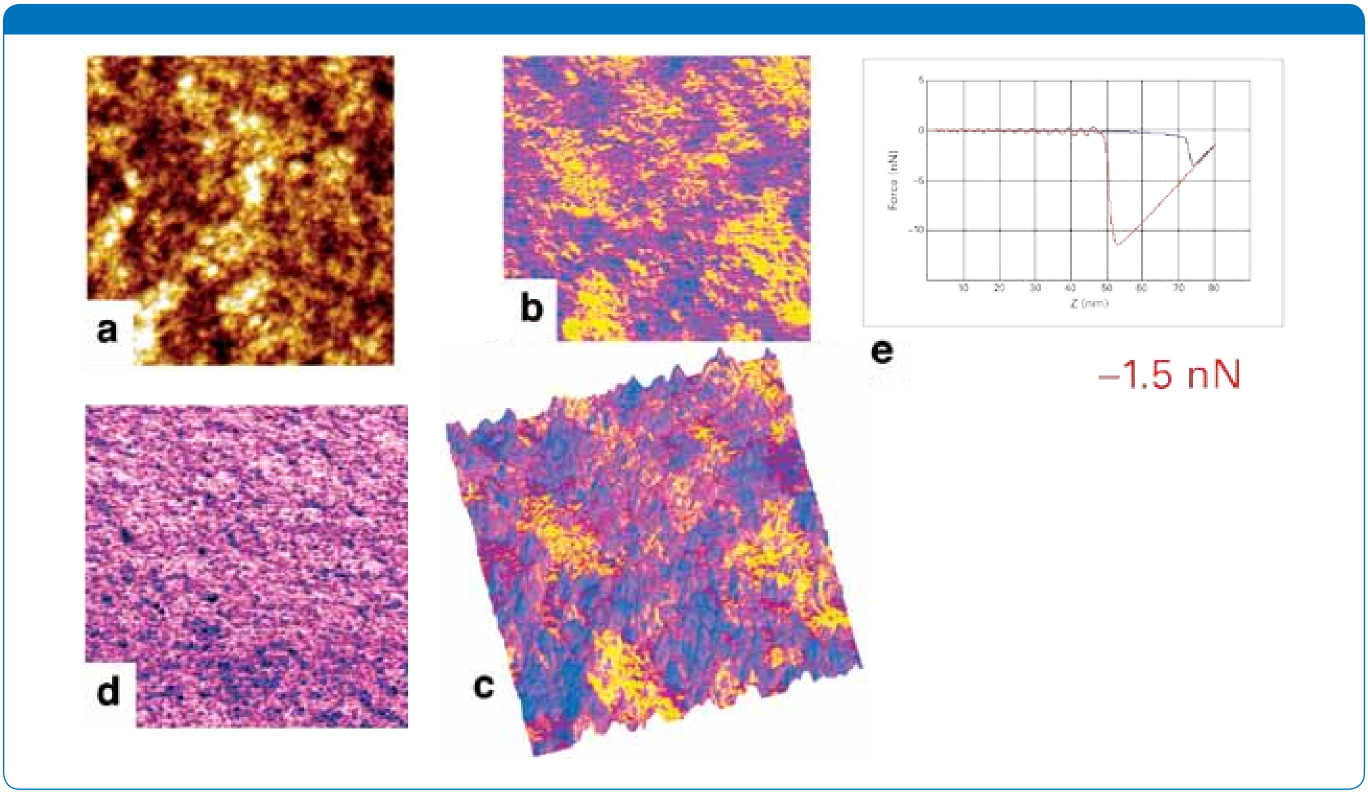

Figure 6. PeakForce TUNA images of P3HT:PCBM solar cell with a PEDOT modified ITO/glass anode. Shown are (a) topography, scale 10nm; (b) Cycle-averaged Current, scale 5pA; (c) Adhesion, scale 8 ~10nN and (d) the overlay of conductivity map on topography. Image size is 2µm × 2µm, taken at 2.5V DC bias, a net-negative PeakForce of -1.5nN is shown in the force curve (e). Bruker's Multimode 8 AFM is used with Bruker's PeakForce TUNA probe (Au coating, spring constant 0.4N/m) in a glove box with below 1ppm O_2 and H_2O. Sample courtesy of Prof. Nguyen, UCSB.

formation of vertical conductive networks. A close look of the current image also reveals fiber-like features, evidence that BHJ networks also exist laterally. Nguyen[6] using conductive AFM (Contact Mode based) to image both the top surface and the cross section of the same device, revealed the nanoscale three-dimensional interpenetrating networks of P3HT and PCBM. The topography (Figure 6a) shows some granular structures that can be polymer aggregates. The adhesion map (Figure 6d) shows features measuring 10~50nm that are quite uniformly dispersed across the whole surface, the length scale falls closely to the hypothesized exciton diffusion length of 6~20nm. This can be a useful criterion in the further optimization of active layer formulation processes. Average conductivity over a certain scan area, and hole and electron motilities extracted from I-V curves were reported to agree with the conversion efficiency of organic solar cells in the general trend.[6] It is worth noting that, as a net-negative PeakForce was used for the imaging, the same tip could last for more than 6 hours without perceivable degradation in resolution and conductivity signal, a stark contrast to Contact Mode–based conductive-AFM.

Applications in Lithium Ion Batteries

Lithium-based battery, as an energy storage device, has enjoyed wide acceptance for its light weight and high energy density. Its applications in consumer electronics are ubiquitous; lithium battery powered vehicles have started to appear on the market. Despite the tremendous achievements in the past decades, only about 10% of the theoretical capacity of lithium has been realized.[7] Much attention is being directed to improve lithium battery chemistry, formulation, and structuring of cathode and anode materials to improve energy density, power density, safety, shelf/cycle life, and cost. Electrode materials are often engineered into micrometer to nanometer sized structures (particles, fibers, pillars and so forth) and held together by additives for mechanical support while leaving some space (measured in porosity) around them for lithium ions to pass. This three-dimensional nanostructure assembly has the following benefits: (1) the large surface area increases capacity; (2) the small size of each individual particle shortens the diffusion length for lithium ion to get in and out of the hosting material, leading to higher charging/discharging rate, or power density. As Tarascon and Armand vividly put, "the arrival of nanomaterials gave lithium-ion

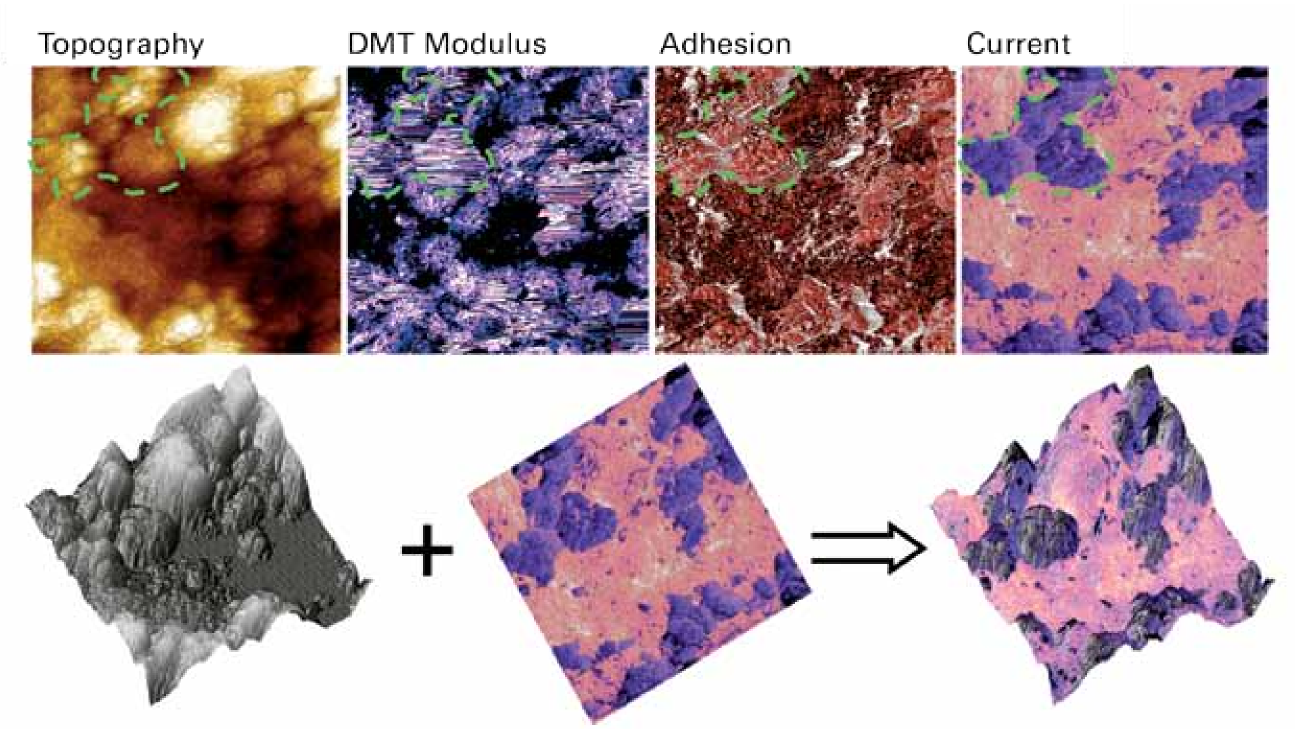

Figure 7. PF-TUNA images of a $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ composite cathode, on the top row are topography, DMT modulus, adhesion and current maps. The overlay of a current map on topography is shown on the bottom row. Images were taken on a Dimension ICON AFM in ambient conditions, with a DDESP probe (spring constant was calibrated to be 93N/m), 50µm scan at a DC sample bias of 500mV. Sample courtesy of Dr. Zheng and Battaglia, Lawrence Berkeley National Laboratory.

batteries a new lease of life."[8, 9] Characterization on the nanoscale is therefore of fundamental importance. The following two examples demonstrate the unique capabilities of PeakForce TUNA in this regard.

Example 1: Material assignments in $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ Composite Cathode

Lithium-ion battery cathode materials often come in a composite form. $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ (L333) is one of the most used cathode materials. Besides this active material, polyvinylidene difluoride (PVDF) was added as the binder polymer to hold L333 particles together; and acetylene black (AB) as the conductive additive to enhance electronic conductivity. PF-TUNA was used to visualize the distribution of each component, and to characterize the elastic modulus and the formation of a conductive network that is intended to connect all the L333 particles together and connect them to the current collector (in this case Al foil). From the topography, particle sizes measuring 3~15µm are seen, which represent the size of L333 particles, as PVDF+AB contribute little given their smaller sizes (AB: ~50nm) and percentage (see figure 7). In the current image, two distinct conductivity levels can be readily seen. The less conductive regions (shown in dark purple color, encircled within the

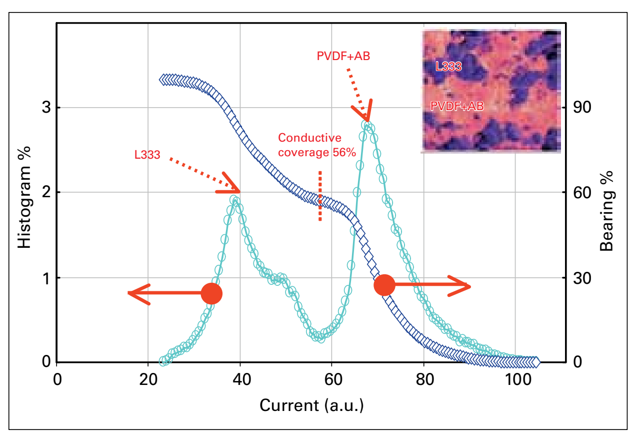

Figure 8. Bearing analysis of the Current map in figure 7.

dotted green line) can be assigned to L333 particles that are not covered with AB+PVDF. This assignment is further supported by the higher modulus seen in the same location. The more conductive regions (light pink color) suggest where the top surface is covered with PVDF+AB. PVDF itself is not conductive, but becomes so when mixed with a sufficient amount of AB nanoparticles (i.e., when the nanoparticles connect with each other to form conductive networks). Those regions also showed smaller elastic modulus and smaller adhesion. The overlay of the current map (denoted by color) atop the topography (denoted by height) clearly shows which L333 particles are covered with PVDF+AB and which are not. Those uncovered particles are electrically isolated from the collecting electrode, and thus do not contribute to the battery capacity and become a dead weight. Offline bearing analysis of the current data map shows two distinct peaks corresponding to L333 (left peak) and PVDF+AB (right peak), the coverage of the conductive network is 56% (see figure 8).

Example 2: Optimizing PVDF+AB Content in $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ Cathode

$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (LiNCA) is another cathode material that is being actively pursued to optimize its performance.10 The variation of PVDF+AB content on the characteristics of the

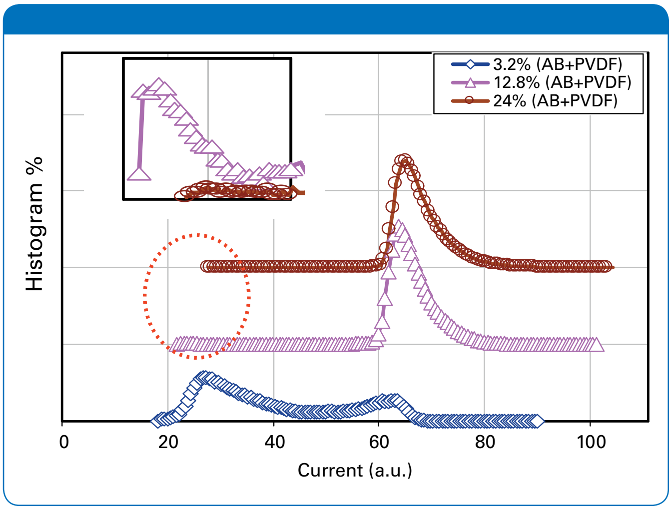

Figure 9. Bearing analysis of the current maps (not shown) of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ composite cathode containing 3.2%, 12.8% and 24% PVDF+AB. Sample courtesy of Dr. Zheng and Battaglia, Lawrence Berkeley National Laboratory.

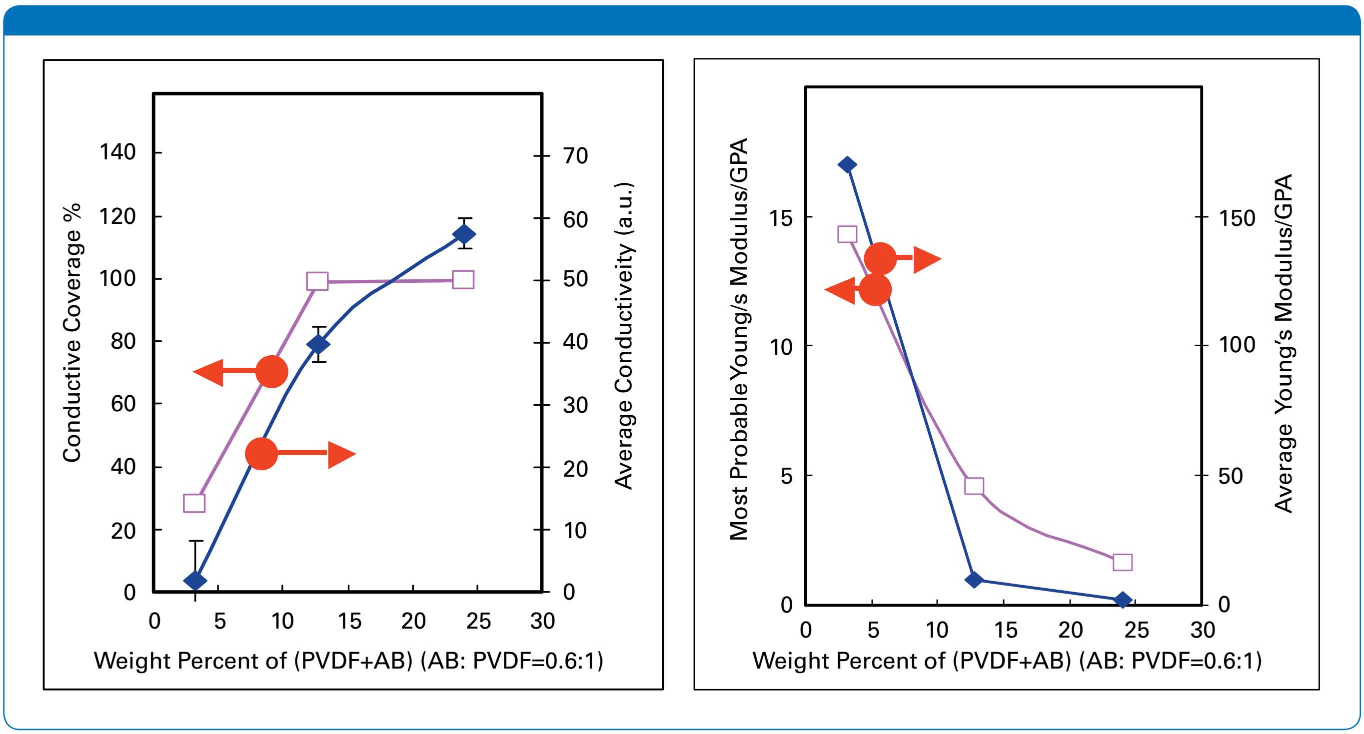

Figure 10. Plot of the conductive network coverage and average conductivity (a) and average elastic modulus (b) over 50μm scan area as a function of the percentage content of PVDF+AB in $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ composite on the same samples used in figure 9.

composite was studied using PeakForce TUNA. Figure 9 shows the bearing analysis of a series of samples containing 3.2%, 12.8% and 24% PVDF+AB (a fixed PVDF:AB ratio 1:0.6). The conductivity peak corresponding to PVDF+AB rapidly increases as more (AB+PVDF) was added. Conductive network coverage approaches completion with 12.8% PVDF+AB (see figure 10a). As a validation of the conductivity measurement, we found good agreement between average conductivity over a 50μm scan area with 4-point probe measurement on the millimeter scale. Higher conductivity translates to less internal resistance of the battery, benefiting high power density. The average elastic modulus decreased with more PVDF+AB content meaning the cathode becomes more flexible, which is important to accommodate volume changes upon lithium-ion insertion into and extraction from the cathode (see figure 10b). Keep in mind that the addition of those inactive materials lowers the energy density, so optimization is needed to balance different performance aspects of the battery. PeakForce TUNA measurements with other complementary techniques can provide direction of optimization to satisfy different application needs.

Although the above examples are on lithium-ion battery cathodes, PeakForce TUNA is similarly useful in the study of anode materials, for example on their aging over time or upon charging/discharging cycling when associated mechanical degradation and resistance increase may occur.

Applications for Nanostructures

Various nanostructures are viewed as the building blocks for the ever shrinking electronic devices. Their electrical behaviors have been the subject of intensive study. The following two examples demonstrate the superiority of PeakForce TUNA for imaging this class of fragile samples, which has been a challenge for Contact Mode AFM-based conductivity measurement.

Figure 11 shows the topography and current map simultaneously taken with PeakForce TUNA of carbon nanotubes connected to conductive pads laid on an

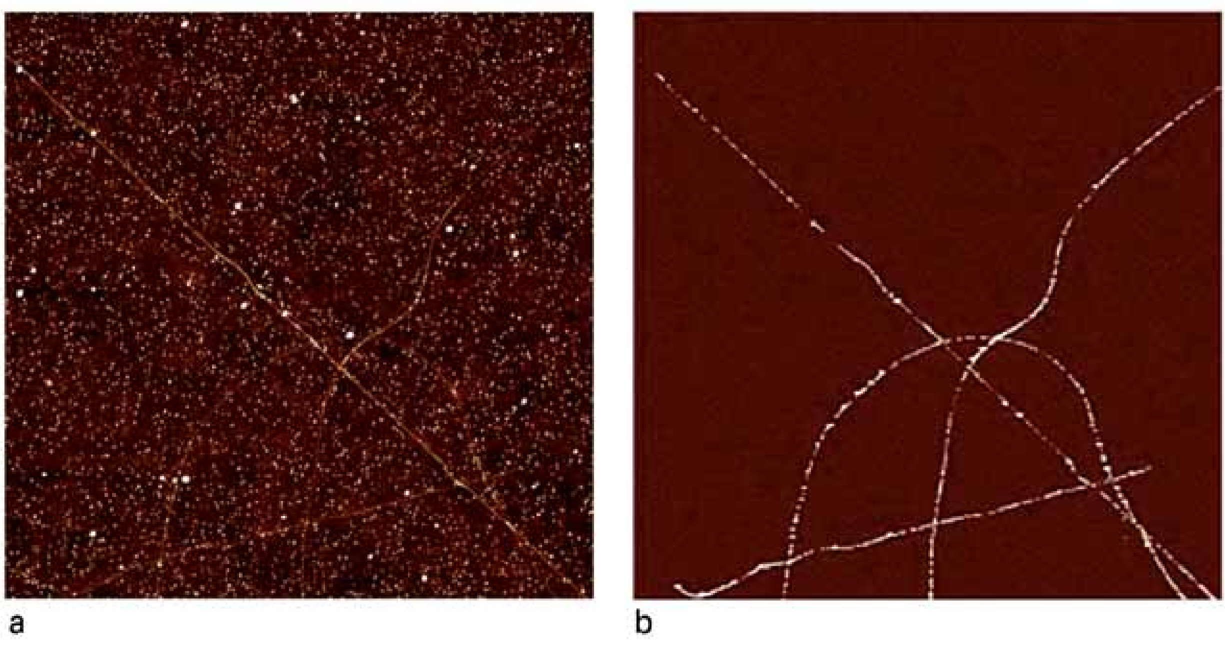

Figure 11. PeakForce TUNA images (a) topography (b) current map of carbon nanotubes lying flat on a SiO_2/Si sample. Images were taken on Bruker's Dimension® Icon® AFM in ambient conditions, with an SCM-PIT probe (spring constant ~4N/m), 5μm scan at a DC sample bias of 500mV. Sample courtesy of Prof. Hague, Rice University.

insulating SiO_2/Si substrate. All the nanotubes present in the topography image are clearly seen in the current map, suggesting they are all conductive and all connected to the conductive pads. The densely packed nanoparticles are residues produced during the sample preparation. Their conductivity can not be assessed as they are not electrically connected to the conductive pads. This is shown as they are clearly not represented in the current map. However, the variation in the conductivity along the tubes may be due to their presence on, or along the tubes. It is worth noting that while the nanotubes are fragile and can be pushed about with an AFM tip (if in Contact Mode), the substrate is hard. With PeakForce TUNA, the SCM-PIT tip (platinum-iridium coating) endured for hours without the coating being worn off by the substrate. For comparison, the same sample was imaged with TR-TUNA. With TR-TUNA the conductivity trace was wider, and it is hypnotized that this increase is due to the lateral dithering of the probe when operating in this mode.

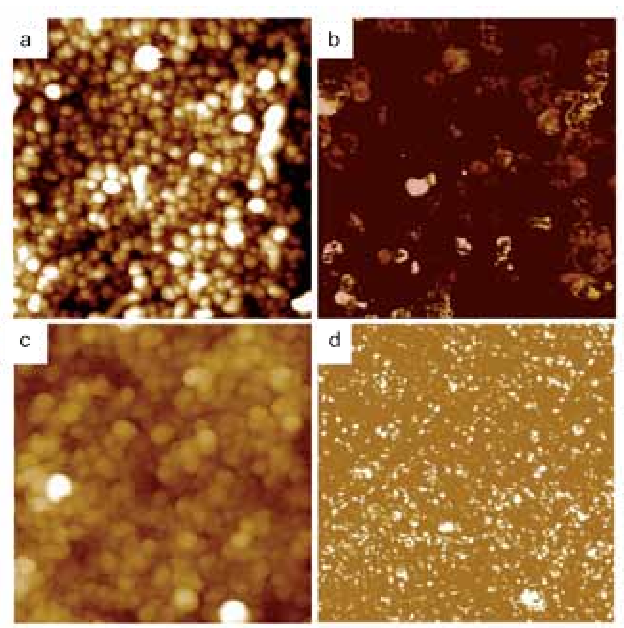

Figure 12. PeakForce TUNA images (a) topography 50nm scale (b) peak current map (1 nA scale) of a vertical multi-walled carbon nanotube mat on a conductive substrate. Images were taken on Bruker's MultiMode 8 AFM in ambient, with SCM-PIT probe (spring constant ~4N/m), 1µm scan at a peak force of 10nN, and DC bias of -1V. TR-TUNA images (c) topography scale 100nm (d) current map (scale 1nA) for comparison.

Figure 12a and b show PeakForce TUNA images of a vertical multi-walled carbon nanotube mat on a conductive substrate. Seen are the end caps of the nanotubes. Initially, it was expected that all of the multi-walled nanotubes would be conductive. However, as observed in the peak current map, this is not the case, but instead the different bundles exhibit different levels of conductivity(see figure 12b). Two possible interpretations are that there is variability in how the nanotubes are connected to the underlying substrate, or that the capping of the tubes is affecting the measured conductivity even if the cylindrical part of the tube is conductive and base attached. The same sample was tried with Contact Mode–based TUNA, however no stable images could be attained. TR-TUNA gave a current image that looked quite different (see figure 12c,d). Several discontinued conductive spots appeared on single tubes, and this is against intuition as we expect more uniformity on each individual tube. The lateral twisting motion of the probe in the Torsional Resonance Mode is likely to be causing an intermittent electrical contact to the surface.

PeakForce TUNA Probe Selection Guide

The spring constant and the conductive coating material are important considerations when selecting a probe. Bruker's newly introduced PeakForce TUNA probes are specifically designed for optimal electrical and mechanical performance and lifetime on soft delicate samples such as conductive polymers, bio-materials, or loosely bound nanostructures; these probes have Au coated tips and a spring constants of ~0.4N/m. SCM-PIT probes which have a Platinum-Iridium coating and a spring constant of ~3N/m, work well for fragile samples, for instance, loosely bound nanostructures, and hard samples, for instance SiO_2 dielectric films. DDESP probes, which have doped diamond coatings and spring constants of ~40N/m, are well suited for samples containing hard components. To attain accurate mechanical property measurements, as a rule of thumb, the match of the spring constant to the elastic modulus of the sample is to be observed. Since the instrument can operate in an inert atmosphere, it is possible to use aluminum or low work-function metal coated silicon probes for organic solar cell characterization.

Conclusions

Through an innovative high-bandwidth, high-gain, low-noise current amplifier design, PeakForce TUNA couples AFM conductivity measurements with Bruker's exclusive PeakForce Tapping technology. Using the unparalleled force control of PeakForce Tapping, PeakForce TUNA enables, for the first time, current imaging on extremely soft and delicate samples, as well as, superior tip lifetime for current imaging on hard samples. In both cases, the enhanced force control improves the repeatability and resolution of conductive AFM imaging. The ScanAsyst algorithm, which is included with PeakForce TUNA, dramatically improves ease of operation by automatically optimizing the AFM's scan parameters (including feedback gain settings). PeakForce TUNA also includes the quantitative nanomechanical property mapping suite of PeakForce QNM, thereby providing electrical information simultaneous with topography and mechanical property information (deformation, adhesion, DMT modulus, and dissipation). Having all of these orthogonal data channels available in a single scan, brings out the PeakForce TUNA's unique ability to correlate the different properties of the sample at the nanometer scale. This technique is complemented by Bruker's AFM specific glove-box offering, enabling proper handling of air-sensitive materials. Both individually and combined, PeakForce TUNA and the ppm capable glove-boxes, will be useful tools in the characterization of fragile samples such as loosely bound nanostructures, organic solar cells, lithium ion batteries, fuel cells, and many others.

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